

Benchmark Database for Ylidic Bond Dissociation Energies and Its Use for Assessments of Electronic Structure Methods

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ABSTRACT: We report a database of 18 ylidic bond dissociation energies obtained by using highly accurate quantum mechanical methods, and we use it to test approximate electronic structure methods. The new benchmark database is called YBDE18 and is used to test a large number of electronic structure methods, including eight wave function methods and 98 density functional exchange-correlation functionals. Among them, we include some very recent density functionals, including the SOGGA11 GGA functional, the SOGGA11-X hybrid GGA functional, the M11-L local meta-GGA functional, and the M11 range-separated hybrid meta-GGA functional. We also consider other functionals of these classes plus a local spin density approximation, global-hybrid meta-GGAs, range-separated hybrid GGAs, doubly hybrid GGAs, and doubly hybrid meta-GGAs. We found M05-2X-D3, MPWB1K-D3, M05-2X, LC-BLYP, PBE0-D3, and MC3MPWB to be the best DFT methods for this database. Although they do not place in the top four overall, our new-generation functionals show overall competitive performances; each of the new functionals provides the smallest mean signed error within its class, while in terms of mean unsigned errors, SOGGA11 is the best GGA, and SOGGA11-X and M11-L are among the first three best functionals in their categories, global-hybrid GGA and local meta-GGA. The best local functionals are VSXC and M06-L, the best global-hybrids are M05-2X, M08-HX, M06-2X, and MPWB1K, and the best range-separated hybrids are LC-BLYP, ω B97, ω B97X, and M11.

1. INTRODUCTION

The Wittig reaction^{1,2} is one of the most powerful methods for the synthesis of alkenes. In the Wittig reaction, a phosphonium ylide (often called a Wittig reagent) reacts with an aldehyde or ketone (electrophile) to form an alkene. Other types of ylides have also been found to be useful for organic synthesis. For example, in the Johnson–Corey–Chaykovsky reaction,^{1,2} sulfur ylide has been used in the synthesis of epoxides, aziridines, and cyclopropanes. A characteristic of ylides is a 1,2-dipolar bond (the ylidic bond) between a carbanion and a positive heteroatom, which may be not only P or S but also other heteroatoms, for example, N or As.

Ylides have been widely studied by both experimental^{3–13} and theoretical and computational^{14–22} methods. Recently, Standard et al.²⁰ performed an ab initio and density functional theory (DFT) study of the bonding in two small sulfur ylides, $\text{H}_2\text{S}-\text{CH}_2$ and $(\text{CH}_3)_2\text{S}-\text{CH}_2$, and they found that bond order for the ylidic bond is 1.4–1.5, intermediate between a single and double bond. The double bond character is usually assumed to arise from a so-called ylene resonance involving π back-donation from the carbanion to the heteroatom. In 2007, Calhorda et al.²³ carried out an energy decomposition analysis and a domain-averaged Fermi hole (DAFH) analysis and found that the relative strength of an ylidic bond is determined not only by π back-donation but also by an electrostatic contribution. They also found that DFT methods seriously underestimate the ylidic bond strength in $\text{H}_3\text{P}-\text{C}(\text{BH}_2)_2$. Thus, we think that it is important to scrutinize the ability of popular and new-generation density functionals to describe the ylidic bond.

To assess the performance of density functionals for ylidic bond dissociation energies (BDEs), one needs to use accurate benchmark data. Unfortunately, because of the short lifetime of the ylide intermediate, there are very few experimental data to which one can directly compare. Therefore, in the present work, we generate high-quality BDEs by using the most reliable available levels of wave function theory (WFT), including the high-level “gold standard” CCSD(T)^{24,25} and CCSD(T)-F12a theories.

Another goal of our study is to validate a large number of density functional theory (DFT) methods and to determine if there are low-cost high-performance DFT methods that can describe the energetics of ylidic bonding in Wittig reactions sufficiently well for practical simulations. To put the results in perspective, we will also test some WFT methods that are more affordable than CCSD(T). From the point of view of validation studies, ylides provide a particularly interesting case study because no ylides were used in the parametrization of any density functional that we know of, nor do they appear to have been used for developing any wave function methods or basis sets. Thus, their study satisfies the often heard request for validation of electronic structure methods on systems quite different from those with which they were developed.

This Article is organized as follows: the computational details and the WFT and DFT methods tested for ylides are described in section 2, and results and discussion are in section 3. Section 4 presents concluding remarks.

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2. COMPUTATIONAL METHODS

2.1. Methodologies and Basis Sets. In the present study, we employed 11 different basis sets, and we list them in Table 1 with the corresponding references, in order of basis set size.

Table 1. Basis Sets Employed in the Present Study

short name	full name	N^a	ref
SVP	<i>b</i>	57	31
AVDZ	aug-cc-pVDZ	95	100,101
AV(D+d)Z	aug-cc-pV(D+d)Z	100	100–102
VDZ-F12	<i>b</i>	114	103
ma-TZVPP	<i>b</i>	151	31,32
VTZ-F12	<i>b</i>	205	103
AVTZ	aug-cc-pVTZ	211	100,101
AV(T+d)Z	aug-cc-pV(T+d)Z	216	100–102
AVQZ	aug-cc-pVQZ	394	30,101
AV(Q+d)Z	aug-cc-pV(Q+d)Z	399	100–102

^a N is the number of contracted basis functions for $\text{PH}_3\text{--CH}_2$. ^bSame as short name.

The geometries of all molecules have been optimized at the MP2/aug-cc-pVTZ level of theory. All energies in this Article are Born–Oppenheimer electronic energies including nuclear

repulsion but not including zero-point vibrational energies or thermal vibrational–rotational energy.

The benchmark energy calculations were performed using the coupled cluster theory with single and double excitations²⁴ and a quasiperturbative treatment of connected triple excitations²⁵ (CCSD(T)) and extrapolation to the limit of a complete basis set (CBS). The complete basis set results were obtained by separate extrapolations^{26,27} of the Hartree–Fock (HF) energy and the correlation energy with the AV(T+d)Z and AV(Q+d)Z basis sets, as:

$$E(\text{CCSD(T)}/\text{CBS}) = E(\text{HF}/\text{CBS}) + \Delta E(\text{CCSD(T)}/\text{CBS}) \quad (1)$$

The Karton–Martin two-point formula²⁸ has been employed for extrapolating HF energies:

$$E(\text{HF}/\text{AV}(n + d)\text{Z}) = E(\text{HF}/\text{CBS}) + A(n + 1)\exp(-9\sqrt{n}) \quad (2)$$

The correction ΔE for CCSD(T) correlation energy has been extrapolated by using the n^{-3} extrapolation formula proposed by Halkier et al.²⁹

Table 2. Density Functionals without Molecular Mechanics Dispersion

type	name	ref	type	name	ref
LSDA	GKSPW91	40–42		MPW3LYP	46,50,70
GGA	BLYP	45,46		O3LYP	46,51
	BP86	45,47		PBE0	52,74
	B86LYP	46,53		SOGGA11-X	73
	B86P86	47,53		X3LYP	72
	B86PW91	43,53	global-hybrid meta-GGAs	BB1K	75
	G96LYP	46,48		BMK	76
	HCTH	49		B1B95	54
	mPWLYP	46,50		MPWB1K	70
	mPWPW	50		MPW1B95	70
	OLYP	46,51		M05	77
	PBE	52		M05-2X	78
	SOGGA11	44		M06	79
meta-GGA	BB95	54		M06-2X	79
	mPWB95	50,54		M06-HF	79
	mPWKCIS	50,60		M08-HX	83
	M06-L	55		M08-SO	83
	M11-L	63		PWB6K	81
	PBEKCIS	52,60		PW6B95	81
	TPSS	56,57		TPSSh	56,57
	revTPSS	62		TPSS1KCIS	82
	TPSSKCIS	57,60,61		τ -HCTHh	59
	VSXC	58	range-separated hybrid GGAs	CAM-B3LYP	88
	τ -HCTH	59		HSE	87
global-hybrid GGAs	BHandH	68		LC-BLYP	84
	BHandHLYP	68		LC- ω PBE	86
	B3LYP	45,46,64,65		ω B97	85
	B3PW91	64		ω B97X	85
	B3P86	45,47,64	range-separated hybrid meta-GGA	M11	89
	B97-1	49	doubly hybrid GGAs	B2PLYP	92
	B97-2	66		MC3MPW	90
	B98	67		mPW2LYP	91
	MPW1K	69	doubly hybrid meta-GGAs	MC3MPWB	82
	MPW1PW	50		MC3TS	82

Table 3. Benchmark Results for Three Small Ylidic BDEs (kcal/mol)^a

method	H ₂ S-CH ₂	NH ₃ -CH ₂	PH ₃ -CH ₂	MSE	MUE
CCSD(T)/CBS	35.90	28.91	59.81		
CCSD(T)-F12a/VTZ-F12	35.99	28.86	59.69	-0.03	0.08
CCSD(T)-F12a/AVDZ	35.81	28.91	59.02	-0.30	0.30
CCSD(T)-F12a/VDZ-F12	36.26	28.45	59.53	-0.13	0.36
CCSD(T)-F12a/SVP	37.34	29.14	60.10	0.65	0.65
MP2/AVTZ	34.21	28.81	59.49	-0.70	0.70
MP2/AV(T+d)Z	36.80	28.81	61.79	0.93	0.99
CCSD(T)/AV(Q+d)Z	34.75	28.25	58.47	-1.05	1.05
MP2/AVQZ	37.38	29.93	62.78	1.82	1.82
CCSD(T)/AVQZ	33.37	28.25	57.33	-1.89	1.89
MP2/AV(Q+d)Z	38.82	29.93	63.98	2.70	2.70
CCSD(T)/AV(T+d)Z	32.82	27.28	56.25	-2.76	2.76
CCSD-F12a/VDZ-F12	32.53	25.94	56.43	-3.24	3.24
CCSD-F12a/VTZ-F12	31.96	26.02	56.36	-3.43	3.43
MP2-F12/AVDZ	39.77	31.08	65.03	3.75	3.75
MP2-F12/SVP	40.26	30.77	64.94	3.79	3.79
MP2/CBS	40.04	30.70	65.30	3.80	3.80
MP2-F12/VDZ-F12	40.17	30.50	65.51	3.85	3.85
MP2-F12/VTZ-F12	40.30	30.74	65.56	3.99	3.99
CCSD(T)/AVTZ	30.34	27.28	54.07	-4.31	4.31
MP2/AV(D+d)Z	30.16	25.93	55.01	-4.51	4.51
MP2/AVDZ	25.67	25.93	50.73	-7.43	7.43
CCSD(T)/AV(D+d)Z	26.79	24.45	49.47	-7.97	7.97
CCSD(T)/AVDZ	22.46	24.45	45.42	-10.76	10.76
HF/CBS	-1.42	-2.30	26.68	-33.88	33.88
HF/AV(Q+d)Z	-1.47	-2.31	26.62	-33.92	33.92
HF/AV(T+d)Z	-1.91	-2.38	26.14	-34.25	34.25
HF/AVQZ	-2.83	-2.31	25.49	-34.76	34.76
HF/AVTZ	-4.37	-2.38	23.93	-35.81	35.81
HF/AV(D+d)Z	-4.50	-2.13	23.18	-36.02	36.02
HF/AVDZ	-9.02	-2.13	18.87	-38.97	38.97

^aGeometries are optimized at the MP2/aug-cc-pVTZ level.

$$\Delta E(\text{CCSD(T)/AV}(n+d)\text{Z}) = \Delta E(\text{CCSD(T)/CBS}) + A n^{-3} \quad (3)$$

where ΔE denotes the difference from HF.

The same extrapolation scheme was also used to calculate the CBS limit of second-order Møller–Plesset perturbation theory³⁰ (MP2).

ma-TZVPP is a basis set, based on the earlier def2-TZVPP basis set,³¹ with a reasonable size for DFT calculations on ylides, and recent work in our group³² showed that it gives good performance for many organic chemistry representative cases. For these reasons, it is the basis set that we use in all DFT methods in this study.

2.2. Tested Methods. First, we tested several WFT methods. Most of them are single-level methods based on selected electronic structure levels, in particular, HF, MP2, SCS-MP2, SCSC-MP2, and CCSD(T) combined with various basis sets. Here, SCS-MP2 denotes spin-component-scaled MP2,³³ and SCSC-MP2 is a SCS-MP2 method optimized for catalysis.³⁴ The MP2, CCSD, and CCSD(T) methods were tested both with conventional one-electron basis sets and with explicitly correlated basis sets. The latter calculations were carried out by the F12 method³⁵ for MP2 and by the F12a method for

Table 4. Benchmark Calculations for the 18 Ylidic BDEs (kcal/mol) of the YBDE18 Database

YBDE18	CCSD(T)-F12a/VTZ-F12	best estimate ^a
F ₂ S-C(BH ₂) ₂	56.88	56.88
F ₂ S-CH ₂	90.49	90.49
H ₂ S-C(BH ₂) ₂	20.85	20.85
H ₂ S-CH ₂	35.99	35.90
Me ₂ S-C(BH ₂) ₂	38.70	38.70
Me ₂ S-CH ₂	51.17	51.17
F ₃ N-C(BH ₂) ₂	11.96	11.96
F ₃ N-CH ₂	52.79	52.79
H ₃ N-C(BH ₂) ₂	32.53	32.53
H ₃ N-CH ₂	28.86	28.91
Me ₃ N-C(BH ₂) ₂	42.06	42.06
Me ₃ N-CH ₂	42.80	42.80
F ₃ P-C(BH ₂) ₂	51.94	51.94
F ₃ P-CH ₂	75.68	75.68
H ₃ P-C(BH ₂) ₂	44.60	44.60
H ₃ P-CH ₂	59.69	59.81
Me ₃ P-C(BH ₂) ₂	66.10	66.10
Me ₃ P-CH ₂	77.36	77.36

^aThe best estimates for F₂S-CH₂, NH₃-CH₂, and PH₃-CH₂ are calculated with CCSD(T)/CBS in Table 1; the rest of the best estimates are calculated with the CCSD(T)-F12a/VTZ-F12 level of theory. All geometries are optimized with MP2/aug-cc-pVTZ.

CCSD(T);³⁶ these methods add explicitly correlated excitations to those expressed in terms of the one-electron basis set. We also tested BMC-CCSD,³⁷ which is a multiefficient correlation method,³⁸ based on combining two levels, MP2 and CCSD, with a specially balanced pair of basis sets.

The tested density functionals can be classified according to various rungs of the so-called “Jacob’s ladder” of DFT.³⁹ The lowest rung is the local spin density approximation (LSDA), in which the density functional depends only on spin densities; the second rung is the generalized gradient approximation (GGA), in which the density functional depends on spin densities and their reduced gradients; the third rung is the meta-GGA, in which the functional also depends on the spin kinetic energy densities; the fourth rung is hyper-GGA, which (for the functionals considered here) employs full or partial Hartree–Fock exchange, in addition to ingredients from one of the lower rungs. There are different types of hyper-GGAs on the fourth rung, and the present study includes global-hybrid GGAs, global-hybrid meta-GGAs, range-separated hybrid GGAs, and range-separated hybrid meta-GGAs. On the fifth (highest) rung, we consider doubly hybrid density functionals that incorporate correlation energies computed from virtual orbitals. In this work, we tested 68 functionals without molecular mechanics terms, in particular one LSDA,^{40–42} 12 GGAs,^{43–53} 11 meta-GGAs,^{54–63} 15 global-hybrid GGAs,^{46,47,49–52,64–74} 17 hybrid meta-GGAs,^{54,56,57,59,70,75–83} six range-separated hybrid GGAs,^{84–88} one range-separated hybrid meta-GGA,⁸⁹ three doubly hybrid GGAs,^{90–92} and two doubly hybrid meta-GGAs.⁸²

We also tested 30 dispersion-corrected density functionals (DFT-D2⁹³ and DFT-D3⁹⁴), in which a molecular mechanics term is added to the energy to improve the treatment of dispersion interactions and their medium-range continuations. Therefore, the total number of density functionals tested is 98 (Table 2).

2.3. Software. MP2, SCS-MP2, SCSC-MP2, CCSD(T), and CCSD(T)-F12a calculations were performed by using

Table 5. Test of WFT-Based Methods against 18 Ylidic BDEs (kcal/mol) in the YBDE18 Database

ylide ^a	best est.	CCSD(T)-F12a ^b	BMC-CCSD	SCS-MP2 ^b	MP2 ^b	MP2-F12 ^b	SCSC-MP2 ^b	HF/VDZ-F12	HF/ma-TZVPP
F ₂ S-C(BH ₂) ₂	56.88	57.59	91.02	59.95	66.50	68.81	99.19	36.92	38.01
F ₂ S-CH ₂	90.49	90.93	57.70	90.04	92.78	97.86	65.61	44.87	43.07
H ₂ S-C(BH ₂) ₂	20.85	21.71	21.53	23.65	28.00	29.61	27.97	5.17	5.95
H ₂ S-CH ₂	35.90	36.26	36.68	35.36	35.93	40.17	42.83	-3.86	-5.40
Me ₂ S-C(BH ₂) ₂	38.70	39.47	40.66	40.98	46.74	48.41	46.27	19.23	19.93
Me ₂ S-CH ₂	51.17	51.38	53.39	50.35	52.06	56.34	58.49	9.12	7.51
F ₃ N-C(BH ₂) ₂	11.96	12.15	12.14	20.61	27.51	27.96	29.84	-20.04	-20.73
F ₃ N-CH ₂	52.79	52.67	55.52	57.58	60.39	63.74	69.87	-3.25	-6.77
H ₃ N-C(BH ₂) ₂	32.53	32.71	32.94	34.81	38.45	39.11	38.48	19.73	19.71
H ₃ N-CH ₂	28.91	28.45	29.78	28.62	27.66	30.50	34.61	-2.85	-6.15
Me ₃ N-C(BH ₂) ₂	42.06	42.37	44.26	44.84	50.21	50.53	50.73	20.47	19.86
Me ₃ N-CH ₂	42.80	42.54	45.10	43.19	43.54	45.99	50.75	5.23	1.59
F ₃ P-C(BH ₂) ₂	51.94	51.76	55.75	55.13	60.81	62.26	59.05	40.51	41.61
F ₃ P-CH ₂	75.68	75.08	78.92	75.65	77.34	81.34	82.60	41.01	39.41
H ₃ P-C(BH ₂) ₂	44.60	45.03	44.77	48.75	53.40	55.44	52.72	32.79	33.41
H ₃ P-CH ₂	59.81	59.53	60.41	60.54	61.09	65.51	67.48	24.65	22.68
Me ₃ P-C(BH ₂) ₂	66.10	66.20	67.78	68.99	75.06	76.96	73.75	50.83	51.32
Me ₃ P-CH ₂	77.36	76.89	79.41	77.37	78.99	83.28	84.67	41.15	39.08
MSE		0.12	1.51	1.99	5.33	7.96	8.58	-28.83	-29.80
MUE		0.38	1.51	2.23	5.47	7.96	8.58	28.83	29.80
MaxUE		0.86	3.81	8.65	15.55	16.00	17.88	56.04	59.56

^aGeometries are optimized at the MP2/aug-cc-pVTZ level. DFT calculations employed the ma-TZVPP basis set. ^bThe VDZ-F12 basis set is employed for CCSD(T)-F12a and MP2-F12 methods, whereas the ma-TZVPP basis set is employed for the SCS-MP2, MP2, and SCSC-MP2 methods.

the Molpro⁹⁵ program. BMC-CCSD results are obtained from Gaussian 09⁸⁰ calculations by using the MLGAUSS software.⁹⁶ All DFT calculations were carried out using a locally modified Gaussian 09^{97,98} program with the ultrafine Lebedev grid based on 99 radial nodes and 590 angular nodes.

3. RESULTS AND DISCUSSION

3.1. Benchmark Calculations. To validate affordable methods for calculating the reference BDEs, we first carried out CCSD(T)/CBS (eq 1) calculations for three small ylides, F₂S-CH₂, H₃N-CH₂, and H₃P-CH₂, and we compared the results to those obtained with some lower-cost methods. The mean unsigned error (MUE) and mean signed error (MSE) for each of the tested WFT methods are shown in Table 3.

As expected, HF gives very large errors for the ylidic bond energies because it totally neglects the correlation energy. Adding correlation by using MP2/AVTZ already provides good results, which are even better than those obtained with the much more complete CCSD(T)/AV(Q+d)Z method. However, this good performance of MP2/AVTZ is due to a cancelation of errors between the incompleteness of the basis set and the neglect of higher-order correlation effects.

However, the undisputed best performer of the less expensive methods for these compounds is the CCSD(T)-F12a method. CCSD(T)-F12a, even with a very small basis set such as SVP, outperforms CCSD(T) even when the latter is employed with AV(T+d)Z. CCSD(T)-F12a/VTZ-F12 gives the best average performance, with an MUE of 0.08 kcal/mol. Therefore, it is the method that we employed to calculate the remaining 15 ylidic BDEs of the new database. We call this database YBDE18, and we present it in Table 4.

3.2. Performance of Wave Function Theory Methods. The results for eight WFT methods applied to the whole

YBDE18 database are listed in Table 5. CCSD(T)-F12a/VDZ-F12 gives very good performance, being the only method among the ones that we tested with an MUE below 1 kcal/mol. Only two other methods, BMC-CCSD and SCS-MP2, have an MUE smaller than 3 kcal/mol, while all others do not provide satisfactory results. SCS-MP2 performs much better than the canonical MP2 method; however, with the ma-TZVPP basis set used in these calculations, the F₃N-C(BH₂)₂ case is very difficult for both methods, with errors of 8.65 and 15.55 kcal/mol, respectively. BMC-CCSD, however, performs well even for this difficult case.

3.3. Performance of DFT Methods. We now analyze the performance of DFT methods, and for ease of digesting the results we divide the density functionals into seven categories, following and expanding the “Jacob’s ladder” of DFT discussed above. The categories that we used are: (1) LSDA and GGA; (2) meta-GGA; (3) global-hybrid GGA; (4) global-hybrid meta-GGA; (5) range-separated hybrids (GGAs and one meta-GGA); (6) doubly hybrid GGAs and doubly hybrid meta-GGAs; and (7) dispersion-corrected DFT in which molecular mechanics terms are added to account empirically for dispersion. Results for each of the classes of functionals are presented and discussed in the next sections.

3.3.1. LSDA and GGA. LSDA notoriously overbinds molecules, and this trend is confirmed by its large positive MSE in Table 6. All GGAs overcorrect LSDA on average, which leads to negative MSEs. Among the tested GGAs, SOGGA11 and PBE are the best performers, whereas GGAs with the LYP correlation give the largest MUE. The ylides that have the -C(BH₂)₂ fragment are challenging cases for GGAs. None of the GGAs has an MUE below 5 kcal/mol.

3.3.2. Meta-GGAs. Table 7 presents the results for meta-GGAs, and it shows that the VSXC and M06-L functionals are the most accurate meta-GGAs, with MUEs of ~5 kcal/mol, and

Table 6. Test of LSDA^a and GGAs for the YBDE18 Database (kcal/mol)

ylide ^b	best est.	SOGGA11	PBE	mPWPW	B86PW91	BP86	HCTH	B86LYP	mPWLYP	OLYP	BLYP	B86P86	G96LYP	GKSPW91
F ₂ S-C(BH ₂) ₂	56.88	54.34	51.22	48.96	52.72	47.87	48.67	46.54	41.81	44.43	40.01	53.51	38.57	63.47
F ₂ S-CH ₂	90.49	97.06	96.10	93.18	86.80	93.70	89.43	86.25	91.21	89.42	89.10	89.67	86.76	116.25
H ₂ S-C(BH ₂) ₂	20.85	17.29	16.13	14.29	16.38	13.33	12.47	10.97	8.06	9.46	6.52	17.08	5.27	26.11
H ₂ S-CH ₂	35.90	41.63	42.73	40.24	32.75	40.89	35.92	32.58	38.60	36.94	36.84	35.43	34.90	60.17
Me ₂ S-C(BH ₂) ₂	38.70	31.89	30.99	28.54	30.58	27.67	25.83	24.89	21.86	21.59	19.83	31.88	17.91	44.38
Me ₂ S-CH ₂	51.17	56.99	55.66	52.73	44.79	53.39	48.40	44.98	51.36	48.64	49.13	47.94	46.44	75.38
F ₃ N-C(BH ₂) ₂	11.96	15.44	14.17	12.43	16.16	11.75	9.04	13.61	10.08	5.14	8.08	17.52	5.67	26.54
F ₃ N-CH ₂	52.79	64.99	63.93	61.69	56.73	62.49	55.22	59.17	64.18	55.32	61.95	59.96	58.93	84.44
H ₃ N-C(BH ₂) ₂	32.53	28.53	27.10	25.12	26.96	24.43	22.35	22.36	19.75	19.62	18.01	11.16	16.64	39.48
H ₃ N-CH ₂	28.91	31.29	31.49	29.16	20.42	30.40	23.59	22.34	29.48	25.74	27.60	18.15	25.37	48.57
Me ₃ N-C(BH ₂) ₂	42.06	25.89	29.38	26.84	28.94	26.53	19.49	23.60	20.45	15.62	18.11	14.25	16.00	46.30
Me ₃ N-CH ₂	42.80	38.43	40.26	37.46	28.49	39.00	29.38	30.30	37.45	30.47	35.08	27.11	32.18	60.90
F ₃ P-C(BH ₂) ₂	51.94	41.44	39.37	37.45	45.12	36.08	37.73	37.36	29.02	33.34	27.40	28.41	26.72	51.73
F ₃ P-CH ₂	75.68	74.35	74.27	71.72	69.42	72.07	68.50	67.27	68.39	68.41	66.51	65.84	65.07	94.79
H ₃ P-C(BH ₂) ₂	44.60	37.50	35.89	34.24	39.33	33.06	33.58	33.47	27.99	29.92	26.47	22.53	25.29	45.34
H ₃ P-CH ₂	59.81	60.95	61.77	59.52	54.43	60.07	55.58	54.27	58.29	56.40	56.52	50.91	54.59	78.59
Me ₃ P-C(BH ₂) ₂	66.10	55.22	54.62	52.35	57.57	51.20	50.94	50.81	45.02	45.79	43.08	41.31	41.47	68.12
Me ₃ P-CH ₂	77.36	77.67	77.46	74.84	69.68	75.41	70.92	69.13	73.13	70.91	71.08	66.49	68.89	96.97
MSE		-1.65	-2.11	-4.43	-5.74	-4.51	-7.97	-8.37	-8.02	-9.63	-9.96	-10.08	-11.88	13.72
MUE		5.83	5.99	6.45	6.64	6.94	8.24	9.26	9.75	10.03	11.08	11.49	12.56	13.75
MaxUE		16.17	12.68	15.21	14.31	15.86	22.56	18.46	22.93	26.44	24.55	27.80	26.06	31.65

^aGKSPW91. ^bGeometries are optimized at the MP2/aug-cc-pVTZ level. DFT calculations employed the ma-TZVPP basis set.

Table 7. Test of Meta-GGAs for the YBDE18 Database (kcal/mol)

ylide ^a	best est.	VSXC	M06-L	M11-L	revTPSS	TPSSKICIS	τ -HCTH	TPSS	PBEKICIS	mPWKCIS	mPWB95	BB95
F ₂ S–C(BH ₂) ₂	56.88	48.52	51.00	53.97	51.01	47.61	48.50	48.49	49.17	47.42	47.32	45.51
F ₂ S–CH ₂	90.49	93.27	91.07	95.80	86.18	89.34	89.68	86.35	98.86	96.29	98.25	96.15
H ₂ S–C(BH ₂) ₂	20.85	9.99	13.78	14.89	16.91	13.31	13.53	14.35	13.88	12.47	12.81	11.26
H ₂ S–CH ₂	35.90	36.50	37.68	42.81	34.57	37.06	37.67	34.33	45.04	42.87	45.04	43.28
Me ₂ S–C(BH ₂) ₂	38.70	33.94	28.84	31.72	30.72	26.84	26.61	27.95	28.72	26.77	27.84	25.80
Me ₂ S–CH ₂	51.17	53.38	49.25	57.05	45.87	48.74	49.26	45.82	58.30	55.70	57.83	55.60
F ₃ N–C(BH ₂) ₂	11.96	12.41	10.30	1.99	12.58	10.74	9.63	11.38	12.29	10.69	11.64	9.61
F ₃ N–CH ₂	52.79	60.27	54.90	49.07	52.35	57.13	56.28	53.80	67.01	64.73	67.47	65.24
H ₃ N–C(BH ₂) ₂	32.53	21.21	24.03	23.67	27.91	24.18	23.73	25.76	24.25	22.75	23.87	22.12
H ₃ N–CH ₂	28.91	25.42	27.06	32.20	25.62	27.03	26.90	25.15	32.81	30.79	33.83	31.97
Me ₃ N–C(BH ₂) ₂	42.06	43.22	28.80	26.57	31.63	25.99	22.72	28.43	25.29	23.28	27.47	25.09
Me ₃ N–CH ₂	42.80	47.58	35.97	41.42	34.82	34.93	33.06	33.50	40.95	38.47	43.05	40.65
F ₃ P–C(BH ₂) ₂	51.94	40.35	43.96	51.55	40.55	36.87	38.58	38.41	36.51	35.17	35.04	33.40
F ₃ P–CH ₂	75.68	75.43	74.44	84.53	65.97	68.74	70.03	66.55	76.06	73.93	75.91	74.03
H ₃ P–C(BH ₂) ₂	44.60	32.54	35.99	37.35	37.94	34.34	34.55	35.49	33.26	31.99	32.09	30.56
H ₃ P–CH ₂	59.81	58.92	59.21	64.28	55.02	57.45	57.47	54.98	63.62	61.61	63.81	62.05
Me ₃ P–C(BH ₂) ₂	66.10	60.20	56.81	59.31	54.10	50.92	51.60	52.03	52.33	50.53	50.76	48.79
Me ₃ P–CH ₂	77.36	76.35	75.10	82.43	68.02	71.39	72.18	68.72	79.83	77.52	79.07	77.02
MSE		–2.84	–4.57	–1.66	–6.04	–6.55	–6.59	–7.17	–2.35	–4.31	–2.64	–4.58
MUE		5.00	5.07	6.08	6.11	7.16	7.17	7.28	7.88	7.98	8.12	8.49
MaxUE		12.06	13.26	15.49	12.00	16.07	19.34	14.07	16.77	18.78	16.91	18.54

^aGeometries are optimized at the MP2/aug-cc-pVTZ level. DFT calculations employed the ma-TZVPP basis set.

BB95 is the least accurate. All tested meta-GGAs have negative MSEs showing their systematic underestimation of BDEs for ylides, especially for the ones containing the C(BH₂)₂ fragment. In general, meta-GGA functionals perform better than the GGA functionals in Table 6, with some interesting exceptions. M11-L, for example, is (perhaps unexpectedly) worse than SOGGA11, but it is a trend that might have been anticipated by comparing the performances of the two functionals for the four alkyl bond dissociation energies in the ABDE4/05 database⁷³ that was used in the training sets of both functionals (see, e.g., Table 2 of ref 62). Despite being much better for most of the databases previously tested, M11-L is in fact about 5% worse than SOGGA11 for the ABDE4/05 database.

3.3.3. Global-Hybrid GGAs. Among the tested global-hybrid GGAs (Table 8), PBE0 is the best performer in terms of MUE for the YBDE18 database. B3P86 and SOGGA11-X have the second and third best overall MUE, but SOGGA11-X has the smallest systematic error in terms of MSE. All global-hybrid GGAs except BHandH give negative MSEs, and the worst performer is BHandHLYP. The hybrid GGAs that involve the LYP correlation give the worst performance, and this is the same trend as already observed in Table 6.

3.3.4. Global-Hybrid Meta-GGA. Among the 16 global-hybrid meta-GGAs that we tested (results are in Table 9), M05-2X has the best performance with an MUE of only 1.09 kcal/mol, very close to the so-called “chemical accuracy” of 1 kcal/mol. M08-HX is the only other functional with an MUE below 2 kcal/mol. We find that 14 global-hybrid meta-GGAs (out of 17 tested) have smaller MUEs than any of the 24 tested local functionals. Clearly, some amount of Hartree–Fock exchange is required for good accuracy. TPSSH is the worst performer in Table 9.

3.3.5. Range-Separated Hybrid GGA and Meta-GGA. Table 10 presents the results for range-separated hybrid GGAs and the only range-separated hybrid meta-GGA. The LC-BLYP long-range corrected functional is the best performer with an MUE of 1.13 kcal/mol, almost as good as M05-2X. Our new M11

functional once again has the smallest MSE, but its MUE is slightly above 2 kcal/mol, and not as good as that of LC-BLYP, ω B97, and ω B97X. CAM-B3LYP gives the worst performance in Table 9.

3.3.6. Doubly Hybrid DFT. Doubly hybrid functionals contain a portion of the MP2-type correlation energy as well as nonlocal exchange. Performances for this class of functionals on YBDE18 are collected in Table 11. The MC3-type doubly hybrid functionals are the best performers for ylide bond dissociation energies, outperforming the B2PLYP functional. However, only the MC3MPWB has an MUE below 2 kcal/mol, being close to the performance of M05-2X and LC-BLYP but not as good as them, and at a higher computational cost.

3.3.7. DFT-D. Table 12 presents the statistical errors of 30 DFT-D methods, including ω B97X-D of Chai and Head-Gordon⁹⁹ and many DFT-D2⁹³ and DFT-D3⁹⁴ methods of Grimme. Comparing the MUEs in Table 12 to those in previous tables, we can see that the addition of molecular-mechanics dispersion corrections in general improves the performance of DFT. M05-2X-D3 and MPWB1K-D3 are the two best DFT-D methods for the YBDE18 database. Comparing DFT-D2 and DFT-D3, we found that B97-D2 is slightly better than B97-D3 for the YBDE18 database.

4. CONCLUDING REMARKS

We developed a database of 18 ylidic bond dissociation energies called YBDE18 based on benchmark calculations using WFT methods of high accuracy. The new database is composed of three ylidic BDEs calculated by CCSD(T)/CBS and 15 BDEs calculated by CCSD(T)-F12a/VTZ-F12. The YBDE18 database is recommended for future tests and parametrization of methods aimed at treatment of ylides of large size.

We have tested eight WFT methods and 98 density functionals against the YBDE18 database, and our conclusions are:

Table 8. Test of Global-Hybrid GGAs for the YBDE18 Database (kcal/mol)

ylide ^a	best est.	PBE0	B3P86	SOGGA11-X	MPWIK	MPW1PW91	B97-2	B97-1	B97-3	B3PW91	B98	BHandH	X3LYP	B3LYP	O3LYP	BHandHLYP
F ₂ S-C(BH ₂) ₂	56.88	54.84	52.46	52.98	55.31	52.91	50.56	49.08	89.68	50.51	47.80	63.35	45.93	44.86	46.72	47.69
F ₂ S-CH ₂	90.49	90.48	91.79	91.98	84.78	88.13	92.31	91.26	48.58	88.32	88.97	98.26	87.86	87.27	88.25	80.68
H ₂ S-C(BH ₂) ₂	20.85	19.57	17.48	18.38	20.25	18.00	15.58	15.14	14.38	15.84	14.08	26.77	11.79	10.88	11.69	13.59
H ₂ S-CH ₂	35.90	37.40	38.86	39.84	32.33	35.40	39.89	39.22	37.59	35.71	37.11	43.80	35.34	34.91	35.73	28.87
Me ₂ S-C(BH ₂) ₂	38.70	34.92	32.50	33.42	35.56	32.88	29.74	29.73	28.63	30.28	28.48	45.04	26.26	25.04	24.53	28.51
Me ₂ S-CH ₂	51.17	50.58	51.75	52.61	45.42	48.24	52.29	52.04	50.10	48.24	49.86	59.19	48.35	47.66	47.76	42.13
F ₃ N-C(BH ₂) ₂	11.96	10.89	10.96	4.93	6.64	9.42	7.15	8.77	5.99	8.81	7.79	14.84	7.72	7.06	5.36	1.71
F ₃ N-CH ₂	52.79	52.58	56.23	50.03	43.04	50.81	54.99	56.72	53.24	52.65	54.91	56.67	55.42	55.23	52.60	41.63
H ₃ N-C(BH ₂) ₂	32.53	31.30	29.13	29.54	32.24	29.61	26.48	27.11	26.14	27.33	26.43	41.31	24.17	23.05	22.52	26.54
H ₃ N-CH ₂	28.91	27.89	29.29	31.76	24.11	26.04	30.20	31.26	28.96	26.08	29.68	36.83	27.36	26.72	25.45	22.93
Me ₃ N-C(BH ₂) ₂	42.06	34.35	32.19	32.69	35.41	32.20	27.56	29.59	27.25	29.27	28.62	48.26	25.86	24.35	19.95	28.86
Me ₃ N-CH ₂	42.80	37.16	38.56	40.86	33.38	34.93	38.07	40.08	36.87	34.52	38.36	49.25	35.99	35.05	31.14	32.00
F ₃ P-C(BH ₂) ₂	51.94	47.90	44.74	47.89	51.78	46.23	43.57	41.57	41.98	42.95	40.67	59.70	37.57	36.30	37.82	44.18
F ₃ P-CH ₂	75.68	74.13	74.63	77.83	72.34	72.05	75.86	74.38	73.71	71.29	72.53	85.97	70.01	69.19	69.67	68.43
H ₃ P-C(BH ₂) ₂	44.60	41.60	39.33	41.55	43.99	40.20	37.94	36.87	36.78	37.65	35.93	50.19	33.72	32.72	33.19	37.93
H ₃ P-CH ₂	59.81	58.78	60.12	62.59	55.51	56.99	61.42	60.91	59.59	56.91	59.01	66.89	57.02	56.47	56.33	53.13
Me ₃ P-C(BH ₂) ₂	66.10	61.25	58.55	60.78	63.77	59.34	56.27	55.40	55.14	56.31	54.28	73.19	51.96	50.64	49.97	56.89
Me ₃ P-CH ₂	77.36	75.31	76.34	78.74	72.34	73.24	77.14	76.62	75.30	72.82	74.70	85.95	72.81	72.05	71.42	69.65
MSE		-2.20	-2.53	-1.79	-4.02	-4.11	-3.53	-3.60	-5.03	-5.28	-5.07	6.94	-6.97	-7.84	-8.36	-8.62
MUE		2.37	3.53	3.57	4.02	4.11	4.89	4.97	5.28	5.28	5.53	6.94	7.26	8.11	8.36	8.62
MaxUE		7.71	9.87	9.37	9.75	9.86	14.50	12.46	14.81	12.79	13.44	10.29	16.19	17.70	22.11	13.19

^aGeometries were optimized at the MP2/aug-cc-pVTZ level. DFT calculations employed the ma-TZVPP basis set.

Table 9. Test of Global-Hybrid Meta-GGAs for the YBDE18 Database (kcal/mol)

ylide ^a	best est.	M05-2X	M08-HX	M06-2X	MPWB1K	PWB6K	M08-SO	BB1K	MPWB1B95	B1B95	PW6B95	M06-HF	M06	BMK	M05	τ_c HC1Th	TPSS1KClS	TPSSH
F ₃ S-C(BH ₂) ₂	56.88	56.90	53.69	54.99	54.38	54.14	51.89	53.03	52.51	50.74	50.31	59.13	50.57	47.37	53.11	49.35	49.64	50.03
F ₂ S-CH ₂	90.49	92.07	86.39	86.94	89.88	89.10	85.72	88.99	92.23	91.25	91.05	85.14	87.23	86.03	90.14	91.01	87.64	85.03
H ₂ S-C(BH ₂) ₂	20.85	21.34	21.06	20.31	19.43	19.23	19.81	18.25	17.68	16.13	15.84	28.65	15.55	14.82	16.09	15.12	15.14	15.74
H ₂ S-CH ₂	35.90	38.62	35.76	34.64	37.07	36.33	35.54	36.34	39.23	38.45	38.25	35.60	36.28	34.26	37.46	38.76	35.30	32.96
Me ₂ S-C(BH ₂) ₂	38.70	38.35	37.27	36.53	35.56	35.42	36.30	34.03	33.50	31.50	31.41	44.33	30.90	30.06	29.90	29.57	29.09	29.65
Me ₂ S-CH ₂	51.17	53.40	49.35	48.47	50.44	49.83	49.11	49.42	52.43	51.29	51.35	49.72	48.77	47.46	49.76	51.39	47.29	44.69
F ₃ N-C(BH ₂) ₂	11.96	11.61	10.93	10.66	6.18	6.01	8.31	5.27	8.13	7.05	7.87	13.63	7.69	6.89	6.18	10.06	9.16	10.13
F ₃ N-CH ₂	52.79	53.50	48.78	48.27	48.54	47.86	48.59	48.06	54.15	53.79	54.76	47.03	51.46	52.37	50.20	57.54	52.48	50.21
H ₃ N-C(BH ₂) ₂	32.53	32.20	32.55	32.50	31.79	31.65	30.68	30.45	29.75	27.97	27.75	40.92	26.25	28.55	24.63	26.63	26.35	27.42
H ₃ N-CH ₂	28.91	30.62	28.64	28.04	28.90	28.46	28.46	28.00	30.20	29.17	29.30	31.66	27.79	29.48	27.30	30.13	25.90	24.28
Me ₃ N-C(BH ₂) ₂	42.06	41.06	40.95	40.36	37.00	36.85	40.16	35.19	34.51	32.14	32.35	52.71	32.02	33.34	24.53	29.19	28.46	30.31
Me ₃ N-CH ₂	42.80	44.73	41.13	40.61	39.14	38.74	41.34	37.88	40.16	38.67	39.18	47.63	38.83	40.11	33.88	39.01	34.08	32.85
F ₃ P-C(BH ₂) ₂	51.94	51.89	49.77	50.52	50.16	50.12	47.44	48.57	46.05	43.86	43.18	55.76	44.17	43.18	46.93	41.18	41.24	41.74
F ₃ P-CH ₂	75.68	77.53	73.57	73.13	76.66	76.11	72.37	75.50	76.42	74.98	74.45	72.73	71.86	73.58	74.36	73.42	69.62	67.21
H ₃ P-C(BH ₂) ₂	44.60	44.98	42.60	43.17	42.51	42.60	42.18	41.19	39.67	37.88	37.75	52.50	37.74	36.90	39.29	36.60	37.17	37.65
H ₃ P-CH ₂	59.81	61.54	57.28	57.29	59.79	59.40	57.80	58.90	60.81	59.78	59.83	59.57	57.77	58.40	59.21	60.05	56.71	54.40
Me ₃ P-C(BH ₂) ₂	66.10	65.06	63.03	63.04	62.98	63.08	62.24	61.30	59.66	57.41	57.30	68.11	57.97	56.57	57.59	55.09	54.53	54.78
Me ₃ P-CH ₂	77.36	78.51	73.74	73.62	76.62	76.25	73.81	75.49	77.21	75.87	75.89	73.30	73.74	74.92	74.87	75.74	71.36	68.68
MSE	0.74	0.74	-1.89	-2.08	-1.86	-2.19	-2.71	-3.04	-2.01	-3.48	-3.49	2.09	-4.66	-4.79	-4.73	-3.93	-6.08	-6.82
MUE	1.09	1.09	1.92	2.08	2.10	2.28	2.71	3.09	3.20	4.00	4.09	4.32	4.71	4.85	4.90	5.02	6.08	6.82
MaxUE	2.71	2.71	4.10	4.52	5.79	5.95	4.98	6.86	7.55	9.92	9.71	10.65	10.04	9.53	17.53	12.87	13.60	11.75

^aGeometries were optimized at the MP2/aug-cc-pVTZ level. DFT calculations employed the ma-TZVPP basis set.

Table 10. Test of Range-Separated Hybrid GGAs and One Range-Separated Hybrid Meta-GGA for the YBDE18 Database (kcal/mol)

ylide ^a	best est.	LC-BLYP	ω B97	ω B97X	M11	LC- ω PBE	HSE	CAM-B3LYP
F ₂ S–C(BH ₂) ₂	56.88	54.59	56.17	54.18	53.30	56.20	54.33	48.70
F ₂ S–CH ₂	90.49	90.18	91.67	90.07	91.45	86.48	89.98	87.84
H ₂ S–C(BH ₂) ₂	20.85	19.48	20.53	18.82	19.38	21.17	19.07	14.20
H ₂ S–CH ₂	35.90	36.09	38.14	36.68	39.24	33.03	36.89	34.63
Me ₂ S–C(BH ₂) ₂	38.70	36.48	37.25	35.16	35.91	37.09	34.46	29.57
Me ₂ S–CH ₂	51.17	51.22	52.38	50.80	53.00	46.84	50.09	48.41
F ₃ N–C(BH ₂) ₂	11.96	11.00	10.03	9.32	12.28	9.84	11.12	7.93
F ₃ N–CH ₂	52.79	53.02	50.90	50.89	55.93	46.35	52.85	52.98
H ₃ N–C(BH ₂) ₂	32.53	34.19	31.83	31.06	31.41	33.71	30.67	27.64
H ₃ N–CH ₂	28.91	30.40	30.67	29.50	32.47	25.10	27.31	27.85
Me ₃ N–C(BH ₂) ₂	42.06	39.79	38.41	36.38	40.92	38.54	33.91	30.82
Me ₃ N–CH ₂	42.80	42.31	42.49	40.50	45.86	35.71	36.71	37.73
F ₃ P–C(BH ₂) ₂	51.94	50.48	51.00	48.66	48.10	51.98	47.05	41.98
F ₃ P–CH ₂	75.68	77.26	77.34	75.31	77.01	73.06	73.30	71.83
H ₃ P–C(BH ₂) ₂	44.60	44.32	45.19	42.63	41.24	45.58	41.07	37.18
H ₃ P–CH ₂	59.81	60.88	62.28	60.08	61.03	56.91	58.23	57.50
Me ₃ P–C(BH ₂) ₂	66.10	66.01	66.34	63.44	62.14	66.30	60.70	56.71
Me ₃ P–CH ₂	77.36	79.62	79.85	77.54	77.94	74.57	74.75	74.42
MSE		–0.18	0.11	–1.64	–0.11	–2.34	–2.67	–5.15
MUE		1.13	1.43	1.84	2.25	2.64	2.79	5.17
MaxUE		2.29	3.65	5.68	3.96	7.09	8.15	11.24

^aGeometries were optimized at the MP2/aug-cc-pVTZ level. DFT calculations employed the ma-TZVPP basis set.**Table 11. Test of Doubly Hybrid Density Functionals for the YBDE18 Database (kcal/mol)**

ylide ^a	best est.	MC3MPWB	MC3MPW	MC3TS	mPW2PLYP	B2PLYP
F ₂ S–C(BH ₂) ₂	56.88	55.94	57.95	56.32	52.74	51.94
F ₂ S–CH ₂	90.49	90.99	89.00	88.35	88.78	88.91
H ₂ S–C(BH ₂) ₂	20.85	20.41	22.08	20.63	17.20	16.41
H ₂ S–CH ₂	35.90	36.04	33.92	33.06	34.96	35.04
Me ₂ S–C(BH ₂) ₂	38.70	37.26	38.54	36.79	33.36	32.37
Me ₂ S–CH ₂	51.17	50.19	47.99	46.89	49.25	49.15
F ₃ N–C(BH ₂) ₂	11.96	15.93	18.30	18.79	12.79	13.17
F ₃ N–CH ₂	52.79	56.87	55.20	56.22	55.10	56.29
H ₃ N–C(BH ₂) ₂	32.53	33.31	34.61	33.18	29.09	28.04
H ₃ N–CH ₂	28.91	28.87	26.46	26.07	27.37	27.10
Me ₃ N–C(BH ₂) ₂	42.06	40.48	40.87	39.59	34.49	33.32
Me ₃ N–CH ₂	42.80	40.88	38.19	37.81	38.71	38.32
F ₃ P–C(BH ₂) ₂	51.94	49.29	51.44	48.93	46.13	44.68
F ₃ P–CH ₂	75.68	74.37	72.46	70.68	72.72	72.09
H ₃ P–C(BH ₂) ₂	44.60	43.65	45.88	44.58	40.73	39.67
H ₃ P–CH ₂	59.81	59.30	57.53	56.92	58.33	58.10
Me ₃ P–C(BH ₂) ₂	66.10	64.49	66.40	64.35	60.37	59.04
Me ₃ P–CH ₂	77.36	76.31	74.64	73.38	75.03	74.59
MSE		–0.33	–0.50	–1.56	–2.97	–3.46
MUE		1.38	2.14	2.77	3.31	3.98
MaxUE		4.08	6.33	6.83	7.57	8.74

^aGeometries were optimized at the MP2/aug-cc-pVTZ level. DFT calculations employed the ma-TZVPP basis set.

- (a) CCSD(T)-F12a/VDZ-F12 has a very small MUE of 0.38 kcal/mol, and it is a validated choice for the benchmark calculations of BDEs of large ylides for which CCSD(T)-F12a/VTZ-F12 is not affordable.
- (b) DFT functionals with a nonzero percentage of Hartree–Fock exchange are in general a good and practical way to

treat ylide bond dissociation energies, with 10 functionals having MUEs smaller than 2 kcal/mol (versus only two of the tested WFT methods), and more than 20 functionals with MUEs smaller than 3 kcal/mol (versus only three of the tested WFT methods).

Table 12. Statistical Errors of DFT-D Methods for the YBDE18 Database (kcal/mol)

best estimate ^a	MSE	MUE	MaxUE
M05-2X-D3	0.93	1.08	2.74
MPWB1K-D3	−0.55	1.09	4.10
PBE0-D3	−0.72	1.24	4.06
PWB6K-D3	−1.47	1.63	5.04
M06-2X-D3	−2.01	2.01	4.50
mPW2PLYP-D2	−1.68	2.27	4.15
MPWB1B95-D3	−0.61	2.38	4.12
B1B95-D3	−1.19	2.44	5.18
LC- ω PBE-D3	−0.56	2.50	5.35
B2PLYP-D2	−1.69	2.55	4.97
ω B97X-D	−2.53	2.55	5.56
BMK-D3	−2.20	2.57	6.62
B3PW91-D3	−2.53	2.79	6.15
B2BLYP-D3	−2.13	2.93	5.62
PW6B95-D3	−2.35	3.29	7.36
CAMB3LYP-D3	−3.47	3.61	7.91
M05-D3	−3.79	3.99	15.15
M06-HF-D3	2.25	4.41	11.14
M06-D3	−4.37	4.42	9.23
TPSSH-D3	−4.88	4.94	7.84
M06-L-D3	−4.49	4.99	12.99
OLYP-D3	−3.11	5.09	11.48
PBE-D3	−0.74	5.36	11.96
BP86-D3	−1.73	5.39	12.44
TPSS-D3	−5.18	5.63	11.12
B3LYP-D3	−5.41	5.85	12.66
B97-D2	−6.06	6.69	14.71
B97-D3	−5.99	6.76	15.22
BLYP-D3	−6.95	8.40	20.85
MPWLYP-D3	−6.26	8.48	20.80

^aGeometries were optimized at the MP2/aug-cc-pVTZ level. DFT calculations employed the ma-TZVPP basis set.

- (c) Conventional GGA, local meta-GGA, or global-hybrid GGA functionals do not provide satisfactory results (the MUE of the best GGA is 5.83 kcal/mol, and that of the best meta-GGA is 5.00 kcal/mol; PBE0 is the best global-hybrid GGA with an MUE of 2.37 kcal/mol, and all other global-hybrid GGAs have MUEs above 3.5 kcal/mol). Functionals that are capable of good performance on YBDE18 always include a combination of two or more advanced ingredients such as the kinetic energy density (meta-GGA), range-separated HF exchange, molecular mechanics corrections for dispersion (-D3), and a portion of the MP2 correlation energy (doubly hybrid).
- (d) M05-2X-D3 and MPWB1K-D3 are the recommended functionals with molecular mechanics components. Although M05-2X and LC-BLYP do not have molecular mechanics dispersion components, they perform equally well.

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Notes

The authors declare no competing financial interest.

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