Hybrid Meta Density Functional Theory Methods for Thermochemistry, Thermochemical Kinetics, and Noncovalent Interactions: The MPW1B95 and MPWB1K Models and Comparative Assessments for Hydrogen Bonding and van der Waals Interactions

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Based on the modified Perdew and Wang exchange functional (MPW) and Becke's 1995 correlation functional (B95), we developed two hybrid meta density functional theory (HMDFT) methods, namely MPW1B95 and MPWB1K. In addition, based on the new X functional of Xin and Goddard, again combined with B95 correlation functional, we developed two other new HMDFT methods, X1B95 and XB1K. MPW1B95 and X1B95 were optimized against a representative database of six atomization energies (AE6). MPWB1K and XB1K were optimized against a kinetics database of three forward barrier heights, three reverse barrier heights, and three energies of reaction for the reactions in the BH6 representative barrier height database. We compared the newly developed methods to other HMDFT and hybrid DFT methods for atomization energies, ionization potentials, electron affinities, barrier heights, saddle point geometries, hydrogen bonding, and weak van der Waals weak interactions. In addition, we optimized scaling factors for calculating zero-point energies from vibrational frequencies. The results show that the MPWB1K and XB1K methods give good results for thermochemistry, thermochemical kinetics, hydrogen bonding, and weak interactions, and they give excellent saddle point geometries. MPW1B95 and X1B95 are suitable for general applications in thermochemistry, and they give good performance for hydrogen bonding and weak interaction calculations.

1. Introduction

Refining functionals for density functional theory (DFT) is an active research area in theoretical chemistry and physics.[1−28] There are two main strategies for developing new functionals, namely the nonempirical approach and the semiempirical approach. The nonempirical approach, favored in physics, is to construct functionals subject to several exact constraints. The typical nonempirical approach is the "Jacob's ladder" scheme[27,29,30] advanced by Perdew and co-workers. This strategy can be viewed as a ladder with five rungs, from the local density approximation (LDA) up to the "divine" exact exchange and exact correlation functional. PBE1PBE[7] is an example of a DFT functional developed by this approach, and it can be said to contain no empirical parameter, although setting the fraction of Hartree−Fock exchange equal to 0.25 was justified by an empirical approach[4] before it was explained[8] theoretically. The semiempirical way to construct functionals, which has been very successful in chemistry, is to choose a flexible mathematical functional form depending on one or more parameters and then to fit these parameters to molecular thermochemical data. B3LYP,[5] B1B95,[6] and B97-2[22] are examples of functionals determined by the empirical approach. These approaches are only partly empirical because the functional forms are guided by theory. Furthermore the most successful semiempirical methods, called hybrid DFT (HDFT),[4,31] doubly hybrid DFT[32] (DHDFT), or hybrid meta DFT[33] (HMDFT), and doubly hybrid MDFT[32] (DHMDFT) are all only partly DFT because they mix a pure DFT functional with, respectively, some Hartree−Fock nonlocal exchange,[4,31] nonlocal exchange with perturbation theory corrections,[32] nonlocal exchange with kinetic energy density,[33] or nonlocal exchange, perturbation theory corrections, and kinetic energy density.[32] In all of these methods, the pure DFT part of the functional depends not only on the local density but also its gradient; this aspect is sometimes called the generalized gradient approximation (GGA).

Besides the refinement of the exchange and correlation functionals, another important problem is the validation of the currently available functionals for different purposes in chemistry and physics. According to our resent assessment,[34] some hybrid DFT and hybrid meta DFT methods such as B3LYP,[5] mPW1PW91,[11] B1B95,[6] and B97-2[22] are successful for thermochemistry but unsatisfactory for kinetics. Our assessments[18,34] showed that MPW1K[18] is an HDFT model with excellent performance for kinetics. Recently, we optimized a Becke88-Becke95 1-parameter model for kinetics (BB1K) against a representative benchmark kinetics database, and we found even better performance for kinetics.[35]

The question arises though of whether one can find an HDFT or HMDFT functional that performs well for the whole spectrum of bond types, that is (i) normal bonds, as in covalently bonded stable molecules; (ii) partial bonds, as at transition states; (iii) hydrogen bonds, and (iv) weak interactions as in dispersion-dominated bonding of van der Waals molecules. Early tests[36] focused on normal bonds and transition states, with the latter judged mainly by barrier heights, and further tests[18,34] for transition states are mentioned in the previous paragraph. Staroverov et al.[37] showed that some HDFT and HMDFT methods can predict hydrogen bond energies within 0.7 and 0.6 kcal/mol, respectively, and Adamo and Barone[11] and Xin and Goddard[28] showed that some HDFT methods give not unreason-

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TABLE 1: Summary of the DFT Methods Examined

method	X	year	type	exchange functional[a] correlation functional[b]	ref(s)[c]
B3LYP	20	1994	HDFT	Becke88 Lee−Yang−Parr	1, 2, 5
B1B95	25	1996	HMDFT	Becke88 Becke95	1, 6
PBE1PBE[d]	25	1996	HDFT	PBE exchange PBE correlation	7
mPW1PW91	25	1998	HDFT	modified Perdew-Wang PW91 correlation	3, 11
B97−1	21	1998	HDFT	B97-1 exchange B97-1 correlation	14
B98	21.98	1998	HDFT	B98 Exchange B98 Correlation	12
MPW1K	42.8	2000	HDFT	modified Perdew-Wang Perdew-Wang91	11, 24
B97−2	21	2001	HDFT	B97-2 exchange B97-2 correlation	14
X3LYP	21.8	2004	HDFT	Becke88+PW91 exchange Lee−Yang−Parr	1, 2, 3, 28
BB1K	42	2004	HMDFT	Becke88 Becke95	1, 6, 35
MPW3LYP	21.8	this work	HDFT	modified Perdew-Wang Lee−Yang−Parr	2, 11, 28, p
X1B95	30	this work	HMDFT	Becke88+PW91 exchange Becke95	1, 2, 3, 6, 28, p
XB1K	43	this work	HMDFT	Becke88+PW91 exchange Becke95	1, 2, 3, 6, 28, p
MPW1B95	31	this work	HMDFT	modified Perdew-Wang Becke95	6, 11, p
MPWB1K	44	this work	HMDFT	modified Perdew-Wang Becke95	6, 11, p

[a] Upper entry. [b] Lower entry. [c] p in this column denotes the present paper. [d] PBE1PBE is also known as PBE0.

able results even for weak interactions. The present article considers all four types of bonding in an attempt to identify generally more satisfactory functionals. In some parts of the discussion, we will group hydrogen bonding and weak interactions together as noncovalent interactions.

In addition, in the present paper, we develop some new methods. First we develop two new methods, namely, MPW1B95 and MPWB1K that are based on the modified Perdew and Wang 1991 exchange functional[3] (mPW or MPW) and Becke's 1995 meta correlation functional[6] (B95), where meta, as explained above, means that it depends on kinetic energy density as well as the density and the gradient of the density. MPW1B95 is optimized against the AE6[38] representative atomization energy database, and it is constructed for general-purpose applications in themochemistry. MPWB1K is an HMDFT model for kinetics, and it was optimized against the Kinetics9 database described[35] in a previous paper.

Weak interactions dominated by dispersion are important for van der Waals molecules, long-range forces, and biological systems. Another important interaction in biological systems is hydrogen bonding. For example, hydrogen bonding plays a key role in protein folding. Recently, Xin and Goddard[28] pointed out that "it is essential that the noncovalent interactions of ligands to proteins be accurately predicted. Thus, it is essential to accurately describe London dispersion forces (van der Waals attraction) along with electrostatic and hydrogen bond interaction". However, in 1998, Kohn et al. point out that "the commonly used LDA and GGA, designed for nonuniform electron gases, fail to capture the essence of vdW energies".[39] Mourik and Gdanitz[40] confirmed this point by showing that the local density approximation (LDA) and some well-established GGA functionals are incapable of accounting for dispersion effects in a quantitative way. However, it is valuable to extend this kind of assessment to a broader range of functionals. In particular, a new-generation of functionals called meta-GGAs or MGGAs has been developed; they incorporate kinetic energy density and are a possible area of systematic improvement.[6,13,17,24,27] The B95 correlation functional used as a component of the two new HMDFTs mentioned above is an example of a meta-GGA. We will also combine the B95 correlation functional with Xin-Goddard functional and optimize a parameter two ways, resulting in some new functionals called X1B95 and XB1K.

In the sections below, we assess our new methods and other DFT-type methods against a wide variety of data. The HDFT and HMDFT methods tested in this paper are listed in the Table 1. This paper does not consider the DHDFT and DHMDFT methods because of their higher cost for large systems, and it does not consider pure DFT because of its generally poor performance (although such methods are improving rapidly[13,14,20,34] and may be a suitable subject for further study in the future). Thus, all considerations are focused on HDFT and HMDFT.

Section 2 presents our training sets and test sets. Section 3 discusses the theory and parametrization of the new methods. Section 4 presents results and discussion.

2. Databases

2.1. AE6. The training set for the MPW1B95 model is the AE6 representative atomization energy database presented previously.[38] The AE6 set of atomization energies consists of SiH_4, S_2, SiO, C_3H_4 (propyne), $C_2H_2O_2$ (glyoxal), and C_4H_8 (cyclobutane). This set of atomization energies was developed[38] such that performance on these database is indicative of performance on a much larger 109-molecule database.[41]

2.2. Kinetics9. To parametrize the MPWB1K model, we used a database of 3 forward barrier heights, 3 reverse barrier heights,

and 3 energies of reaction for the three reactions in the BH6 database;[38] and this 9-component database is called Kinetics9. We have previously used this training set to optimize the BB1K method.[35]

2.3. AE109/3 Test Set. The AE109/3 test set consists of 109 atomization energies (AEs). This AE test set contains a diverse set of molecules including organic and inorganic compounds. All 109 data are pure electronic energies, i.e., zero-point energies and thermal vibrational−rotational energies have been removed. The 109 zero-point-exclusive atomization energies are part of Database/3 and are identical to those used previously.[41,42]

2.4. BH42/04 Test Set. The BH42/04 test set consists of 42 transition state barrier heights. The barrier height data are mostly of open-shell hydrogen transfer reactions. The barrier height database has also been published previously.[32,35] The best estimates for the barrier heights were obtained, as explained elsewhere,[18,32,35,42−44] from a combination of experimental and theoretical kinetics data.

2.5. Ionization Potential and Electron Affinity Test Set. The zero-point-exclusive ionization potential (IP) and electron affinity (EA) test set is taken from a previous paper.[41] This data set is also part of Database/3, and it consists of six atoms and seven molecules for which the IP and EA are both present in the G3 data set.[45] These databases are called IP13/3 and EA13/3, respectively.

2.6. Saddle Point Geometries. The database of saddle point geometries comes from previous work.[43,44] The test set consists of five reactions where very high-level calculations of saddle point geometries are available.[46−49] The perpendicular looseness has been defined[43,44] as the sum of the forming and breaking bond distances; this is a measure of the looseness of the saddle point structure in the direction perpendicular to the reaction coordinate. The breaking bond length, forming bond length, and perpendicular looseness constitute 15 data that are called the SPG15/01 database.

2.7. Vibrational Zero-Point Energies Database. A database of 13 anharmonic vibrational zero-point energies (ZPEs) has been presented in a previous paper,[50] based on the work of Martin.[51] This is called the ZPE13/99 database. We will employ this vibrational ZPE database to develop scale factors for vibrational frequencies calculated by MPW1B95, MPWB1K, and MPW3LYP. The scale factors are optimized to minimize the root-mean-square errors in the calculated ZPEs for these 13 molecules. These scale factors are important for theoretical enthalpy, free energy, and kinetics calculations.

2.8. Weak Interaction Test Set. The weak interaction test set is new in the present paper. It consists of four rare gas dimers, in particular HeNe, NeNe, HeAr, and NeAr. They represent dispersion interactions that are expected to be typical of hydrogen-first row, first row -first row, hydrogen-second row, and first row − second row elements, respectively. The best estimates for the dimers are taken from Ogilvie and Wang's work.[52,53] The set of four equilibrium dissociation energies D_e and four equilibrium bond distance R_e is called WI4/04 database.

2.9. Hydrogen Bonding Test Set. The hydrogen bonding test set consists of four hydrogen bonding dimers, in particular $(HF)_2$, $(H_2O)_2$, $(HCOOH)_2$, and $(HCONH_2)_2$. The D_e and R_e values are taken from high-level calculations[54−57] or experimental results.[58,59] This set is called the HB4/04 database.

2.10. Database Availability. For convenience, the weak interaction test set is in Table 2, the hydrogen bonding test set is in Table 3, and the other seven databases (including training sets and test sets) are given in the Supporting Information and are also available at the Truhlar group website.[60]

TABLE 2: WI4/04 Database

	D_e (kcal/mol)	R_e (Å)	ref
HeNe	0.041	3.031	53
NeNe	0.084	3.091	52
HeAr	0.057	3.480	53
NeAr	0.134	3.489	53

TABLE 3: HB4/04 Database[a]

	D_e (kcal/mol)	R_e (Å)	ref
$(HF)_2$	4.60	2.730	54
$(H_2O)_2$	5.02	2.912	55
$(HCOOH)_2$	14.40	2.696	58,59
$(HCONH_2)_2$	13.53	2.904	56,57

[a] R_e denotes the heavy atom distance (F−F, O−O, or N−O) in the dimer. For the two large dimers, there are two hydrogen bonds each, but the two heavy atom distances (O−O in one case and N−O in the other) are equal by symmetry.

3. Theory and Parametrization

3.1. Geometries, Basis Sets, and Spin−Orbit Energy. Parametrization of MPWB1K and the tests against the databases of sections 2.6, 2.7, 2.8, and 2.9 involve geometry optimization with each level of theory tested. All other calculations are single-point calculations at QCISD/MG3 geometries, where QCISD is quadratic configuration interaction with single and double excitations,[61] and MG3 is the modified[62,63] G3Large[45] basis set. The MG3 basis set,[62] also called G3LargeMP2,[63] is the same as 6-311++G(3d2f, 2df, 2p)[64] for H−Si, but improved[45] for P−Ar. The QCISD/MG3 geometries for molecules and saddle points in the AE109/3 and BH42/03 databases can be obtained from the Truhlar group database website.[60]

We tested the MPW1B95 and MPWB1K methods with two highly recommended basis sets, namely a recommended[41,44] augmented polarized valence double-ζ set, 6-31+G(d,p),[65,66] and a recommended[41,42] augmented polarized triple-ζ set, MG3S.[41] In tables, 6-31+G(d,p) is abbreviated DIDZ (desert-island double-ζ). The MG3S basis is the same as MG3[62,63] except it omits diffuse functions on hydrogens.

In all of the calculations presented in this paper, the spin−orbit stabilization energy was added to atoms and open-shell molecules for which it is nonzero, as described previously.[62]

3.2. Counterpoise Corrections and Software. For rare gas dimers and hydrogen bonding dimers, we perform calculations with and without the counterpoise corrections[67,68] for basis set superposition error (BSSE). All calculations were performed with the *Gaussian03* program.[69] Note that we locally implemented the Xin-Goddard exchange method in *Gaussian03* to perform all X-type calculations.

3.3. Theory. The one-parameter hybrid Fock−Kohn−Sham operator can be written as follows:[6,18]

$$F = F^{H} + (X/100)\,F^{HFE} + [1 - (X/100)]\,(F^{SE} + F^{GCE}) + F^{Cor} \quad (1)$$

where F^H is the Hartree operator (i.e., the nonexchange part of the Hartree−Fock operator), F^{HFE} is the Hartree−Fock exchange operator, X is the percentage of Hartree−Fock exchange, F^{SE} is the Dirac−Slater local density functional for exchange,[70,71] F^{GCE} is the gradient correction for the exchange functional, and F^{Cor} is the total correlation functional including both local and gradient-corrected parts and (where applicable) a dependence on kinetic energy density. In the MPW1B95 and MPWB1K models, we used Adamo and Barone's mPW exchange functional[11] for F^{GCE} and the Becke95[6] functional for F^{Cor}. For the

TABLE 4: Parameters for MPW1B95, MPWB1K, *X*1B95, *X*B1K, and MPW3LYP

methods	c_1	c_2	X
MPW1B95			31
MPWB1K			44
X1B95			30
XB1K			43
MPW3LYP	0.72[a]	0.81[a]	20[a]

[a] Not re-optimized; same as in ref 28.

MPW1B95 model, we optimize the X to minimize the root-mean-square error (RMSE) for the AE6 representative atomization energy database. For the MPWB1K model, X was adjusted to minimize the RMSE for the Kinetics9 database. We also combined the X exchange functional of Xu and Goddard[28] with the B95 correlation functional, and we parametrized two methods, namely X1B95 and XB1K. X1B95 is parametrized against the AE6 database, and XB1K is parametrized against the Kinetics9 database.

Becke's three parameter hybrid Fock-Kohn−Sham operator can be written as eq 2

$$F = F^{H} + (X/100)\,F^{HFE} + [1 - (X/100)]\,F^{SE} + c_1 F^{GCE} + F^{LSD-Cor} + c_2 F^{GC-Cor} \quad (2)$$

where $F^{LSD-Cor}$ is the density-only part of the correlation functional,[72] and F^{GC-Cor} is the gradient corrected correlation functional. In Becke's hybrid DFT method B3PW91, he used Becke88 for F^{GCE} and the PW91 correlation functional for F^{GC-Cor}, and then he determined the X, c_1, and c_2 by a fit to experimental data. He obtained $X = 20$, $c_1 = 0.72$, and $c_2 = 0.81$. Stephens et al.[5] used Becke's three parameters and the Lee−Yang−Parr correlation functional to construct the popular B3LYP method. Recently, Xu and Goddard developed a HDFT method, X3LYP,[28,73] where the X exchange functional is a linear combination of the Becke88 and PW91 exchange functionals. They optimized the three parameters, and their parameters are $X = 21.8$, $c_1 = 0.782$, and $c_2 = 0.871$. In the present paper, we use the three parameters in X3LYP with the mPW exchange functional substituted for the X one to construct the MPW3LYP method.

Table 4 gives all of the parameters for the methods that are used in the present paper.

4. Results and Discussion

In this section, we will gauge the quality of the results by mean unsigned errors (MUEs), which are the averages of the absolute deviations of calculated values from database values, and by mean signed errors (MSE), which are used to detect systematic deviations. However, for atomization energies, we use MUE per bond (MUEPB) and MSE per bond (MSEPB) because this allows[32,34,35] more transferable comparison between databases with different average sizes of molecules. Root-mean-square errors (RMSEs) are given in the Supporting Information, but in the text, we discuss mean unsigned rather than root-mean-square errors because the former is more robust;[74] that is, it is less sensitive to departures of the error distribution from the idealized case of a Gaussian error distribution.

To make the trends more clear, in every table we will list the methods in increasing order of the values in the key error column.

TABLE 5: Mean Errors[a]

	AE109/3		IP13/3		EA13/3			
methods	MSEPB	MUEPB	MSE	MUE	MSE	MUE	TMUE	MTMUE
X1B95/DIDZ[b]	−0.68	0.97	0.94	2.34	1.90	3.33	1.33	1.16
X1B95/MG3S	0.02	0.52	1.10	2.76	2.96	3.10	0.99	
B1B95/DIDZ	−0.94	1.02	0.72	2.38	1.98	3.39	1.38	1.17
B1B95/MG3S	−0.23	0.56	−0.13	2.18	3.02	3.16	0.97	
B97−2/DIDZ	−0.94	1.00	1.20	2.36	1.35	3.05	1.33	1.18
B97−2/MG3S	−0.20	0.66	0.46	2.21	2.41	2.89	1.02	
MPW1B95/DIDZ	−0.36	1.04	1.22	2.38	1.64	3.14	1.37	1.19
MPW1B95/MG3S	0.31	0.63	0.36	2.14	2.72	2.91	1.00	
B97−1/DIDZ	−1.28	1.31	1.83	2.86	0.01	2.33	1.56	1.32
B97−1/MG3S	−0.39	0.76	0.99	2.84	1.09	2.02	1.08	
B98/DIDZ	−1.43	1.45	2.83	3.45	−0.75	2.24	1.72	1.37
B98/MG3S	−0.50	0.65	1.99	3.21	0.30	1.84	1.01	
MPW3LYP/DIDZ	−1.02	1.34	3.50	4.35	−1.74	2.87	1.77	1.46
MPW3LYP/MG3S	−0.19	0.64	2.72	4.32	−0.70	2.14	1.14	
PBE1PBE/DIDZ	−0.67	1.34	3.25	3.43	0.35	2.97	1.69	1.51
PBE1PBE/MG3S	0.11	0.92	2.44	3.23	1.50	2.76	1.32	
mPW1PW91/DIDZ	−1.53	1.59	3.97	3.99	−0.05	2.83	1.94	1.64
mPW1PW91/MG3S	−0.73	0.89	3.17	3.72	1.09	2.62	1.33	
MPWB1K/DIDZ	−1.53	1.74	1.45	2.82	2.83	4.29	2.09	1.74
MPWB1K/MG3S	−0.83	0.97	0.51	2.05	3.99	4.11	1.38	
B3LYP/DIDZ	−1.56	1.71	4.35	4.91	−2.51	3.24	2.16	1.78
B3LYP/MG3S	−0.69	0.90	3.58	4.72	−1.51	2.29	1.40	
XB1K/DIDZ	−1.78	1.86	1.03	2.57	3.03	4.45	2.18	1.85
XB1K/MG3S	−1.06	1.12	0.18	2.16	4.17	4.26	1.52	
BB1K/DIDZ	−2.05	2.06	1.07	2.73	3.16	4.56	2.37	2.04
BB1K/MG3S	−1.32	1.34	0.13	2.09	4.28	4.36	1.70	
X3LYP/DIDZ	−2.12	2.22	3.35	4.71	−1.43	3.60	2.59	2.24
X3LYP/MG3S	−1.26	1.41	2.58	4.73	−0.41	3.04	1.88	
MPW1K/DIDZ	−3.16	3.17	4.32	4.49	1.51	4.11	3.39	2.99
MPW1K/MG3S	−2.33	2.34	3.41	3.53	2.79	3.71	2.59	

[a] kcal/mol for ionization potentials (IP) and electron affinities (EA) and kcal/mol per bond for atomization energies (AE). MUEPB denotes mean unsigned error (MUE) per bond. MSE denotes mean signed error. RMSE denotes root−mean−square error. TMUE denotes total MUE, and it is defined as TMUE = [MUEPB × 109 +MUE(IP) × 13+ MUE(AE) × 13]/135. MTMUE denotes mean TMUE, and it is defined as MTMUE = [TMUE(DIDZ) + TMUE(MG3S)]/2. QCISD/MG3 geometries are used for calculations in this table. [b] DIDZ denotes 6-31+G(d,p) basis set.

4.1. AE, IP, and EA Results. Table 5 summarizes the errors in AEs, IPs, and EAs for all HDFT and HMDFT methods in Table 1. Among these methods, B1B95 and B97−2 were found to be the two best methods for thermochemisty in our recent test,[34] whereas B3LYP, PBE1PBE, MPW1K, and BB1K are included because of their wide popularity or their quality for kinetics, B97-1, B98, and mPW1PW91 are included because of their general high quality, X3LYP is included because it is so new, MPW3LYP is included mainly for comparison with X3LYP, and MPW1B95, MPWB1K, X1B95, and XB1K are included as the new HMDFT methods developed in the present study. To compare their performance for thermochemistry, we defined the TMUE (total MUE) and MTMUE (mean TMUE) as follows:

$$TMUE = [MUEPB(\mathrm{AE}) \times 109 + MUE(\mathrm{IP}) \times 13 + MUE(\mathrm{EA}) \times 13]/135 \quad (3)$$

$$MTMUE = [TMUE(\mathrm{DIDZ}) + TMUE(\mathrm{MG3S})]/2 \quad (4)$$

The motivation for MTMUE is that it is desirable for a HDFT or HMDFT method to give good results for both polarized double-ζ and polarized triple-ζ basis sets. The smaller basis sets are important because one of the attractive features of hybrid DFT is its applicability to large systems, for which larger basis sets can be cost prohibitive.

Table 5 shows that the X1B95, B1B95, B97-2, and MPW1B95 methods give the best results for AE and IP calculations. B98 and B97-1 have the best performance for EA calculations.

From Table 5, we can see that, for the DIDZ basis, the best methods are B97-2 and X1B95, and MPW1B95 and B1B95 are only slightly less accurate is the second best, as shown by their low TMUE value. For the MG3S basis, B1B95 is the best, X1B95 is the second best, and MPW1B95, B97-2, and B97-1 are only slightly less accurate.

If we use MTMUE as a criterion to justify the performance of a DFT method for thermochemistry, we can see from Table 5 that, the performance of X1B95 and MPW1B95 is comparable to B1B95 and B97-2. The performance of MPW3LYP is worse than B97-1 and B98, but better than PBE1PBE, mPW1PW91, MPWB1K, B3LYP, and X3LYP. However, a final choice of method for many applications should probably be based more on a broader assessment with more diverse data than on small differences in Table 5, and one of the chief goals of the rest of this paper is to present such an assessment.

First, though, a few additional issues deserve discussion. Even though we incorporated 44% HF exchange in the MPWB1K model, which is for thermochemical kinetics, MPWB1K outperforms the most popular HDFT method B3LYP as shown by its lower MTMUE value. MPWB1K has the best performance for thermochemistry among the four DFT model designed for kinetics.

Another important point is that MPW1B95 and X1B95 are parametrized only against the AE6 representative set. Even though the MPW1B95 and X1B95 models are parametrized on this small data set, both of them show good performance for the much larger AE109/3 database and for the IP and EA databases. This confirms the point addressed in a previous paper, i.e., a representative small dataset "would be very useful not only for testing but also to help in developing new theoretical methods".[38]

4.2. AE6 and BH6 Benchmarks Results. Table 6 gives the mean errors for the AE6 and BH6 benchmarks. We also tabulated a value for MMUE (mean MUE) as defined in previous papers.[34,35]

TABLE 6: Mean Errors for BH6 and AE6 Benchmarks with QCISD/MG3 Geometries[a]

	BH6		AE6		
method	MSE	MUE	MSEPB	MUEPB	MMUE[b]
XB1K/DIDZ	−1.18	1.35	−1.58	1.76	1.35
XB1K/MG3S	−1.18	1.22	−0.90	1.06	
MPWB1K/DIDZ	−1.44	1.49	−1.23	1.72	1.41
MPWB1K/MG3S	−1.44	1.44	−0.57	0.99	
BB1K/DIDZ	−1.03	1.42	−1.84	1.84	1.42
BB1K/MG3S	−1.03	1.14	−1.1	1.28	
B1B95/DIDZ	−3.23	3.23	−0.82	0.94	1.97
B1B95/MG3S	−3.14	3.14	−0.16	0.57	
B97−2/DIDZ	−2.87	3.12	−0.84	0.84	1.98
B97−2/MG3S	−2.88	3.21	−0.15	0.73	
X1B95/DIDZ	−3.26	3.26	−0.57	0.96	2.00
X1B95/MG3S	−3.19	3.19	0.34	0.57	
MPW1K/DIDZ	−1.05	1.42	−3.08	3.08	2.04
MPW1K/MG3S	−1.14	1.40	−2.26	2.26	
MPW1B95/DIDZ	−3.59	3.59	0.15	0.84	2.19
MPW1B95/MG3S	−3.50	3.50	0.47	0.82	
B98/DIDZ	−4.08	4.14	−1.31	1.31	2.52
B98/MG3S	−4.00	4.00	−0.41	0.63	
B97−1/DIDZ	−4.23	4.23	−1.20	1.20	2.62
B97−1/MG3S	−4.14	4.14	−0.34	0.91	
mPW1PW91/DIDZ	−3.94	3.94	−1.59	1.65	2.62
mPW1PW91/MG3S	−3.95	3.95	−0.81	0.94	
PBE1PBE/DIDZ	−4.61	4.61	−0.81	1.47	2.96
PBE1PBE/MG3S	−4.62	4.62	−0.06	1.12	
B3LYP/DIDZ	−4.99	5.03	−1.46	1.52	2.98
B3LYP/MGS3S	−4.72	4.72	−0.60	0.66	
X3LYP/DIDZ	−5.18	5.18	−1.35	1.41	3.01
X3LYP/MG3S	−4.91	4.91	−0.51	0.56	
MPW3LYP/DIDZ	−5.56	5.56	−0.96	1.08	3.05
MPW3LYP/MG3S	−5.27	5.27	−0.14	0.31	

[a] MUEPB denotes mean unsigned error (MUE) per bond (kcal mol^{-1} bond^{-1}). MSE denotes mean signed error (kcal/mol). [b] MMUE is defined in eq 5 and it is a measure of the quality of a method for kinetics, averaged over two basis sets.

$$\mathrm{MMUE} = 1/4[\mathrm{MUE(BH6,DIDZ)} + \mathrm{MUE(BH6, MG3S)} + \mathrm{MUEPB(AE6, DIDZ)} + \mathrm{MUEPB(AE6, MG3S)}] \quad (5)$$

where MUEPB is MUE per bond for the AE6 database.

The MMUE is a criterion to evaluate the performance of electronic structure methods for kinetics. The motivation for this criterion, as presented previously,[34,35] is that it is desirable for a method used for practical kinetics calculations to give good results for both bond energies and barrier heights with both polarized double-ζ and polarized triple-ζ basis sets.

Table 6 shows that MPW1K and BB1K are slightly better than MPWB1K for barrier height calculations, but MPWB1K outperforms MPW1K and BB1K for atomization energy calculations.

If we use MMUE to judge methods for thermochemical kinetics, we conclude that XB1K, MPWB1K, and BB1K, which are all new methods developed after our comprehensive assessment[34] published earlier this year, are the three best DFT-type methods for thermochemical kinetics. They each have an MMUE of about 1.4 kcal/mol. MPW1B95, B1B95, B97-2, MPW1K, and X1B95 are next line with MMUEs in the range of 2.0−2.2 kcal/mol. All other methods in Table 6 have MMUEs in the range 2.5−3 kcal/mol, about twice large as the three methods at the top of the list.

4.3. AE109/3 and BH42/04 Results. Table 7 gives the mean errors for AE109/3 database and BH42/04 database with the large basis set. We also tabulated a value for AMUE (average MUE) as defined in previous papers.[32]

$$AMUE = 0.5[MUEPB(\mathrm{AE109/3}) + MUE(\mathrm{BH42/03})] \quad (6)$$

TABLE 7: Mean Errors for AE109/3 and BH42/04 Database[a]

	AE109/3		BH42/04		
methods	MSEPB	MUEPB	MSE	MUE	AMUE
MPWB1K/MG3S	−0.83	0.97	−0.89	1.29	1.13
XB1K/MG3S	−1.06	1.12	−0.75	1.23	1.18
BB1K/MG3S	−1.32	1.34	−0.61	1.16	1.25
X1B95/MG3S	0.02	0.52	−2.82	2.82	1.67
B1B95/MG3S	−0.23	0.56	−2.80	2.80	1.68
MPW1B95/MG3S	0.31	0.63	−3.01	3.01	1.82
MPW1K/MG3S	−2.33	2.34	−0.75	1.40	1.87
B97−2/MG3S	−0.20	0.66	−2.91	3.13	1.90
mPW1PW91/MG3S	−0.73	0.89	−3.62	3.63	2.26
B98/MG3S	−0.50	0.65	−4.08	4.08	2.37
B97−1/MG3S	−0.39	0.76	−4.24	4.24	2.50
B3LYP/MG3S	−0.68	0.90	−4.40	4.31	2.60
PBE1PBE/MG3S	0.11	0.92	−4.29	4.29	2.72
MPW3LYP/MG3S	−0.19	0.64	−4.76	4.80	2.72
X3LYP/MG3S	−1.26	1.41	−4.20	4.28	2.84

[a] kcal/mol for barriers and kcal/mol per bond for atomization energies. MUEPB denotes mean unsigned error (MUE) per bond. MSE denotes mean signed error. RMSE denotes root−mean-square error. Average mean unsigned error (AMUE) is defined by eq 6. QCISD/MG3 geometries are used for calculations in this table.

TABLE 8: Mean Errors (Å) in Internuclear Distances at Saddle Point of the Five Reactions in the Saddle Point Geometry Database[a]

	bond distance		perpendicular looseness		15 distances
method	MSE	MUE	MSE	MUE	MUE
XB1K/MG3S	−0.00	0.02	−0.01	0.01	0.01
BB1K/MG3S	0.00	0.02	0.00	0.01	0.01
MPW1K/MG3S	−0.01	0.01	−0.02	0.02	0.02
MPWB1K/MG3S	−0.01	0.02	−0.01	0.01	0.02
QCISD/MG3	−0.01	0.02	−0.01	0.02	0.02
MPW1B95/MG3S	*0.02*	*0.04*	*0.04*	*0.05*	*0.04*
X1B95/MG3S	*0.02*	*0.04*	*0.04*	*0.05*	*0.04*
B1B95/MG3S	*0.02*	*0.04*	*0.05*	*0.05*	*0.04*
mPW1PW91/MG3S	*0.02*	*0.04*	*0.05*	*0.05*	*0.04*
B97−2/MG3S	*0.03*	*0.06*	*0.05*	*0.06*	*0.06*
X3LYP/MG3S	*0.03*	*0.05*	*0.07*	*0.07*	*0.06*
MPW3LYP/MG3S	*0.03*	*0.05*	*0.07*	*0.07*	*0.06*
B3LYP/MG3S	*0.04*	*0.06*	*0.07*	*0.07*	*0.06*

[a] MPW3LYP, MPW1B95, X1B95, B97-2, B1B95, B3LYP, and mPW1PW91 do not yield a finite-distance saddle point for $F + H_2 \rightarrow HF + H$. Therefore, in computing errors for these methods, the error in the forming bond length and perpendicular looseness for this reaction were arbitrarily set equal to 0.15 and 0.18 Å, respectively, which are respectively 1.5 times the largest errors that any other method makes in these quantities. Since this an underestimate (the true error is infinite), these values are in italics.

The use of atomization energies rather than reaction energies, the use of the larger databases, and the use of only the large basis set provide a test of whether our conclusions about quality of the various functionals are sensitive to the testing methodology. It is very encouraging that we find the same breakdown into three methods with a first class grade, five methods in a second class, and seven in a third class, with each method finding itself in the same class as inferred from Table 6. This confirms the success of the representative database. Furthermore, we conclude that the division of the methods into three classes is meaningful, although the order in a given class is probably not meaningful.

4.4. Saddle Point Geometries. We tested several methods for the prediction of transition state geometries and compared them with other methods; Table 8 summarizes the error in $R^{\neq}_{\text{forming bond}}$ and $R^{\neq}_{\text{breaking bond}}$ and in perpendicular looseness for the five reactions (four for MPW3LYP, MPW1B95, X1B95, X3LYP, B97-2, B1B95, B3LYP, and mPW1PW91) in the SPG15/01 database. In addition to all of the first and second class methods from Tables 6 and 7, Table 8 contains four of the third class methods plus QCISD/MG3, which is a good comparison because QCISD is well-known to be especially accurate for saddle point geometries.[75,76] For the reaction $F + H_2 \rightarrow HF + H$, the MPW3LYP, MPW1B95, X1B95, X3LYP, B97-2, B1B95, B3LYP, and mPW1PW91 methods predict that there is a monotonically downhill reaction path for this reaction; thus, they predict that the highest-energy point on the reaction path is at reactants where the forming bond length is ∞. Therefore, in computing errors for these methods, the error in the forming bond length and perpendicular looseness for this reaction were arbitrarily set equal to 0.15 and 0.18 Å, respectively, which are respectively 1.5 times the largest errors that any other method makes in these quantities. Since this is an underestimate (the true error is infinite), these values are in italics.

Table 8 shows that the three first class thermochemical kinetics methods (MPWB1K, XB1K, and BB1K) and the one second class method that was designed for kinetics (MPW1K) are, by a clear margin, the four best methods for the prediction of saddle point geometries. If, instead, we focus on the four best methods of Table 5 for thermochemistry (MPW1B95, B97−2, B1B95, and X1B95), we can see that MPW1B95, B1B95, and X1B95 give the best results for saddle point geometry calculations, even though none of them predict the saddle point of the reaction $F + H_2 \rightarrow HF + H$. The B97-2 method scored poorly for saddle point geometries.

Table 7 showed that MPW3LYP, MPW1B95, X3LYP, B97-2, B1B95, B3LYP, and mPW1PW91 systematically underestimate the barrier heights as indicated by their high negative MSE. As a consequence, one would have expected, by the Hammond postulate,[77] that the saddle points are too early for exothermic reactions, and this is consistent with their positive MSE for the perpendicular looseness.

TABLE 9: Mean Unsigned Error and Scale Factor for Calculating Zero-Point Energies

	MUE in ZPE[a]			
method	unscaled	scaled	scale factor	ref[b]
B3LYP/MG3S	0.19	0.09	0.9851	35
MPW3LYP/DIDZ	0.21	0.09	0.9825	this work
MPW1B95/DIDZ	0.35	0.10	0.9721	this work
X1B95/DIDZ	0.36	0.10	0.9709	this work
MPW3LYP/MG3S	0.21	0.11	0.9846	this work
B1B95/MG3S	0.32	0.11	0.9758	35
MPW1B95/MG3S	0.33	0.11	0.9746	this work
XB1K/DIDZ	0.56	0.11	0.9549	this work
MPWB1K/DIDZ	0.58	0.11	0.9537	this work
X1B95/MG3S	0.35	0.12	0.9733	this work
BB1K/MG3S	0.52	0.14	0.9590	35
MPW1K/MG3S	0.54	0.14	0.9581	35
XB1K/MG3S	0.54	0.15	0.9579	this work
MPWB1K/MG3S	0.56	0.15	0.9567	this work
HF/MG3S	1.03	0.23	0.9210	35

[a] kcal/mol. [b] Reference in which scale factor was first reported.

4.5. Vibrational Frequencies Scale Factor. We employed the database[50,51] of 13 anharmonic vibrational zero-point energies to determine the vibrational frequency scale factor for the five new methods (MPW1B95, MPWB1K, X1B95, XB1K, and MPW3LYP). These scale factors are listed with scale factors for other methods in Table 9. Use of the scale factor reduces the MUE calculated by MPW1B95 by about 0.2 kcal/mol, and the scale factor reduces RMS error calculated by MPWB1K by

TABLE 10: Mean Errors for the HB4/04 and WI4/04 Noncovalent Interaction Test Sets with Counterpoise Correction for BSSE[a]

	D_e (kcal/mol)					R_e (Å)				
	HB		WI			HB		WI		
method	MSE	MUE	MSE	MUE	MMUE	MSE	MUE	MSE	MUE	MMUE
B98/DIDZ	0.38	0.39	−0.01	0.02	0.20	0.02	0.03	0.07	0.07	0.05
B98/MG3S	−0.11	0.38	−0.01	0.02		0.02	0.03	0.04	0.09	
MPW1B95/DIDZ	0.20	0.33	0.00	0.03	0.22	0.01	0.02	0.06	0.08	0.05
MPW1B95/MG3S	−0.29	0.48	0.00	0.03	0.22	0.01	0.02	0.04	0.09	
B97−1/DIDZ	0.61	0.61	0.01	0.02	0.22	0.02	0.02	−0.05	0.05	0.04
B97−1/MG3S	0.14	0.26	0.01	0.02		0.02	0.02	−0.08	0.08	
MPWB1K/DIDZ	0.42	0.42	−0.01	0.02	0.23	0.01	0.01	0.04	0.10	0.06
MPWB1K/MG3S	−0.10	0.46	−0.01	0.02		0.00	0.02	0.04	0.09	
MPW1PW91/DIDZ	0.30	0.40	−0.02	0.03	0.26	−0.01	0.03	0.33	0.33	0.19
MPW1PW91/MG3S	−0.19	0.60	−0.03	0.03		−0.01	0.03	0.35	0.35	
XB1K/DIDZ	0.03	0.31	−0.10	0.10	0.27	0.01	0.02	0.22	0.22	0.10
XB1K/MG3S	−0.49	0.59	−0.11	0.11		0.01	0.02	0.14	0.14	
X3LYP/DIDZ	0.70	0.70	−0.03	0.04	0.28	0.00	0.01	0.01	0.05	0.04
X3LYP/MG3S	0.23	0.34	−0.03	0.04		0.00	0.02	−0.05	0.09	
MPW1K/DIDZ	0.54	0.54	−0.04	0.04	0.30	−0.02	0.03	0.35	0.35	0.19
MPW1K/MG3S	0.01	0.57	−0.04	0.04		−0.02	0.03	0.36	0.36	
B3LYP/DIDZ[b]	0.13	0.35	−0.23	0.23	0.32	0.01	0.02	1.44	1.44	0.63
B3LYP/MG3S[b]	−0.33	0.45	−0.23	0.23		0.01	0.02	1.02	1.02	
BB1K/DIDZ	−0.35	0.38	−0.13	0.13	0.38	0.02	0.02	0.46	0.46	0.18
BB1K/MG3S	−0.85	0.85	−0.16	0.16		0.02	0.03	0.22	0.22	
PBE1PBE/DIDZ	0.96	0.96	−0.02	0.03	0.39	−0.02	0.03	0.09	0.10	0.06
PBE1PBE/MG3S	0.47	0.55	−0.02	0.03		−0.02	0.03	0.06	0.09	
MPW3LYP/DIDZ	1.15	1.15	0.15	0.15	0.53	−0.01	0.01	−0.21	0.21	0.11
MPW3LYP/MG3S	0.68	0.68	0.14	0.14		−0.01	0.01	−0.22	0.22	
B97−2/DIDZ	−0.76	0.76	−0.05	0.05	0.53	0.04	0.04	0.37	0.37	0.21
B97−2/MG3S	−1.25	1.25	−0.05	0.05		0.04	0.05	0.38	0.38	
B1B95/DIDZ	−0.74	0.74	−0.14	0.14	0.56	0.03	0.04	0.96	0.96	0.43
B1B95/MG3S	−1.21	1.21	−0.15	0.15		0.03	0.03	0.68	0.68	
X1B95/DIDZ	−1.37	1.43	−0.14	0.14	0.61	−0.14	0.18	0.06	0.13	0.14
X1B95/MG3S	−0.75	0.75	−0.11	0.11		0.02	0.03	0.21	0.22	

[a] HB denotes hydrogen bonding, and WI denotes weak interaction. MMUE is defined in eq 7. [b] When counterpoise is included, B3LYP/DIDZ does not predict the van der Waals well for 3 of the 4 rare gas dimers, and B3LYP/MG3S does not predict any van der Waals well for any of the four rare gas dimers. In those cases, we arbitrarily set absolute magnitude of the errors in D_e and R_e to 1.5 times the largest error that any other method makes for that quantity. The error in D_e is treated as negative, and the error in R_e is treated as positive. Values computed with these assumptions are in italics.

about 0.4∼0.5 kcal/mol. Table 9 also shows that the scale factor for these new methods is not too far from unity, which is a serious problem for Hartree−Fock theory. The scale factors will be useful for applying the new methods to theoretical kinetics calculations.

4.6. Hydrogen Bonding and Weak Interaction Results. *4.6.1. Results with Counterpoise Correction for BSSE.* Table 10 presents a summary of the counterpoise corrected results for the WI4/04 and HB4/04 databases. The counterpoise correction[67] is a standard way to try to correct for basis-set superposition error (BSSE). We define the mean MUE (MMUE) as

$$\mathrm{MMUE} = 1/4[\mathrm{MUE(HB,DIDZ)} + \mathrm{MUE(HB, MG3S)} + \mathrm{MUE(WI, DIDZ)} + \mathrm{MUE(WI, MG3S)}] \quad (7)$$

which is similar in spirit to the MMUE for thermochemical kinetics defined in section 4.2.

Table 10 shows that B98, MPW1B95, B97-1, and MPWB1K give the best results for hydrogen bonding and weak interactions as indicated by their low MMUE for both D_e and R_e. The performances of MPW1PW91, XB1K, X3LYP, and MPW1K are close behind the three leaders for noncovalent interactions, and among all the methods, B97-1 and X3LYP give the best results for R_e.

Note that BB1K and B1B95 greatly underestimate the strengths of noncovalent interaction as shown by their large negative MSE. BB1K and B1B95 predict negative D_e for all rare gas dimer in WI4/04 database. At first this seems to confirm Becke's comments in his 1997 paper[9] that the B95 correlation functional "is problematic in very weakly bound systems (e.g., van der Waals systems)". However MPWB1K and MPW1B95 give good performance for weak interactions even though both of them use B95 correlation functional. Therefore, we conclude that the poor performance of B1B95 and BB1K for weak interaction is due to the Becke88 correlation functional, and this is confirmed by the results for B3LYP, which does not predict the existence of van der Waals wells for most dimers in WI4/04 database. Because there is 76.5% of Becke88 in the X exchange functional, the performance of XB1K is slightly better than BB1K but much worse than MPWB1K for weak interactions. Similarly, X1B95 is slightly better than B1B95 but worse than MPW1B95 for weak interactions.

Another interesting conclusion from Table 10 is that six of the methods in the present paper give more accurate predictions of the energies of noncovalent interactions than X3LYP. X3LYP was developed "to significantly improve the accuracy of hydrogen-bonded and van der Waals complexes ..." as compared to B3LYP.[28] The test set in the X3LYP paper includes two rare gas dimers and one hydrogen-bonded system, whereas the present test sets include four of each. Although X3LYP does improve on B3LYP for rare gas dimers, so does every other method tested. For dissociation energies of hydrogen-bonded complexes, X3LYP improves over B3LYP with one basis set but not the other. X3LYP is, nevertheless, one of the better

TABLE 11: Mean Errors for the HB4/04 and WI4/04 Noncovalent Interaction Test Sets without Counterpoise Correction for BSSE[a]

	D_e (kcal/mol)					R_e (Å)				
	HB		WI			HB		WI		
method	MSE	MUE	MSE	MUE	MMUE	MSE	MUE	MSE	MUE	MMUE
X1B95/DIDZ	0.36	0.51	−0.02	0.04	0.27	0.00	0.01	−0.05	0.13	0.07
X1B95/MG3S	−0.30	0.49	−0.02	0.04		0.01	0.02	−0.09	0.10	
XB1K/DIDZ	0.66	0.66	0.00	0.04	0.30	−0.01	0.01	−0.16	0.16	0.08
XB1K/MG3S	−0.03	0.45	−0.04	0.04		0.00	0.02	0.11	0.12	
BB1K/DIDZ	0.27	0.49	−0.06	0.08	0.31	0.00	0.01	0.14	0.16	0.10
BB1K/MG3S	−0.40	0.56	−0.09	0.09		0.01	0.02	0.21	0.21	
B3LYP/DIDZ	0.75	0.75	0.04	0.13	0.32	−0.01	0.01	0.07	0.24	0.14
B3LYP/MG3S	0.12	0.38	−0.05	0.05		0.00	0.02	0.23	0.31	
B97−2/DIDZ	−0.10	0.44	0.07	0.10	0.34	0.01	0.02	0.13	0.14	0.10
B97−2/MG3S	−0.76	0.76	0.01	0.04		0.02	0.04	0.21	0.21	
B1B95/DIDZ	−0.14	0.46	−0.06	0.10	0.35	0.01	0.01	0.20	0.21	0.16
B1B95/MG3S	−0.77	0.77	−0.09	0.09		0.02	0.03	0.38	0.38	
MPW1B95/DIDZ	0.84	0.84	0.16	0.16	0.36	−0.01	0.01	0.02	0.11	0.06
MPW1B95/MG3S	0.17	0.37	0.08	0.08		0.00	0.02	0.03	0.09	
MPW1PW91/DIDZ	0.99	0.99	0.11	0.12	0.40	−0.04	0.04	0.12	0.15	0.10
MPW1PW91/MG3S	0.35	0.43	0.04	0.06		−0.03	0.03	0.20	0.20	
B98/DIDZ	1.02	1.02	0.15	0.15	0.41	−0.01	0.02	−0.10	0.14	0.07
B98/MG3S	0.37	0.39	0.07	0.07		0.00	0.02	−0.06	0.10	
MPWB1K/DIDZ	1.07	1.07	0.12	0.12	0.42	−0.02	0.02	0.02	0.11	0.06
MPWB1K/MG3S	0.37	0.41	0.06	0.06		−0.01	0.02	0.03	0.09	
MPW1K/DIDZ	1.25	1.25	0.07	0.09	0.48	−0.04	0.04	0.13	0.14	0.10
MPW1K/MG3S	0.55	0.55	0.02	0.04		−0.04	0.04	0.19	0.20	
X3LYP/DIDZ	1.33	1.33	−0.03	0.04	0.52	−0.02	0.02	0.01	0.14	0.07
X3LYP/MG3S	0.69	0.69	−0.03	0.04		−0.01	0.01	−0.05	0.09	
B97−1/DIDZ	1.25	1.25	0.19	0.19	0.54	−0.01	0.01	−0.18	0.18	0.09
B97−1/MG3S	0.60	0.60	0.11	0.11		0.00	0.02	−0.16	0.16	
PBE1PBE/DIDZ	1.65	1.65	0.14	0.14	0.71	−0.04	0.04	−0.10	0.15	0.08
PBE1PBE/MG3S	0.98	0.98	0.06	0.06		−0.04	0.04	−0.06	0.10	
MPW3LYP/DIDZ	1.80	1.80	0.15	0.15	0.81	−0.03	0.03	−0.21	0.21	0.12
MPW3LYP/MG3S	1.15	1.15	0.14	0.14		−0.02	0.02	−0.23	0.23	

[a] HB denotes hydrogen bonding, and WI denotes weak interaction. MMUE is defined in eq 7.

methods for weak interactions, and with some methods of ranking (putting more emphasis on R_e and the larger basis set and less on D_e and the smaller basis set), it might be considered second only to B97-1 and B98. The reason that was given[28] for the success of X3LYP for weak interactions was the dependence of the gradient-corrected exchange functional F^{GCE} on the reduced gradient density s defined by

$$s = \frac{|\nabla\rho|}{(24\pi^2)^{1/3}\rho^{4/3}} \tag{8}$$

This dependence is given by

$$F^{GCE}(\rho, s) = F^{SE}(\rho)\,[F(s) - 1] \tag{9}$$

where $F(s)$ is the GGA enhancement factor.

Figure 1 shows the behavior of the GGA enhancement factor of the Beck88 (as in B3LYP), mPW (as in mPW1PW91, MPW1K, MPW1B95, MPWB1K, and MPW3LYP), PW91 (as in the original Perdew and Wang 1991 exchange functional[78]), and X (as in X3LYP and XB1K) functionals. If we compare the enhancement factors of the four exchange functionals in the figure, we see that mPW differs slightly more from Becke88 than does X. Adamo and Barone[11] had already showed that this deviation from the Becke88 functional should improve the noncovalent interactions, and the present tests confirm this. The direct comparison of MPW3LYP to X3LYP indicates that X is close to optimum for weak interactions when combined with LYP correlation. However when we use the B95 correlation functional, the performance of the MPW exchange functional is better than X, and X is better than Becke88 as indicated by

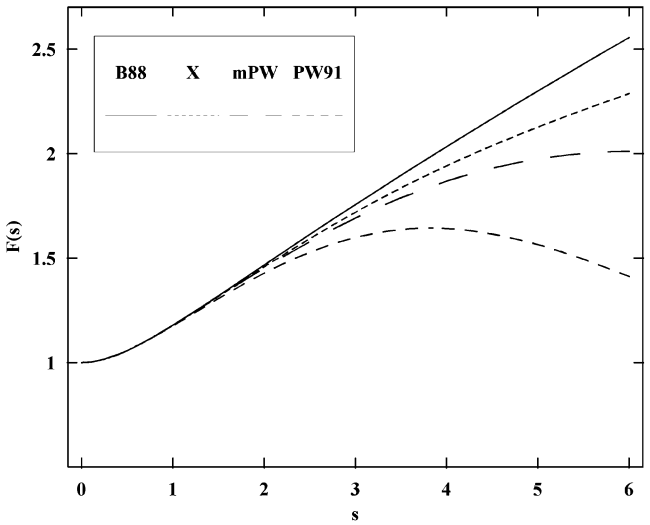

Figure 1. The GGA enhancement factors for Becke88, X, mPW, and PW91 exchange functionals.

the relative performances of MPWB1K, XB1K, and BB1K for noncovalent interactions.

4.6.2. Results without Counterpoise Correction for BSSE. Table 11 summarizes the results for WI4/04 and HB4/04 database without the counterpoise correction for BSSE. These results are very relevant for applications because for most molecular dynamics simulations, it is prohibitive to do counterpoise corrections during the simulation. The good performance without counterpoise corrections may be due in part to error cancellation (as may be the good performance *with* counterpoise corrections−our understanding of the source of

TABLE 12: Overall Results[a]

	thermochemistry	barrier heights	noncovalent interaction with BSSE[b]		noncovalent interaction without BSSE[b]		
method	MTMUE	MUE	MMUE (D_e)	MMUE (R_e)	MMUE (D_e)	MMUE (R_e)	row sum
MPWB1K	1.74	1.39	0.23	0.11	0.42	0.11	3.99
XB1K	1.85	1.27	0.27	0.19	0.30	0.15	4.03
BB1K	2.04	1.29	0.38	0.35	0.31	0.19	4.55
MPW1B95	1.19	3.30	0.22	0.10	0.36	0.11	5.27
X1B95	1.16	3.04	0.61	0.26	0.27	0.12	5.46
MPW1K	2.99	1.41	0.30	0.36	0.48	0.20	5.73
B97-2	1.18	3.12	0.53	0.40	0.34	0.19	5.76
B1B95	1.17	3.01	0.56	0.81	0.35	0.30	6.21
B98	1.37	4.11	0.20	0.10	0.41	0.13	6.31
B97-1	1.32	4.23	0.23	0.09	0.54	0.17	6.58
mPW1PW91	1.64	3.79	0.26	0.35	0.40	0.20	6.64
PBE1PBE	1.51	4.45	0.39	0.12	0.71	0.15	7.33
X3LYP	2.24	4.73	0.28	0.08	0.52	0.13	7.98
MPW3LYP	1.46	5.18	0.53	0.21	0.81	0.23	8.42
B3LYP	1.78	4.68	0.32	1.19	0.32	0.27	8.57
average	1.64	3.27	0.35	0.31	0.44	0.18	6.19

[a] MTMUE is from Table 5, the MUE in barrier heights is the average of the DIDZ MUE for BH6 from Table 6 and the MG3S MUE for BH42/04 in Table 7, and MMUE (D_e) and MMUE (R_e) for noncovalent interaction are from the Tables 10 and 11. Errors in energies are in kcal/mol per bond for atomization energies and kcal/mol for other energetic quantities; and errors in R_e are in a_0. [b] This includes hydrogen bonding and weak interactions.

errors is imperfect), but we still want to know for practical work which methods are good for noncovalent interactions without BSSE corrections. Furthermore, although counterpoise corrections are well-known to improve the results for very small basis sets, their justification with larger basis sets is less secure.[68]

When the BSSE contribution is included, B3LYP can predict van der Waals wells for all rare gas dimers, which differs from the situation in the previous section. Table 11 shows that X1B95, XB1K, BB1K, and B3LYP give the best uncorrected results for hydrogen bonding and weak interactions, as indicated by their low MMUE for D_e. However, MPW1B95 is also as good energetically, but gives very good geometries, so its overall performance is better than B3LYP and comparable to BB1K. The performances of B97−2, B1B95, mPW1PW91, B98, and MPWB1K are also reasonably good for noncovalent interactions, and among the 10 methods do best energetically, MPW1B95 and MPWB1K give the best results for R_e, with X1B95, XB1K, and B98 only slightly behind. In the next subsection, we will try to combine what was learned from Tables 9 and 10 with what was learned from Tables 5−7.

4.7. Overall Performance. Table 12 is a summary of the performance of the tested DFT methods for thermochemistry, thermochemical kinetics, and noncovalent interactions. The final column is the row sum for the columns included in this table. This is a somewhat arbitrary way to weight all the results, but readers who think this is an unbalanced assessment or who are interested in performance for a specific quantity such as electron affinity may concentrate on the more relevant of the myriad of other tabulated results in this paper. To make the very small MMUE (R_e) values count more in the row sum of Table 12, we converted them to bohrs for this table. A very rough attempt at providing an overall ranking for noncovalent interaction is to add the four MMUE columns in Table 12; this would give the following rank for the methods that do best: MPW1B95 (0.79), B98 (0.84), XB1K (0.91), MPWB1K (0.97), X3LYP (1.01), and B97-1 (1.03), with no other method below 1.21. Of these methods, X3LYP does best on weak interactions, which have less effect on the row sums than do hydrogen bonds. In Table 12, the methods are listed in order of increasing row sum for all six columns. Using other methods of weighting the various quantities gives similar orderings of the methods although of course the precise order depends on the weights.

Using the row sum of Table 12 as the measure of quality, we can see that MPWB1K is the best of all of the tested methods, and MPW1K is the best of the tested methods that do not contain kinetic energy density.

An alternative to using the ordering in Table 12 is to use the results obtained for noncovalent interactions, as summarized in the MMUE columns of Tables 10−12, to discriminate among the best performing methods of Tables 5−8. First consider thermochemistry and recall that Table 5 showed that X1B95, B1B95, B97-2, and MPW1B95 are the best methods for thermochemistry of covalent bonds. Examination of Tables 10-12 shows that, on average, MPW1B95 is the best of these methods for noncovalent interactions, and B1B95 is worst. MPW1B95 is also very good for zero-point energies, and so it can be recommended as an excellent general purpose method for thermochemistry. Unfortunately, Tables 6−8 show that none of the methods mentioned in this paragraph is particularly good for barrier heights or saddle point geometries; thus, for thermochemical kinetics, one would certainly make another choice.

Our criteria for thermochemical kinetics still include an atomization energy or energy of reaction component, but it is weighted 50:50 with barrier heights. As already discussed above, when we include barrier heights in this way, Tables 6 and 7 show that BB1K, XB1K, and MPWB1K all perform similarly and seem to be the best choice for thermochemical kinetics. Table 8 showed that these methods give similar accuracy for saddle point geometries, and Table 9 shows that performance for zero-point energies does not significantly distinguish them either. Thus, their relative performance for noncovalent interactions can be decisive. On average MPWB1K and XB1K perform similarly for noncovalent interactions, with BB1K coming in third among these three methods. It is encouraging that the final overall ranking of the methods by this human judgment line of reasoning agrees quite well with the ranking in Table 12, giving at least a little confidence that this numerical ranking is not unreasonable.

Of the fifteen methods in Table 12, seven of them have a row sum better than the average, and of these, the MPWB1K, XB1K, MPW1B95, and X1B95 can all be highly recommended if a computer program that supports kinetic energy density is available. Based on the row sum, MPW1K is the best of the tested methods from among those that do not contain kinetic

energy density. Nevertheless, one should be cautious about overgeneralizing these results. For example, although MPW1K is certainly the best of the HDFT methods for kinetics and has the best overall row sum, it is not the best in all categories. The best method without kinetic energy density for thermochemistry is B97-2, and the best method without kinetic energy density for noncovalent interactions is B98. Similarly, although MPWB1K appears to be the best method overall, XB1K, BB1K, and MPWB1K give similar accuracy for barrier heights, MPW1B95, X1B95, B97-2, and B1B95 are the best for thermochemistry, and MPWB1K, XB1K, B98, and MPW1B95 are the best for noncovalent interactions.

4.8. Concluding Remarks. This paper developed four new hybrid meta DFT methods and one new hybrid DFT method for thermochemistry and thermochemical kinetics. The resulting methods were comparatively assessed against the AE109/3 atomization energy database, against the BH42/04 barrier height database, against the AE6 representative atomization energy database, against the BH6 representative barrier height database, against the SPG15/02 saddle point geometries database, against the ZPE13/99 zero-point energy database, against the new HB4/04 hydrogen bonding database, and against the new WI4/04 weak interaction database. From the above assessment and comparison, we obtain the following conclusions:

(1) The mPW and X exchange functional are very similar and both appear better than other exchange functionals.

(2) MPWB1K and XB1K give the best results for a combination of thermochemistry, thermochemical kinetics, hydrogen bonding, and weak interactions, especially for thermochemical kinetics and noncovalent interaction.

(3) X1B95 and MPW1B95 are the best methods for covalent and noncovalent thermochemistry, but these methods are not accurate for barrier height calculations.

(4) B98 and B97-1 give good performance for hydrogen bonding and weak interactions with BSSE corrections. They are not accurate for barrier height calculations.

(5) X1B95, XB1K, MPW1B95, and BB1K perform well for hydrogen bonding and weak interactions without BSSE corrections. BB1K and MPWB1K are also good methods for thermochemical kinetics.

It is important to be able to draw general conclusions as well as to do numerical comparisons. The present paper, which involves a broader assessment than our previous work but builds on that work in the selection of methods, leads us to believe that the mPW exchange functional performs better than the Becke88 one in essentially all respects, and the Becke95 correlation functional likewise performs better than the LYP correlation functional. In addition, when both exchange functionals are used with the Becke95 correlation functional, mPW appears to be slightly better on average than the newer but very similar X functional, but for some purposes (or with the LYP correlation functional), the X functional is sometimes better. This assessment now includes noncovalent interactions, in addition to thermochemical data and barrier heights. Thus we recommend MPW1B95 for general purpose application and MPWB1K for kinetics. Both methods are among the best performers for noncovalent interactions.

The keywords required in Gausssian03[69] to carry out MPW1B95/DIDZ calculations are:

#mpwb95/6-31+G(d,p)

IOp(3/76=0690003100)

The keywords required in Gausssian03[69] to carry out MPWB1K/DIDZ calculations are:

#mpwb95/6-31+G(d,p)

IOp(3/76=0560004400)

We can also recommend X1B95 and XB1K for some purpose, but they are not available in any distributed computer packages.

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Supporting Information Available: Training sets and the AE109/03, BH42/03, and SPG15/01 databases. This material is available free of charge via the Internet at http://pubs.acs.org.

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