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Benchmark Databases for Nonbonded Interactions and Their Use to Test Density Functional Theory

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Abstract.

We present four benchmark databases of binding energies for nonbonded complexes. Four types of nonbonded interactions are considered: hydrogen bonding, charge transfer, dipole interactions, and weak interactions. We tested 44 DFT methods and 1 WFT method against the new databases; one of the DFT methods (PBE1KCIS) is new, and all of the other methods are from the literature. Among the tested methods, the PBE, PBE1PBE, B3P86, MPW1K, B97-1, and BHandHLYP functionals give the best performance for hydrogen bonding. MPWB1K, MP2, MPW1B95, MPW1K, and BHandHLYP give the best performances for charge transfer interactions; and MPW3LYP, B97-1, PBE1KCIS, B98, and PBE1PBE give the best performance for dipole interactions. Finally, MP2, B97-1, MPWB1K, PBE1KCIS, and MPW1B95 give the best performance for weak interactions. Overall, MPWB1K is the best of all the tested DFT methods, with a relative error (highly averaged) of only 11%, and MPW1K, PBE1PBE, and B98 are the best of the tested DFT methods that do not contain kinetic energy density. Moving up the rungs of Jacob's ladder for nonempirical DFT, PBE improves significantly over the LSDA, and TPSS improve slightly over PBE (on average) for nonbonded interactions.

1. Introduction

One can classify interatomic interactions as bonded or nonbonded. One can further subdivide bonded interactions into ionic, metallic, covalent, coordinate covalent, and partial bonds (as at transition states), and one can subdivide nonbonded interactions into charge transfer interactions, hydrogen bonds, dipolar interactions, dispersion (London forces), and so forth. Mixed cases are also possible, such as polar covalent (e.g., an HF bond is about 50% ionic and 50% covalent[1]) or a much more complicated range of possibilities[2] for nonbonded interactions. Nevertheless the distinctions and the broadly defined categories of interactions are useful for understanding chemical phenomena and for testing the abilities of approximate theories and models to understand chemical phenomena.

Density functional theory (DFT[3-87] and wavefunction theory (WFT)[31,34,44,55,88-119] have been widely compared for their abilities to treat bonds and transition states, but comparisons are less complete for nonbonded interactions. There are two reasons for this. First, it has been realized for a long time that DFT, at least with the early functionals, is less accurate for nonbonded interactions than for bonded ones,[16-18] and this can be understood in part by the fact that current functionals are not designed to treat dispersion interactions, which are sometimes dominant in nonbonded interactions. Second, no standard databases (analogous to the G3 database[106,107,110] or Database/3[114] for bond energies, ionization potentials, and electron affinities; the latter also includes partial bond strengths as measured by barrier heights) are available for nonbonded interactions. The purpose of the present article is to remedy the latter problem and to use newly created databases for nonbonded interactions for a systematic comparison of DFT and WFT methods.

Considerable insight into how DFT works can be obtained by detailed analysis of the functionals and the Kohn-Sham electron density. In particular it should be recognized that, for molecules, the separation of exchange-correlation effects into exchange and

correlation are different in WFT and DFT.[10,21,28,46,49] In particular, DFT exchange includes a certain amount of what is called nondynamical (also called static or internal or, in certain contexts, left-right) correlation in WFT.[10,28,43,49] Handy and Cohen[49] have shown that DFT with an exchange functional (Becke88, or B88X[8]) but no correlation functional gave lower energies than Hartree-Fock for the multi-center system (for example, molecules), and they concluded that local exchange functionals must introduce nondynamical correlation. Furthermore, He et al[46] found that even for closed-shell systems that are well described without nondynamical correlation (so called single-reference systems), densities obtained by DFT with an exchange functional but no correlation functional look more like those obtained with fourth-order perturbation theory (MP4) than those obtained by uncorrelated Hartree-Fock.[46] They concluded that " even though the DFT exchange functional does not include any Coulomb correlation effects by construction, it simulates orbital relaxation, pair correlation, …".[46] However the resulting electron density is too high in the van der Waals region, and correlation functionals contract the density toward high-density regions (where there is more favorable correlation energy), thus improving the description of van der Waals interactions.[46] Since correlation functionals make up for deficiencies in exchange functionals, and since the exchange functional gives a much larger contribution to molecular interactions than the correlation one, it is important that the correlation functional be well matched to the exchange functional with which it is used.

Although the usual DFT functionals do not contain dipolar dispersion interactions, there is some debate as to whether DFT methods, with either the usual functionals or new ones, might nevertheless produce useful results for the attractive interaction between rare gas atoms.[120-123] Furthermore DFT, even with the usual functionals, does contain the polarizabilities.[124] Our goal in the present paper is not, however, to pursue lines of research based on explicit inclusion of dipole polarization, but rather to check which of the density functionals in current widespread use disqualify themselves by predicting

unrealistic interaction potentials in regimes where the real interaction potentials are dominated by dispersion forces or other nonbonded interactions, and which density functionals yield reasonable results in such situations, for whatever reason.

In addition to lacking explicit R^{-6} terms, DFT (without Hartree-Fock exchange) predicts no interaction energy for molecules so far apart that they do not overlap (because the density is the same as for infinitely separated molecules). At the equilibrium distance of nonbonded complexes, the lack of explicit R^{-6} terms need not be a serious issue because the higher terms (R^{-8}, etc.) in the asymptotic expansion are not negligible.[125,126] Furthermore, the overlap and exchange forces are also not negligible at the equilibrium internuclear distance of nonbonded complexes.[125,127] Thus DFT is not excluded as a potentially useful theory for nonbonded interactions, as is sometimes claimed.

In summary, our goal is to understand the performance of existing density functionals for nonbonded interactions and to compare this performance to that of WFT with the same basis sets. We therefore develop four new databases for such testing:

- A hydrogen bond database
- A charge transfer complex database
- A dipole complex database
- A weak interaction database

Whereas hydrogen bonds are dominated by electrostatic and polarization (also called induction) interactions (with a smaller contribution from charge transfer), charge transfer complexes derive a considerable portion of their stabilization from electron transfer between the two centers. Dipole complexes involve much smaller amounts of intermolecular charge transfer and have no hydrogen bonds. Weak complexes are defined here as those that are dominated by dispersion interactions.

In the literature, there are many theoretical studies of hydrogen bonds,[29,31,39,44,47,54,70,82,85,100,102,111-113,116,128,129] charge transfer complexes,[18,19,27,29,34,71,117] and weak interactions.[29,44,54,62,84,93,94,97,115] However there are very few studies[31,39,47,69] of

dipolar interaction complexes. Several studies[39,47,69] treated $(HCl)_2$ dimer as a hydrogen bond complex, but in the present study we will treat $(HCl)_2$ dimer as a dipole interaction complex since there is no classical hydrogen bond in $(HCl)_2$ dimer.

The databases are used to test several types of DFT: (i) the local spin density approximation (LSDA, in which the density functional depends only on density), (ii) the generalized gradient approximation (GGA, in which the density functional depends on density and its reduced gradient), (iii) meta GGA (in which the functional also depends kinetic energy density), (iv) hybrid GGA (a combination of GGA with Hartree-Fock exchange), and (v) hybrid meta GGA (a combination of meta GGA with Hartree-Fock exchange). In addition we study one level of WFT: Møller-Plesset second order perturbation theory[88] (MP2).

Section 2 explains the theories, databases, and functionals used in the present work. Section 3 presents results and discussion, and Section 4 has concluding remarks.

2. Theory and Databases

2.1. Weizmann 1 (W1) Theory. It is difficult to extract the zero-point-exclusive binding energies D_e from experiment for nonbonded complexes due to the uncertainties in the experimental ground-state dissociation energy D_0 and due to the uncertain effect of anharmonicity on the zero point vibrational energy of these loose complexes. To obtain the best estimates for the binding energies in the new database, we employed the W1 method for most of the nonbonded complexes, and we also took some theoretical and experimental results from the literature.

W1 theory was developed by Martin and Oliveira, and it is a method designed to extrapolate to the complete basis limit of a CCSD(T)[90] calculation. Thus W1 theory should be good enough for obtaining best estimates of binding energies of these nonbonded complexes. Boese et. al[69,81] have already used W1 and W2 theory to calculate best estimates for some hydrogen bonding dimers, and we will employ W1

theory for several more nonbonded complexes in the present work. The strengths and limitations of W1 theory have been described elsewhere.[98,105,108,109,119]

2.2. HB6/04 Database. The hydrogen bond database consists of binding energies of six hydrogen bonding dimers, namely $(NH_3)_2$, $(HF)_2$, $(H_2O)_2$, $NH_3\cdots H_2O$, $(HCONH_2)_2$, and $(HCOOH)_2$. The binding energies of $(NH_3)_2$, $(HF)_2$, $(H_2O)_2$, and $NH_3\cdots H_2O$ are taken from Boese and Martin's[81] W2 calculations. The best estimates of D_e for $(HCONH_2)_2$ and $(HCOOH)_2$ are calculated here by the W1 theory. This database is called the HB6/04 database.

2.3. CT7/04 Database. The charge transfer (CT) database consists of binding energies of seven charge transfer complexes, in particular $C_2H_4\cdots F_2$, $NH_3\cdots F_2$, $C_2H_2\cdots ClF$, $HCN\cdots ClF$, $NH_3\cdots Cl_2$, $H_2O\cdots ClF$, and $NH_3\cdots ClF$. The best estimates of D_e for all complexes in the charge transfer database are calculated here by the W1 model. This database is called the CT7/04 database.

2.4. DI6/04 Database. The dipole interaction (DI) database consists of binding energies of six dipole inteaction complexes: $(H_2S)_2$, $(HCl)_2$, $HCl\cdots H_2S$, $CH_3Cl\cdots HCl$, $CH_3SH\cdots HCN$, and $CH_3SH\cdots HCl$. The binding energy of $(HCl)_2$ is taken from Boese and Martin's[81] W2 calculation. The best estimates of D_e for the other complexes in the dipole interaction database are calculated here by the W1 theory. This database is called the DI6/04 database.

2.5. WI9/04 Database. The weak interaction database consists of binding energies of weak interaction complexes, namely HeNe, HeAr, Ne_2, NeAr, $CH_4\cdots Ne$, $C_6H_6\cdots Ne$, $(CH_4)_2$, $(C_2H_2)_2$, and $(C_2H_4)_2$. The binding energies of HeNe, HeAr, Ne_2, and NeAr are taken from Ogilvie and Wang's[130,131] analysis. The binding energy of $C_6H_6\cdots Ne$ is taken from Cappelletti et al.'s[132] experimental study. The best estimates of D_e for $CH_4\cdots Ne$, $(CH_4)_2$, $(C_2H_2)_2$, and $(C_2H_4)_2$ are calculated by W1 theory. This database is called the WI9/04 database.

2.6. AE6 Benchmark Database. We parametrized one new hybrid meta GGA method, namely PBE1KCIS (see Table 3). It has one parameter, the fraction *X* of Hartree-Fock exchange, and this was optimized against the AE6[133] benchmark database of atomization energies for six covalently bonded nonmetallic molecules. We have previously used this database as a training set to optimize the MPW1B95,[79] TPSS1KCIS,[86] and MPW1KCIS[87] methods.[76] The AE6 database is listed for reference in the supporting information.

To parametrize the PBE1KCIS model, we optimize the fraction of Hartree-Fock exchange, *X,* to minimize the root mean square error (RMSE) for the six data in the AE6 database. The optimized *X* parameter for the PBE1KCIS method is given in Table 3.

2.7. Theoretical Methods Tested. We tested a number of DFT-type methods against the new four-part (HB6, CT7, DI6, WI9) nonbonded-interaction database. In particular, we assessed three LSDAs: SVWN3,[5,134] SVWN5,[5,134] and SPWL.[12,134] We tested twelve GGAs: BP86,[7,8] BLYP,[8,9] BPW91,[8,11] BPBE,[8,22] mPWPBE,[22,135] G96LYP,[9,20] HCTH,[33] mPWLYP,[9,29] mPWPW91,[29] OLYP,[9,49] PBE[22], and XLYP.[74] We tested seven meta GGA methods: BB95,[21] mPWB95,[21,29] mPWKCIS,[29,37,38,60,70,72] PBEKCIS,[22,37,38,60] TPSS,[70,72] TPSSKCIS[37,38,60,70,72] and VSXC.[32] We assessed thirteen hybrid GGA methods: B3LYP,[9,14,15] B3P86,[7,14] B3PW91,[11,14] BHandHLYP,[136] B97-1,[33] B97-2,[53] B98,[30] mPW1PW91,[29] MPW1K,[45] MPW3LYP,[9,29,79] O3LYP,[49,50] PBE1PBE,[22]and X3LYP[74] and we also assessed nine hybrid meta GGA methods: B1B95,[21] BB1K, [76] MPW1B95,[79] MPWB1K,[79] MPW1KCIS,[87] MPWKCIS1K,[87] PBE1KCIS, TPSS1KCIS,[37,38,60,70,72,86] and TPSSh.[70,72]

Since the theory behind the various DFT functionals is explained in the original paper, we refer the readers to the original references for those details; however, a few comments are needed about these LSDAs. All these use the same exchange functional, due to Dirac and Slater,[134] but they differ in the correlation functional. Although SVWN3 is incorporated (apparently by mistake) in the popular B3LYP functional, it is based upon

the inaccurate random phase approximation for the electron gas of uniform density, where VWN5 and SPWL are more properly (from a theoretical point of view) based on the homogeneous electron gas results of Ceperly and Alder.[137] The difference between VWN3 and VWN5 has been discussed, for example, by Hertwig and Koch.[26] A complete summary of all DFT methods considered in this article is given in Table 3.

We also tested one ab initio WFT method: MP2.[88]

2.8. Computational Methods. All MP2, W1, and DFT calculations were carried out using the *Gaussian03*[138] and MOLPRO[139] programs, but a few aspects of the calculations require some comments.

PBE1KCIS is not available with standard keywords in *Gaussian03*; the keywords required in *Gaussian03* to carry out the the PBE1KCIS calculation are:

#PBEKCIS

IOp(3/76= 0780002200)

Some workers have had difficulty with SCF convergence when using the B95 correlation functional, and the usefulness of the functional has been questioned for this reason. However, we have discovered the source of this problem, and it is easily remedied without changing the functional. In the B95 functional,[21] the parallel-spin component of the correlation energy is given in terms of the uniform electron gas (UEG) expression by

$$E_C^{\sigma\sigma} = \frac{D_\sigma}{\frac{3}{5}\left(6\pi^2\right)^{2/3}\rho_\sigma^{5/3}} E_{C\sigma\sigma}^{UEG} \qquad (1)$$

where D_σ is a function of kinetic energy density and the reduced gradient density, and ρ_σ is the electron density for spin σ. This energy expression vanishes when the density goes to zero, and *Gaussian03* sets it equal to zero when the denominator is less than 10^{-15}; however, for values of the denominator in the range 10^{-15}–10^{-6}, $E_C^{\sigma\sigma}$ is still negligible, but eq. (1) has numerical instabilities because it is ~0/0. Changing the criterion for neglecting $E_C^{\sigma\sigma}$ from a denominator of 10^{-15} to a denominator of 10^{-6} solves

the problem. This can be accomplished by changing the density tolerance variable DTol in subroutine bc95ss.f from 10^{-15} to 10^{-6}. We have checked that this eliminates problems for counterpoise calculations, ionization potential calculations, metal-metal bonds, and metal-ligand bonds. The effect on the computed results is negligible, for example, an average error of 10^{-8} hartrees for the data in Database/3[65,114] and < 10^{-4} cm^{-1} for the vibrational frequencies of methanethiol.

All DFT calculations use ultrafine grids in *Gaussian03*.

Except in the final table, which involves DFT geometries optimization with 20 different functionals, geometries for all molecules in this paper are optimized at the MC-QCISD/3 level, where MC-QCISD is the multi-coefficient QCISD method,[103,114] which is one of the most cost efficient of the multi-coefficient correlation methods (MCCMs). Figures 1, 2, 3, and 4 show the geometries of the complexes studied in the present paper. All W1 and MP2 calculations use the MC-QCISD/3 geometries, and we also presented results for all 43 DFT methods with these geometries. The MC-QCISD/3 geometries for all monomers and complexes in this paper can be obtained from the Truhlar group database website.[140]

We tested all DFT methods in Table 3 with three basis sets: DIDZ (which denotes 6-31+G(d,p)),[89] aug-cc-pVTZ,[91] and MG3S. The MG3S basis[65] is the same as MG3 except it omits diffuse functions on hydrogens. MG3 is the modified[99,101] G3Large[96] basis set. It is also called the G3LargeMP2[99] basis set, and it is the same as 6-311++G(3d2f, 2df, 2p)[141] for H-Si, but improved[96] for P-Ar.

2.9. Counterpoise Corrections. For all nonbonded complexes, we perform calculations with and without the counterpoise corrections[142,143] for basis set superposition error (BSSE).

3. Results and Discussion

3.1.W1 Results. Table 1 summarizes the 17 new W1 calculations carried out for the new databases. From this table, it can be seen that the Hartree-Fock (HF) component

of the calculations underestimates all binding energies; the magnitudes of CCSD correlation contributions to the binding energies for the two hydrogen bonding dimers in Table 1 are in a range from 3 to 4 kcal/mol, and those for the seven charge transfer complexes are in a range from 1.9 to 6.3 kcal/mol. The (T) correlation contributes about 1 kcal/mol to the binding energies for the two hydrogen bonding cases, and from 0.4 to 1.9 kcal/mol for the charge transfer cases. Note that HF theory gives negative binding energies for the $C_2H_4\cdots F_2$, $NH_3\cdots F_2$, and $C_2H_2\cdots ClF$ complexes, that is, the complex is not bound at the MC-QCISD/3 geometry.

The magnitudes of CCSD correlation contributions to the binding energies for the five dipole interaction complexes are in a range from 1.5 to 3.6 kcal/mol, whereas the magnitudes of the (T) correlation contributions are in a range from 0.3 to 0.6 kcal/mol, which makes the (T) contribution relatively less important for the dipole interaction cases than for the previous two types. The validity of various DFT methods might be correlated with the relative importance of (T) contributions because the relative importance of (T) contributions might be a rough measure of multi-reference character, and some DFT methods are better than others for multi-reference cases.

The magnitudes of CCSD correlation contributions to the binding energies for the four weak interaction complexes are in a range from 0.3 to 2 kcal/mol, and the magnitudes of (T) correlation contributions are in a range from 0.0 to 0.4 kcal/mol, again relatively small. Note that HF theory give negative binding energies for $CH_4\cdots Ne$, $(CH_4)_2$, and $(C_2H_4)_2$. This agrees with Tsuzuki and Luthi's theoretical study.[54] They have shown that HF predicts purely repulsive intermolecular potentials for the $(CH_4)_2$ and $(C_2H_4)_2$ dimers.

3.2. Benchmark Databases for Nonbonded Interactions. The new databases are presented in Table 2. The magnitudes of the binding energies are in the range 3.2 to 16.2 kcal/mol for the HB6/04 database, 1.1 to 10.6 kcal/mol for the CT7/04 database, 1.7 to 4.2 kcal/mol for the DI6/04 database, and 0.04 to 1.42 kcal/mol for the WI9/04 database.

The last row gives the average binding energy for each type, but we note that each database in Table 2 contains strong, medium, and weak complexes for each particular kind of nonbonded interaction. Furthermore, the CT7/04, DI6/04, and WI9/04 databases contain complexes for the first and second row atoms. In the WI9/04 database, we have rare gas-rare gas complexes (HeAr, NeAr, etc.), a rare gas-π interaction complex (C_6H_6-Ne), an sp^2-sp^2 interaction complex ($(C_2H_4)_2$), an *sp*-*sp* interaction complex ($(C_2H_2)_2$), and a rare gas-sp^3 interaction (CH_4-Ne). These diverse data for nonbonded interactions were especially chosen to be suitable for testing theoretical methods.

3.3. Tests of Theoretical Methods. The mean errors of the tested methods are listed in Tables 4, 5, 6, 7, and 8. In these tables we tabulate the mean unsigned error (MUE, also called mean absolute deviation) and mean signed error (MSE). We use "no-cp" to denote calculations without the counterpoise correction for the BSSE, and we use "cp" to denote calculations that do include the counterpoise correction for the BSSE. The calculated binding energies with the MG3S basis set are listed in the supporting information.

In order to make it a little easier to put the large number of results in this paper in perspective, we define the following quantities:

MMUE = [MUE(no-cp) + MUE(cp)]/2

MMMUE = [MMUE(DIDZ) + MMUE(aug-cc-pVTZ) + MMUE(MG3S)]/3

MMMMUE= [MMMUE(HB) + MMMUE(CT) + MMMUE(DI) + MMMUE(WI)]/4

Our discussion will focus *mainly* on the highly averaged MMMUEs and MMMMUEs because they provide measures for broad usefulness for various kinds of calculations. Specialists interested in one or another subjects of the results are invited to make their own comparisons and draw their own conclusions.

3.3.1 Results for Hydrogen Bonding. Table 4 summarizes the results for the hydrogen bonding calculations. Among the LSDA and GGA methods, PBE gives the lowest MMMUE for binding energies in the HB6/04 database. VSXC is the best meta

GGA, B3P86 and PBE1PBE are the best hybrid GGAs, and PBE1KCIS is the best hybrid meta GGA for hydrogen bonding calculation. Overall, PBE1PBE, B3PB86, and PBE give the best performance for calculating the binding energies for the hydrogen bonding dimers in the HB6/04 database. This result is consistent with the results of Ireta and coworkers.[82] They used ab initio pseudopotentials, a plane wave basis set, and periodic boundary conditions to integrate the Kohn-Sham equations for the calculation of the energetics of several hydrogen bonded dimers, and they found that PBE gives very good accuracy.

From Table 4, we can also see that B3P86 and MPW1K are the best performers for the DIDZ basis set. Good performance for the small basis is important because one of the attractive features of DFT is its applicability to large systems, for which larger basis sets can be cost prohibitive. Note that MP2 only works well with the aug-cc-pVTZ basis, and this will limit its application to large systems.

Table 4 shows that the two DFT methods that contain the OPTX exchange functional, OLYP and O3LYP, give very bad results for hydrogen bonding dimers. OLYP is even worse than LSDA. Note that in one of our previous papers, we found that OLYP gives good performance for atomization energy calculations on chemically bonded systems. From this point of view, we conclude that the OPTX exchange functional may have been fitted to a too restricted set of thermochemical data; anyway it is not suitable for hydrogen bonding calculation.

3.3.2 Results for Charge Transfer. Table 5 summarizes the results for the charge transfer calculations. Among the LSDA and GGA methods, G96LYP give the lowest MMMUE for calculating the binding energies in the CT7/04 database. BB95 is the best meta GGA, BHandHLYP and MPW1K are the best hybrid GGAs, and MPWB1K is the best hybrid meta GGA for charge transfer calculations. Overall, MPWB1K and MPW1B95 give the best performance for calculating the binding energies of the charge transfer complexes, and both of them outperform MP2. This is encouraging because

MPWB1K and MPW1B95 are among the newest functionals, and so far they have proved to be good general-purpose functionals.

Table 5 shows that all LSDA, GGA and meta GGA functionals systematically overestimate the binding energies of the complexes in the CT7/04 database. Ruiz et al[19] have pointed out that " the wrong asymptotic behavior and the derivative discontinuity of the exchange and correlation energy in DFT lead to a reduction of the HOMO-LUMO gap …". The small HOMO-LUMO gap leads to too much charge transfer and is the ultimate cause of the overestimation of the strength of the charge transfer interaction. Inclusion of HF exchange in the DFT calculation improves the performance,[18] as shown here by the low MMMUE obtained by some hybrid and hybrid meta GGA methods.

From Table 5, we can see that MPWB1K and BHandHLYP are the best performers for the DIDZ basis set.

3.3.3 Results for Dipole Interaction. Table 6 summarizes the results for the dipole interaction complexes. Among the LSDA and GGA methods, mPWLYP gives the lowest MMMUE for calculating the binding energies in the DI6/04 database. PBEKCIS is the best meta GGA, B97-1 and MPW3LYP are the best hybrid GGAs, and PBE1KCIS is the best hybrid meta GGA for dipole interaction calculations. Overall, B97-1 and MPW3LYP give the best performance for calculating the binding energies for the dipole interaction complexes in the DI6/04 database.

Since hydrogen bonding interactions and dipole interactions are physically very similar, the good performers for hydrogen bonding, PBE and PBE1PBE, also work well for the dipole interaction calculation

From Table 6, we can see that MPW3LYP is the best performer for the DIDZ basis set.

3.3.4 Results for Weak Interaction. Table 7 summarizes the results for the weak interaction complexes. PBEKCIS is the best meta GGA, B97-1 is the best hybrid GGA, and MPWB1K is the best hybrid meta GGA for weak interactions. Overall, B97-1 and

MP2 give the best performance for calculating the binding energies for the weak interaction complexes in the WI9/04 database.

In principle, a DFT method can yield the exact ground state energy, including long range van der Waals (vdW) energies. However, in 1998, Kohn et al. pointed out, "the commonly used LDA and GGA, designed for non-uniform electron gases, fail to capture the essence of vdW energies."[144] It seems that this statement is true because the best method, B97-1, has a mean unsigned error (0.19 kcal/mol) that is 40% of the mean value of the binding energy (0.47 kcal/mol, see Table 2). However, even MP2 has a 34% error by this kind of assessment, so from the practical point of view, DFT is almost competitive in accuracy at a much lower cost. Other methods with errors of less than 50% are MPWB1K, and MPW1B95. We have recently pointed out[79] that the X and mPW exchange functionals have similar behavior in the large reduced-gradient region (which corresponds to the polarizable low-density outer fringe of atoms and moleculaes) and that seems to account for their good behavior for nonbonded interactions. Table 7 bears this out: mPWLYP and XLYP are better than BLYP, mPWB95 is better than BB95, MPW3LYP and X3LYP are better than B3LYP, MPWB1K is better than BB1K, and MPW1B95 is better than B1B95.

From Table 7, we can see that B97-1 is the best performer for the DIDZ basis set.

3.4. Overall Results. Table 8 is a summary of the performance of the tested methods for nonbonded interactions. The rank order is according to the final column, which is the average of the four database columns included in this table. Clearly the exact position in the ranking is not as meaningful as the general trends, but it provides a way to organize the discussion. The five smallest average errors for each of the individual databases and the ten smallest average errors overall are in bold.

From Table 8, we can see that the best performers for hydrogen bonding are: PBE, PBE1PBE, B3P86, MPW1K, B97-1, and X3LYP. The best performers for charge transfer interaction are: MPWB1K, MP2, MPW1B95, MPW1K, and B1B95. The best performers

for dipole interaction are: MPW3LYP, B97-1, PBE1KCIS, B98, and PBE1PBE. The best performers for weak interaction are: MP2, B97-1, MPWB1K, MPW1B95, and PBE1KCIS.

Using MMMMUE in Table 12 as the overall, summarizing measure of quality for nonbonded interactions, we can see that MPWB1K is the best of all the tested DFT methods, and MPW1K is the best of the tested DFT methods that do not contain kinetic energy density. Both of these DFT methods have three bold entries. B97-1 has four bold entries, but it is only 27% better than average of all 43 DFT methods for charge transfer complexes (the averages are in the last row of the table).

LSDA, PBE, and TPSS are the first three rungs of Perdew's nonempirical Jacob's ladder[51,61,72] for organizing DFT approximations. Perdew, Scuseria, and coworkers have recently made extensive comparisons of LSDA, PBE, and TPSS for atoms, molecules, solids, and surfaces.[70,72,83] In every case, TPSS was either significantly better than the other two nonempirical functionals or about the same as the better of the other. Recently we also found this pattern holds for barrier height calculations.[87] From Table 8, we can see that this pattern also holds for nonbonded interaction calculations in general, even though it does not hold for hydrogen bonding. As we climb the nonempirical ladder, the nonbonded interaction calculations improve significantly from LSDA to PBE (MMMMUE reduces from 3.67 to 1.05 kcal/mol), but only improve slightly from PBE to TPSS (MMMMUE reduces from 1.05 to 0.95 kcal/mol).

Averaging the four averages in Table 2 yields 4.13 kcal/mol for a mean binding energy characterizing the tests in this paper. The smallest error in Table 8, namely 0.46 kcal/mol, is only 11% of this. This is quite good, especially considering that DFT is often described as inaccurate for nonbonded interactions. The same calculation yield an 18% error for B3LYP, which is the most popular DFT functional, and 93% for the least accurate method (SVWN3) in Table 8.

Progress in DFT can be gauged by a statistical analysis of the 14 DFT methods that perform better than the popular B3LYP method in Table 8. We find two methods from 1993 (BHandHLYP and B3P86), one from 1996 (PBE1PBE), one from 2000 (MPW1K), six from 2004 (MPWB1K, MPW1B95, X3LYP, MPW3LYP, MPW1KCIS, and TPSS1KCIS), and one from this article (PBE1KCIS). Thus, half of the best methods date from the past year. This is encouraging, and we hope that the variety of new databases and systematic tests currently being reported will lead to even more improvements in the near future.

3.5. Comparison of the mean errors by consistently optimized geometries. To investigate the ability of DFT methods to predict accurate energetics when they are also used to predict the geometries of the complexes, we also performed calculations with consistently optimized geometries for the B3LYP, B97-1, B97-2, B98, BLYP, HCTH, MP2, MPW1B95, MPW1K, MPW3LYP, MPWB1K, PBE, PBE1KCIS, PBE1PBE, SPWL, TPSS, TPSS1KCIS, TPSSh, X3LYP, and XLYP methods with MG3S basis set, and the results are given in Table 9.

Table 9 shows that the mean errors only slightly changed for hydrogen bonding, dipole interactions, and weak interactions by using consistently optimized geometries as compared to using the MC-QCISD geometries. For charge transfer interactions, the mean errors for the B97-1, B97-2, MP2, MPWB1K, MPW1B95, MPW1K, PBE1KCIS and PBE1PBE methods change slightly, but mean errors for B3LYP, HCTH, MPW3LYP, PBE, SPWL, TPSS, TPSS1KCIS, and TPSSh change more significantly. This is due to the systematical underestimation of the intermolecular distance by these methods, a problem for many DFT methods that was studied ten years ago by Ruiz et al.[18] For SPWL applied to weak interactions the strong overbinding shown by the results in Table 9 is consistent with previous work.[145-147]

The HCTH, XLYP, and X3LYP results in Table 9 are particularly interesting because these methods contained some non-bonded complexes in their training set. The

training set of HCTH contains nine hydrogen bonded dimers, and the training set of XLYP and X3LYP contains two van der Waals complexes (He_2 and Ne_2). However, Table 9 shows that HCTH does poorly for hydrogen bonding, and XLYP and X3LYP do poorly for weak interaction. These results show that including nonbonded interaction complexes in the training set does not guarantee that one will produce a good functional for nonbonded interaction; one needs to choose a good functional form, an appropriate training set, and a good weighting scheme to accurately parametrize a semiempirical DFT functional for nonbonded interactions.

The last three columns of Table 9 give the information about the maximum errors for each functional. For hydrogen bonding, $(HCOOH)_2$ and $(HCONH_2)_2$ are difficult cases for all DFT methods. This is partly due to the fact that both complexes have two hydrogen bonds. For charge transfer interactions, NH_3-F_2 is the most difficult case for those DFT methods that have low or zero percentage of Hartree-Fock exchange, and NH_3-ClF is the worst case for DFT methods that have a moderate or high percentage of Hartree-Fock exchange. CH_3Cl-HCl and CH_3SH-HCl are two difficult cases for DFT for dipole interactions. For weak interactions, $(C_2H_4)_2$ is the worst case for most DFT methods. This is because $(C_2H_4)_2$ is a $\pi\cdots\pi$ stacking complex, and it is very difficult to describe this type of weak interaction by DFT methods. It is encouraging that MPW1K and MPWB1K have smaller maximum errors than MP2, and the maximum errors in MPW1B95and PBE1KCIS are only 4% and 22% larger, respectively, than the maximum error in MP2. If we judge the methods solely by the maximum errors, we would conclude that MPW1K, MPWB1K, and MPW1B95 (in that order) are the best DFT methods in Table 9 with PBE1KCIS ranked fourth. It is encouraging that this is very similar to the conclusion drawn form Table 8. A key difference between Tables 8 and 9 is that Table 8 average over three basis sets, whereas Table 9 is based on a single basis set. For this reason we based on our overall evaluation on Table 8.

4. Concluding Remarks

In this paper, we developed four benchmark databases of binding energies for nonbonded interaction complexes. We tested 43 DFT methods and 1 WFT method against the new databases.

Among the tested methods, the PBE, PBE1PBE, B3P86, MPW1K, B97-1, and BHandHLYP functionals give the best performance for hydrogen bonding, and MPWB1K, MP2, MPW1B95, MPW1K, and BHandHLYP give the best performance for charge transfer interactions. MPW3LYP, B97-1, PBE1KCIS, B98, and PBE1PBE give the best performance for dipole interactions, and MP2, B97-1, MPWB1K, PBE1KCIS, and MPW1B95 give the best performance for weak interactions.

Overall, MPWB1K is the best of all the tested DFT methods, and MPW1K, PBE1PBE, and B98 are the best of the tested DFT methods that do not contain kinetic energy density. Interestingly, MPWB1K is found to be more accurate than MP2 for nonbonded interactions.

Moving up the rungs of Jacob's ladder for DFT, PBE improves significantly over the LSDA, and TPSS improve slightly (on average) over PBE for nonbonded interactions.

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Supporting Information Available: The AE6 database and the calculated binding energies on nonbonded complexes with the MG3S basis are given as PDF file in the first supporting information file, and the MC-QCISD/3 geometries are given as a text file in the second supporting information file. This material is available free of charge via the Internet at http://pubs.acs.org.

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Table 1: Components of W1 Calculations for Binding Energies D_e (kcal/mol)

Complex	SCF[a] limit	CCSD[b] limit	(T) [c] limit	core corr. & Relativistic	Final D_e
Hydrogen Bonding					
$(HCONH_2)_2$	9.98	3.93	0.97	0.06	14.94
$(HCOOH)_2$	12.05	3.15	0.94	0.00	16.15
Charge Transfer					
$C_2H_4\cdots F_2$	-1.24	1.90	0.40	-	1.06
$NH_3\cdots F_2$	-1.21	2.45	0.57	-	1.81
$C_2H_2\cdots ClF$	-0.64	3.47	0.98	-	3.81
$HCN\cdots ClF$	1.73	2.50	0.64	-	4.86
$NH_3\cdots Cl_2$	0.62	3.27	0.98	-	4.88
$H_2O\cdots ClF$	2.33	2.34	0.68	-	5.36
$NH_3\cdots ClF$	2.37	6.34	1.90	-	10.62
Dipole Interaction					
$(H_2S)_2$	-0.18	1.51	0.32	0.00	1.65
$HCl\cdots H_2S$	0.70	2.14	0.49	0.02	3.35
$CH_3Cl\cdots HCl$	0.39	2.57	0.59	-	3.55
$HCN\cdots CH_3SH$	1.53	1.64	0.42	-	3.59
$CH_3SH\cdots HCl$	0.10	3.62	0.43	-	4.16
Weak Interaction					
$CH_4\cdots Ne$	-0.09	0.27	0.03	0.01	0.22
$(CH_4)_2$	-0.53	0.91	0.13	0.00	0.51
$(C_2H_2)_2$	0.27	0.90	0.19	-0.01	1.34
$(C_2H_4)_2$	-0.92	1.99	0.35	-0.01	1.42

[a] Hartree-Fock

[b] coupled clusters theory with single and double excitations

[c] quasiperturbative triple excitations

Table 2: Benchmark Databases of Binding Energies D_e (kcal/mol) for Hydrogen Bonding (HB), Charge Transfer (CT), Dipole Interaction (DI), and Weak Interaction (WI)

HB6/04			CT7/04			DI6/04			WI9/04		
Complex	D_e	Ref.	Complex	D_e	Ref.	Complex	D_e	Ref.	Complex	D_e	Ref.
$(NH_3)_2$	3.15	81	C2H4···F2	1.06	This work	$(H_2S)_2$	1.66	This work	HeNe	0.04	131
$(HF)_2$	4.57	81	NH3···F2	1.81	This work	$(HCl)_2$	2.01	81	HeAr	0.06	131
$(H_2O)_2$	4.97	81	C2H2···ClF	3.81	This work	$HCl···H_2S$	3.35	This work	Ne_2	0.08	130
$NH_3···H_2O$	6.41	81	HCN···ClF	4.86	This work	$CH_3Cl···HCl$	3.55	This work	NeAr	0.13	131
$(HCONH_2)_2$	14.94	This work	NH3···Cl2	4.88	This work	$HCN···CH_3SH$	3.59	This work	$CH_4···Ne$	0.22	This work
$(HCOOH)_2$	16.15	This work	H2O···ClF	5.36	This work	$CH_3SH···HCl$	4.16	This work	$C_6H_6···Ne$	0.47	132
			NH3···ClF	10.62	This work				$(CH_4)_2$	0.51	This work
									$(C_2H_2)_2$	1.34	This work
									$(C_2H_4)_2$	1.42	This work
Average	8.37			4.63			3.05			0.47	

Table 3: Summary of the DFT Methods Tested (in chronological order)

Method	X [a]	Year	Type	Ex. functional [b] Corr. functional[c]	Ref(s).
SVWN3[d]	0	1981	LSDA	Slater's local Ex. VWN no.3	5, 134
SVWN5[e]	0	1981	LSDA	Slater's local Ex. VWN no.5	5, 134, 26
BP86	0	1988	GGA	Becke88 Perdew's 1986 GGA	7, 8
BLYP	0	1988	GGA	Becke88 Lee-Yang-Parr	8, 9
SPWL	0	1992	LSDA	Slater's local Ex. Perdew-Wang local	12, 134
BPW91	0	1992	GGA	Becke88 Perdew-Wang91	8, 11
B3P86	20	1993	hybrid GGA	Becke88 Perdew's 1986 GGA	7, 8
B3PW91	20	1993	hybrid GGA	Becke88 Perdew-Wang91	8, 11
BHandHLYP	50	1993	hybrid GGA	Becke88 Lee-Yang-Parr	8, 9, 136
B3LYP	20	1994	hybrid GGA	Becke88 Lee-Yang-Parr	8, 9, 15
G96LYP	0	1996	GGA	Gill96 Lee-Yang-Parr	9,20
BB95	0	1996	meta GGA	Becke88 Becke95	8, 21
B1B95	25	1996	hybrid meta GGA	Becke88 Becke95	8, 21
PBE	0	1996	hybrid GGA	PBE Ex. PBE Corr.	22
PBE1PBE[f]	25	1996	hybrid GGA	PBE Ex. PBE Corr.	22

BPBE	0	1996	GGA	Becke88 PBE Corr.	8,22
mPWPW91[g]	0	1998	GGA	modified PW91 Perdew-Wang91	11, 29
mPW1PW91[h]	25	1998	hybrid GGA	modified PW91 Perdew-Wang91	11, 29
mPWPBE	0	1998	GGA	modified PW91 PBE Corr.	22,29
mPWLYP	0	1998	GGA	modified PW91 Lee-Yang-Parr	9, 29
mPWB95	0	1998	meta GGA	modified PW91 Becke95	21,29
VSXC	0	1998	meta GGA	VSXC Ex. VSXC Corr.	32
HCTH	0	1998	GGA	HCTH Ex. HCTH Corr.	33
B97-1	21	1998	hybrid GGA	B97-1 Ex. B97-1 Corr.	33
B98	21.98	1998	hybrid GGA	B98 Ex. B98 Corr.	30
MPW1K	42.8	2000	hybrid GGA	modified PW91 Perdew-Wang91	29, 24
B97-2	21	2001	hybrid GGA	B97-2 Ex. B97-2 Corr.	33
OLYP	0	2001	GGA	OPTX Lee-Yang-Parr	9,49,50
O3LYP	11.61	2001	hybrid GGA	OPTX Lee-Yang-Parr	9,49,50
TPSS	0	2003	meta GGA	TPSS Ex. TPSS Corr.	70,72
TPSSh	10	2003	hybrid meta GGA	TPSS Ex. TPSS Corr.	70,72
MPWKCIS	0	2004	hybrid meta GGA	modified PW91 KCIS Corr.	21, 37,38,60

PBEKCIS	0	2004	hybrid meta GGA	TPSS Ex. KCIS Corr.	22,37,38,60
TPSSKCIS	0	2004	hybrid meta GGA	TPSS Ex. KCIS Corr.	37,38,60,70,72
X3LYP	21.8	2004	hybrid GGA	Becke88+PW91 Lee-Yang-Parr	8, 9, 11, 74
BB1K	42	2004	hybrid meta GGA	Becke88 Becke95	8, 21, 76
MPW3LYP	21	2004	hybrid GGA	modified PW91 Lee-Yang-Parr	9, 29, 79
MPW1B95	31	2004	hybrid meta GGA	modified PW91 Becke95	21, 29, 79
MPWB1K	44	2004	hybrid meta GGA	modified PW91 Becke95	21, 29, 79
TPSS1KCIS	13	2004	hybrid meta GGA	TPSS Ex. KCIS Corr.	37,38,60,70,72,86
MPW1KCIS	15	2004	hybrid meta GGA	modified PW91 KCIS Corr.	21, 37,38,60, 87
MPWKCIS1K	41	2004	hybrid meta GGA	modified PW91 KCIS Corr.	21, 37,38,60, 87
PBE1KCIS	22	2005[h]	hybrid meta GGA	PBE Ex. KCIS Corr.	22,37,38,60, this work

[a] X denotes the percentage of HF exchange in the functional.
[b] Upper entry
[c] Lower entry
[d] also called SVWN and SVWNIII
[e] also called SVWN (expression V) where the final V is Roman numeral 5.
[f] also called PBE0
[g] also called mPWPW
[h] also called mPW1PW, mPW0, and MPW25

Table 4 Mean Errors (kcal/mol) for the HB6/04 Database [a] [b]

Method	DIDZ					aug-cc-pVTZ					MG3S					MMMUE
	MSE		MUE		MMUE	MSE		MUE		MMUE	MSE		MUE		MMUE	
	no-cp	cp	no-cp	cp		no-cp	cp	no-cp	cp		no-cp	cp	no-cp	cp		
LSDA																
SPWL	4.41	4.29	4.41	4.29	4.35	5.44	4.72	5.44	4.72	5.08	4.64	4.20	4.64	4.20	4.42	4.62
SVWN5	5.45	4.73	5.45	4.73	5.09	4.42	4.30	4.42	4.30	4.36	4.65	4.21	4.65	4.21	4.43	4.63
SVWN3	5.69	4.98	5.69	4.98	5.34	4.67	4.55	4.67	4.55	4.61	4.90	4.46	4.90	4.46	4.68	4.87
GGA																
PBE	1.02	0.32	1.09	0.65	0.87	0.01	-0.09	0.26	0.25	0.26	0.22	-0.19	0.45	0.32	0.39	0.50
mPWLYP	0.70	-0.02	1.11	0.88	0.99	-0.29	-0.40	0.50	0.56	0.53	-0.08	-0.49	0.65	0.62	0.64	0.72
mPWPW91	0.23	-0.48	0.85	0.71	0.78	-0.52	-0.96	0.57	0.96	0.77	-0.52	-0.96	0.57	0.96	0.77	0.77
mPWPBE	0.20	-0.52	0.84	0.72	0.78	-0.80	-0.93	0.80	0.93	0.86	-0.56	-1.00	0.60	1.00	0.80	0.82
BP86	0.01	-0.65	0.74	0.78	0.76	-0.90	-1.01	0.90	1.01	0.95	-0.72	-1.10	0.72	1.10	0.91	0.88
XLYP	0.12	-0.56	1.07	0.85	0.96	-0.84	-0.96	0.84	0.96	0.90	-0.65	-1.04	0.74	1.04	0.89	0.92
BLYP	-0.42	-1.10	1.04	1.12	1.08	-1.37	-1.48	1.37	1.48	1.42	-1.18	-1.56	1.18	1.56	1.37	1.29
BPW91	-0.90	-1.58	1.13	1.58	1.36	-1.84	-1.97	1.84	1.97	1.91	-1.64	-2.05	1.64	2.05	1.84	1.70
BPBE	-0.93	-1.62	1.15	1.62	1.39	-1.89	-2.01	1.89	2.01	1.95	-1.68	-2.09	1.68	2.09	1.88	1.74
HCTH	-0.78	-1.51	1.47	1.51	1.49	-1.83	-1.94	1.83	1.94	1.88	-1.68	-2.12	1.68	2.12	1.90	1.76
G96LYP	-2.24	-2.87	2.24	2.87	2.55	-3.11	-3.22	3.11	3.22	3.17	-2.95	-3.30	2.95	3.30	3.13	2.95
OLYP	-2.67	-3.50	2.67	3.50	3.08	-3.83	-3.95	3.83	3.95	3.89	-3.60	-4.09	3.60	4.09	3.84	3.60
meta GGA																
VSXC	0.26	-0.46	0.70	0.64	0.67	-0.46	-0.59	0.47	0.60	0.54	-0.34	-0.77	0.45	0.79	0.62	0.61
TPSS	0.42	-0.28	0.77	0.60	0.69	-0.59	-0.73	0.59	0.73	0.66	-0.37	-0.82	0.45	0.82	0.63	0.66
PBEKCIS	0.59	-0.09	1.09	0.86	0.98	-0.37	-0.47	0.48	0.54	0.51	-0.19	-0.58	0.62	0.62	0.62	0.70
TPSSKCIS	0.35	-0.36	0.90	0.70	0.80	-0.67	-0.80	0.67	0.80	0.74	-0.46	-0.89	0.55	0.89	0.72	0.75
mPWB95	0.05	-0.65	0.98	0.80	0.89	-0.96	-1.09	0.96	1.09	1.02	-0.72	-1.12	0.72	1.12	0.92	0.94
mPWKCIS	-0.22	-0.92	1.05	1.01	1.03	-1.17	-1.30	1.17	1.30	1.24	-0.97	-1.39	0.97	1.39	1.18	1.15
BB95	-1.08	-1.74	1.24	1.74	1.49	-2.04	-2.16	2.04	2.16	2.10	-1.83	-2.21	1.83	2.21	2.02	1.87

hybrid GGA																
B3P86	0.70	0.06	0.83	0.37	0.60	-0.23	-0.34	0.40	0.42	0.41	-0.05	-0.44	0.33	0.44	0.38	0.46
PBE1PBE	1.01	0.33	1.03	0.55	0.79	-0.02	-0.13	0.28	0.27	0.27	0.19	-0.23	0.40	0.28	0.34	0.47
BHandHLYP	0.76	0.14	0.93	0.56	0.74	-0.23	-0.34	0.36	0.40	0.38	-0.04	-0.43	0.42	0.48	0.45	0.52
B97-1	0.75	0.10	0.94	0.71	0.82	-0.21	-0.31	0.29	0.36	0.32	-0.04	-0.43	0.45	0.45	0.45	0.53
MPW1K	0.65	-0.03	0.84	0.45	0.64	-0.40	-0.53	0.44	0.53	0.49	-0.17	-0.61	0.33	0.61	0.47	0.53
X3LYP	0.73	0.08	0.95	0.65	0.80	-0.24	-0.35	0.34	0.41	0.37	-0.05	-0.44	0.45	0.48	0.47	0.55
MPW3LYP	1.04	0.38	1.12	0.69	0.91	0.06	-0.05	0.35	0.34	0.35	0.26	-0.14	0.51	0.41	0.46	0.57
B98	0.54	-0.12	0.87	0.68	0.78	-0.44	-0.54	0.44	0.54	0.49	-0.26	-0.66	0.45	0.66	0.55	0.61
mPW1PW91	0.43	-0.25	0.75	0.54	0.65	-0.58	-0.72	0.58	0.72	0.65	-0.36	-0.79	0.39	0.79	0.59	0.63
B3LYP	0.22	-0.42	0.86	0.69	0.78	-0.73	-0.84	0.73	0.84	0.78	-0.55	-0.93	0.60	0.93	0.76	0.77
B3PW91	-0.26	-0.92	0.78	0.94	0.86	-1.23	-1.35	1.23	1.35	1.29	-1.03	-1.43	1.03	1.43	1.23	1.13
B97-2	-0.43	-1.11	0.95	1.11	1.03	-1.43	-1.55	1.43	1.55	1.49	-1.22	-1.64	1.22	1.64	1.43	1.32
O3LYP	-1.86	-2.63	1.86	2.63	2.25	-2.99	-3.10	2.99	3.10	3.04	-2.77	-3.23	2.77	3.23	3.00	2.76
hybrid meta GGA																
PBE1KCIS	0.59	-0.06	0.93	0.73	0.83	-0.37	-0.48	0.40	0.48	0.44	-0.20	-0.59	0.49	0.59	0.54	0.60
MPWB1K	0.52	-0.13	0.79	0.55	0.67	-0.53	-0.65	0.53	0.65	0.59	-0.31	-0.70	0.41	0.70	0.56	0.61
TPSSh	0.45	-0.24	0.76	0.56	0.66	-0.57	-0.71	0.57	0.71	0.64	-0.36	-0.80	0.41	0.80	0.60	0.63
TPSS1KCIS	0.39	-0.30	0.84	0.65	0.74	-0.63	-0.76	0.63	0.76	0.70	-0.43	-0.86	0.49	0.86	0.67	0.71
MPW1B95	0.34	-0.32	0.79	0.61	0.70	-0.69	-0.81	0.69	0.81	0.75	-0.46	-0.86	0.50	0.86	0.68	0.71
MPWKCIS1K	0.20	-0.45	0.79	0.64	0.72	-0.78	-0.91	0.78	0.91	0.85	-0.59	-1.00	0.59	1.00	0.80	0.79
MPW1KCIS	-0.11	-0.78	0.95	0.87	0.91	-1.07	-1.19	1.07	1.19	1.13	-0.87	-1.28	0.87	1.28	1.07	1.04
BB1K	-0.18	-0.82	0.72	0.82	0.77	-1.20	-1.56	1.20	1.56	1.38	-0.99	-1.37	0.99	1.37	1.18	1.11
B1B95	-0.52	-1.16	0.89	1.16	1.02	-1.52	-1.63	1.52	1.63	1.58	-1.31	-1.69	1.31	1.69	1.50	1.37
ab initio WFT																
MP2	0.48	-1.20	0.88	1.20	1.04	0.28	-0.44	0.28	0.44	0.36	0.24	-0.93	0.26	0.93	0.60	0.66

[a] MUE denotes mean unsigned error (also called mean absolute deviation). MSE denotes mean signed error. MMUE=[MUE(no-cp) + MUE(cp)]/2. MMMUE= [MMUE(DIDZ) + MMUE(aug-cc-pVTZ) + MMUE(MG3S)]/3

[b] We use "no-cp" to denote the calculation without the counterpoise correction for the BSSE, and use "cp" to denote the calculation with the counterpoise correction for the BSSE. DIDZ denotes 6-31+G(d,p) basis.

Table 5 Mean Errors (kcal/mol) for the CT7/04 Database [a] [b]

Method	DIDZ					aug-cc-pVTZ					MG3S					MMMUE
	MSE		MUE		MMUE	MSE		MUE		MMUE	MSE		MUE		MMUE	
	no-cp	cp	no-cp	cp		no-cp	cp	no-cp	cp		no-cp	cp	no-cp	cp		
LSDA																
SPWL	6.41	6.30	6.41	6.30	6.36	7.59	6.89	7.59	6.89	7.24	6.78	6.41	6.78	6.41	6.59	6.73
SVWN5	7.59	6.89	7.59	6.89	7.24	6.42	6.30	6.42	6.30	6.36	6.78	6.41	6.78	6.41	6.60	6.73
SVWN3	7.80	7.10	7.80	7.10	7.45	6.63	6.51	6.63	6.51	6.57	6.99	6.62	6.99	6.62	6.80	6.94
GGA																
G96LYP	0.61	0.01	1.59	1.38	1.48	-0.42	-0.51	1.24	1.28	1.26	-0.18	-0.46	1.20	1.28	1.24	1.33
HCTH	1.77	1.17	2.04	1.59	1.81	0.71	0.63	1.26	1.25	1.26	0.94	0.63	1.31	1.22	1.26	1.45
BPBE	1.88	1.28	2.13	1.60	1.87	0.79	0.69	1.21	1.18	1.19	1.12	0.79	1.37	1.22	1.29	1.45
BPW91	1.92	1.32	2.15	1.63	1.89	0.83	0.73	1.22	1.19	1.20	1.16	0.83	1.39	1.23	1.31	1.47
OLYP	0.03	-0.60	1.77	1.55	1.66	-1.10	-1.18	1.56	1.59	1.58	-0.78	-1.14	1.57	1.58	1.57	1.60
BLYP	2.46	1.83	2.48	1.94	2.21	1.36	1.28	1.43	1.38	1.41	1.63	1.32	1.67	1.42	1.54	1.72
BP86	2.80	2.19	2.80	2.23	2.52	1.74	1.64	1.74	1.68	1.71	2.03	1.71	2.03	1.73	1.88	2.03
XLYP	2.98	2.33	2.98	2.33	2.66	1.85	1.77	1.85	1.77	1.81	2.14	1.82	2.14	1.82	1.98	2.15
mPWPBE	2.98	2.35	2.98	2.37	2.68	1.83	1.74	1.83	1.77	1.80	2.21	1.85	2.21	1.85	2.03	2.17
mPWPW91	3.02	2.40	3.02	2.40	2.71	2.25	1.89	2.25	1.89	2.07	2.25	1.89	2.25	1.89	2.07	2.28
mPWLYP	3.55	2.89	3.55	2.89	3.22	2.40	2.32	2.40	2.32	2.36	2.70	2.37	2.70	2.37	2.54	2.71
PBE	3.76	3.14	3.76	3.14	3.45	2.63	2.55	2.63	2.55	2.59	2.95	2.63	2.95	2.63	2.79	2.94
meta GGA																
BB95	2.09	1.49	2.26	1.74	2.00	0.98	1.28	1.27	1.36	1.31	1.30	0.99	1.48	1.27	1.38	1.56
mPWKCIS	2.63	2.01	2.63	2.10	2.36	1.52	1.43	1.57	1.52	1.55	1.84	1.50	1.85	1.58	1.71	1.87
TPSSKCIS	2.91	2.32	2.91	2.32	2.61	1.82	1.74	1.82	1.74	1.78	2.17	1.84	2.17	1.84	2.01	2.13
TPSS	2.91	2.34	2.91	2.34	2.63	1.84	1.74	1.84	1.74	1.79	2.20	1.86	2.20	1.86	2.03	2.15
mPWB95	3.18	2.56	3.18	2.56	2.87	2.02	1.94	2.02	1.94	1.98	2.38	2.05	2.38	2.05	2.21	2.36
PBEKCIS	3.42	2.79	3.42	2.79	3.10	2.31	2.23	2.31	2.23	2.27	2.58	2.27	2.58	2.27	2.43	2.60
VSXC	3.61	3.05	3.61	3.05	3.33	2.55	2.47	2.55	2.47	2.51	2.84	2.53	2.84	2.53	2.68	2.84

hybrid GGA																
BHandHLYP	0.31	-0.23	0.74	0.44	0.59	-0.67	-0.77	0.67	0.77	0.72	-0.42	-0.73	0.42	0.73	0.58	0.63
MPW1K	0.53	-0.03	0.94	0.69	0.81	-0.54	-0.65	0.63	0.70	0.67	-0.21	-0.56	0.44	0.66	0.55	0.68
mPW1PW91	1.26	0.68	1.38	0.91	1.15	0.19	0.08	0.51	0.52	0.51	0.53	0.18	0.65	0.51	0.58	0.75
B97-2	0.65	0.08	1.12	0.79	0.96	-0.42	-0.52	0.65	0.71	0.68	-0.10	-0.43	0.56	0.67	0.61	0.75
B3LYP	1.38	0.79	1.45	1.02	1.24	0.35	0.26	0.54	0.54	0.54	0.61	0.30	0.71	0.54	0.63	0.80
B3PW91	0.89	0.32	1.29	0.92	1.11	-0.14	-0.25	0.66	0.72	0.69	0.17	-0.17	0.64	0.69	0.66	0.82
X3LYP	1.73	1.14	1.73	1.18	1.46	0.69	0.61	0.70	0.65	0.67	0.96	0.65	0.96	0.68	0.82	0.98
B98	1.63	1.05	1.66	1.16	1.41	0.60	0.51	0.68	0.63	0.65	0.87	0.55	0.91	0.66	0.79	0.95
PBE1PBE	1.80	1.22	1.80	1.26	1.53	0.74	0.64	0.76	0.70	0.73	1.04	0.71	1.04	0.75	0.90	1.05
B3P86	1.79	1.22	1.79	1.28	1.54	0.78	0.67	0.84	0.80	0.82	1.05	0.73	1.05	0.83	0.94	1.10
B97-1	1.95	1.37	1.95	1.39	1.67	0.91	0.83	0.91	0.86	0.89	1.17	0.86	1.17	0.89	1.03	1.20
O3LYP	-0.21	-0.81	1.33	1.17	1.25	-1.30	-1.38	1.38	1.44	1.41	-0.99	-1.34	1.20	1.41	1.30	1.32
MPW3LYP	2.16	1.56	2.16	1.56	1.86	1.10	1.01	1.10	1.01	1.06	1.39	1.06	1.39	1.06	1.22	1.38
hybrid meta GGA																
MPWB1K	0.61	0.07	0.84	0.50	0.67	-0.45	-0.55	0.45	0.55	0.50	-0.12	-0.45	0.24	0.45	0.34	0.50
MPW1B95	1.11	0.54	1.20	0.74	0.97	0.03	-0.06	0.31	0.33	0.32	0.36	0.04	0.47	0.31	0.39	0.56
B1B95	0.46	-0.09	1.00	0.68	0.84	-0.58	-0.68	0.71	0.76	0.73	-0.27	-0.59	0.53	0.72	0.62	0.73
MPWKCIS1K	0.21	-0.34	0.79	0.55	0.67	-0.80	-0.91	0.80	0.91	0.86	-0.52	-0.85	0.52	0.85	0.69	0.74
BB1K	0.05	-0.48	0.75	0.63	0.69	-0.98	-1.09	0.98	1.09	1.04	-0.68	-1.00	0.68	1.00	0.84	0.86
PBE1KCIS	1.64	1.06	1.64	1.14	1.39	0.61	0.52	0.66	0.61	0.63	0.87	0.56	0.89	0.63	0.76	0.93
MPW1KCIS	1.46	0.87	1.59	1.12	1.36	0.39	0.30	0.68	0.68	0.68	0.70	0.37	0.85	0.68	0.77	0.93
TPSS1KCIS	1.90	1.34	1.93	1.43	1.68	0.85	0.77	0.94	0.88	0.91	1.18	0.85	1.22	0.95	1.08	1.22
TPSSh	2.13	1.57	2.13	1.64	1.89	1.08	0.98	1.14	1.08	1.11	1.43	1.09	1.44	1.16	1.30	1.43
ab initio WFT																
MP2	0.59	-1.00	0.71	1.00	0.86	0.65	0.16	0.65	0.25	0.45	0.73	-0.21	0.73	0.26	0.49	0.60

[a] MUE denotes mean unsigned error (also called mean absolute deviation). MSE denotes mean signed error. MMUE=[MUE(no-cp) + MUE(cp)]/2. MMMUE= [MMUE(DIDZ) + MMUE(aug-cc-pVTZ) + MMUE(MG3S)]/3

b We use “no-cp” to denote the calculation without the counterpoise correction for the BSSE, and use “cp” to denote the calculation with the counterpoise correction for the BSSE. DIDZ denotes 6-31+G(d,p) basis.

Table 6 Mean Errors (kcal/mol) for the DI6/04 Database [a] [b]

Method	DIDZ					aug-cc-pVTZ					MG3S					MMMUE
	MSE		MUE		MMUE	MSE		MUE		MMUE	MSE		MUE		MMUE	
	no-cp	cp	no-cp	cp		no-cp	cp	no-cp	cp		no-cp	cp	no-cp	cp		
LSDA																
SPWL	2.89	2.77	2.89	2.77	2.83	3.27	2.95	3.27	2.95	3.11	2.93	2.73	2.93	2.73	2.83	2.93
SVWN5	3.27	2.95	3.27	2.95	3.11	2.89	2.77	2.89	2.77	2.83	2.93	2.73	2.93	2.73	2.83	2.93
SVWN3	3.42	3.11	3.42	3.11	3.27	3.05	2.93	3.05	2.93	2.99	3.08	2.89	3.08	2.89	2.98	3.08
GGA																
mPWLYP	0.17	-0.07	0.43	0.44	0.44	-0.19	-0.26	0.39	0.41	0.40	-0.11	-0.30	0.38	0.41	0.39	0.41
PBE	0.67	0.39	0.68	0.54	0.61	0.31	0.24	0.42	0.41	0.42	0.38	0.20	0.46	0.40	0.43	0.49
mPWPW91	0.01	-0.27	0.58	0.61	0.60	-0.28	-0.47	0.56	0.59	0.57	-0.28	-0.47	0.56	0.59	0.57	0.58
HCTH	-0.31	-0.53	0.44	0.53	0.49	-0.63	-0.68	0.63	0.68	0.66	-0.55	-0.71	0.55	0.71	0.63	0.59
mPWPBE	-0.01	-0.30	0.59	0.63	0.61	-0.36	-0.46	0.58	0.60	0.59	-0.30	-0.49	0.57	0.61	0.59	0.60
XLYP	-0.29	-0.53	0.55	0.58	0.56	-0.65	-0.72	0.65	0.72	0.68	-0.58	-0.76	0.58	0.76	0.67	0.64
BP86	-0.21	-0.49	0.68	0.71	0.69	-0.58	-0.67	0.68	0.74	0.71	-0.54	-0.71	0.66	0.76	0.71	0.71
BLYP	-0.70	-0.95	0.70	0.95	0.82	-1.06	-1.13	1.06	1.13	1.10	-1.00	-1.18	1.00	1.18	1.09	1.00
BPW91	-0.87	-1.15	0.88	1.15	1.02	-1.21	-1.32	1.21	1.32	1.27	-1.17	-1.35	1.17	1.35	1.26	1.18
BPBE	-0.89	-1.18	0.90	1.18	1.04	-1.24	-1.34	1.24	1.34	1.29	-1.19	-1.38	1.19	1.38	1.29	1.20
OLYP	-2.14	-2.39	2.14	2.39	2.26	-2.46	-2.51	2.46	2.51	2.48	-2.35	-2.53	2.35	2.53	2.44	2.40
G96LYP	-2.25	-2.49	2.25	2.49	2.37	-2.61	-2.69	2.61	2.69	2.65	-2.57	-2.74	2.57	2.74	2.65	2.56
meta GGA																
PBEKCIS	0.43	0.18	0.54	0.46	0.50	0.07	0.01	0.35	0.37	0.36	0.14	-0.03	0.37	0.37	0.37	0.41
TPSSKCIS	0.00	-0.27	0.52	0.54	0.53	-0.34	-0.40	0.49	0.51	0.50	-0.26	-0.43	0.49	0.52	0.50	0.51
mPWB95	-0.02	-0.27	0.51	0.54	0.52	-0.38	-0.45	0.52	0.56	0.54	-0.29	-0.47	0.48	0.57	0.52	0.53
TPSS	-0.03	-0.32	0.53	0.56	0.55	-0.35	-0.44	0.52	0.54	0.53	-0.29	-0.46	0.52	0.56	0.54	0.54
mPWKCIS	-0.25	-0.51	0.56	0.59	0.58	-0.60	-0.69	0.61	0.69	0.65	-0.54	-0.72	0.57	0.72	0.65	0.62
VSXC	1.21	0.98	1.21	0.98	1.10	1.14	1.08	1.15	1.11	1.13	1.10	0.95	1.10	1.02	1.06	1.10
BB95	-0.90	-1.15	0.90	1.15	1.02	-1.26	-1.33	1.26	1.33	1.29	-1.18	-1.35	1.18	1.35	1.27	1.19

hybrid GGA																
B97-1	0.41	0.14	0.48	0.37	0.42	0.06	0.00	0.28	0.30	0.29	0.09	-0.06	0.28	0.30	0.29	0.33
MPW3LYP	0.15	-0.10	0.36	0.36	0.36	-0.19	-0.26	0.32	0.34	0.33	-0.14	-0.30	0.31	0.36	0.34	0.34
B98	0.15	-0.12	0.41	0.39	0.40	-0.20	-0.27	0.35	0.37	0.36	-0.17	-0.32	0.34	0.40	0.37	0.38
PBE1PBE	0.35	0.05	0.47	0.42	0.45	-0.02	-0.09	0.36	0.38	0.37	0.03	-0.13	0.35	0.38	0.37	0.39
X3LYP	-0.14	-0.39	0.42	0.44	0.43	-0.48	-0.54	0.48	0.54	0.51	-0.43	-0.59	0.45	0.59	0.52	0.49
B3P86	0.03	-0.27	0.52	0.55	0.53	-0.34	-0.44	0.50	0.55	0.53	-0.32	-0.49	0.50	0.57	0.54	0.53
MPW1K	-0.15	-0.49	0.43	0.51	0.47	-0.53	-0.62	0.53	0.62	0.58	-0.51	-0.67	0.52	0.67	0.60	0.55
mPW1PW91	-0.13	-0.44	0.50	0.53	0.51	-0.49	-0.59	0.55	0.60	0.57	-0.46	-0.63	0.53	0.63	0.58	0.55
BHandHLYP	-0.44	-0.72	0.44	0.72	0.58	-0.77	-0.83	0.77	0.83	0.80	-0.75	-0.89	0.75	0.89	0.82	0.73
B3LYP	-0.48	-0.74	0.52	0.74	0.63	-0.82	-0.89	0.82	0.89	0.86	-0.78	-0.94	0.78	0.94	0.86	0.78
B97-2	-0.55	-0.83	0.58	0.83	0.71	-0.91	-0.98	0.91	0.98	0.94	-0.87	-1.02	0.87	1.02	0.94	0.86
B3PW91	-0.64	-0.94	0.69	0.94	0.82	-1.00	-1.10	1.00	1.10	1.05	-0.97	-1.14	0.97	1.14	1.06	0.97
O3LYP	-1.73	-1.99	1.73	1.99	1.86	-2.06	-2.10	2.06	2.10	2.08	-1.97	-2.13	1.97	2.13	2.05	2.00
hybrid meta GGA																
PBE1KCIS	0.14	-0.14	0.40	0.37	0.39	-0.22	-0.27	0.33	0.36	0.34	-0.17	-0.32	0.32	0.38	0.35	0.36
TPSS1KCIS	-0.09	-0.37	0.47	0.50	0.49	-0.43	-0.50	0.49	0.53	0.51	-0.37	-0.53	0.46	0.55	0.50	0.50
MPWB1K	-0.18	-0.47	0.36	0.48	0.42	-0.55	-0.55	0.55	0.55	0.55	-0.50	-0.65	0.50	0.65	0.57	0.52
MPW1B95	-0.17	-0.45	0.41	0.49	0.45	-0.54	-0.60	0.54	0.60	0.57	-0.48	-0.63	0.50	0.63	0.56	0.53
TPSSh	-0.09	-0.39	0.50	0.53	0.52	-0.42	-0.51	0.51	0.56	0.54	-0.38	-0.54	0.49	0.58	0.54	0.53
MPW1KCIS	-0.35	-0.63	0.51	0.63	0.57	-0.71	-0.78	0.71	0.78	0.75	-0.66	-0.82	0.66	0.82	0.74	0.69
MPWKCIS1K	-0.42	-0.72	0.44	0.72	0.58	-0.78	-0.85	0.78	0.85	0.81	-0.75	-0.90	0.75	0.90	0.83	0.74
BB1K	-0.69	-0.98	0.69	0.98	0.84	-1.06	-1.13	1.06	1.13	1.09	-1.02	-1.16	1.02	1.16	1.09	1.01
B1B95	-0.80	-1.07	0.80	1.07	0.94	-1.16	-1.23	1.16	1.23	1.20	-1.11	-1.26	1.11	1.26	1.19	1.11
ab initio WFT																
MP2	-0.23	-1.41	0.23	1.41	0.82	0.74	0.22	0.74	0.22	0.48	0.45	-0.08	0.45	0.25	0.35	0.55

[a] MUE denotes mean unsigned error (also called mean absolute deviation). MSE denotes mean signed error. MMUE=[MUE(no-cp) + MUE(cp)]/2. MMMUE= [MMUE(DIDZ) + MMUE(aug-cc-pVTZ) + MMUE(MG3S)]/3.

b We use “no-cp” to denote the calculation without the counterpoise correction for the BSSE, and use “cp” to denote the calculation with the counterpoise correction for the BSSE. DIDZ denotes 6-31+G(d,p) basis.

Table 7 Mean Errors (kcal/mol) for the WI9/04 Database [a] [b]

Method	DIDZ					aug-cc-pVTZ					MG3S					MMMUE
	MSE		MUE		MMUE	MSE		MUE		MMUE	MSE		MUE		MMUE	
	no-cp	cp	no-cp	cp		no-cp	cp	no-cp	cp		no-cp	cp	no-cp	cp		
LSDA																
SPWL	0.42	0.38	0.42	0.38	0.40	0.47	0.33	0.47	0.33	0.40	0.44	0.36	0.44	0.36	0.40	0.40
SVWN5	0.47	0.33	0.47	0.33	0.40	0.41	0.38	0.41	0.38	0.40	0.44	0.36	0.44	0.36	0.40	0.40
SVWN3	0.51	0.38	0.51	0.38	0.44	0.46	0.42	0.46	0.42	0.44	0.49	0.40	0.49	0.40	0.44	0.44
GGA																
PBE	-0.11	-0.26	0.30	0.29	0.30	-0.23	-0.26	0.26	0.28	0.27	-0.19	-0.26	0.26	0.28	0.27	0.28
HCTH	0.11	-0.04	0.43	0.35	0.39	0.02	-0.01	0.33	0.33	0.33	0.02	-0.05	0.39	0.34	0.36	0.36
mPWLYP	-0.08	-0.25	0.46	0.40	0.43	-0.22	-0.26	0.38	0.39	0.38	-0.17	-0.24	0.39	0.39	0.39	0.40
mPWPW91	-0.40	-0.55	0.54	0.56	0.55	-0.47	-0.55	0.49	0.56	0.52	-0.47	-0.55	0.49	0.56	0.52	0.53
mPWPBE	-0.41	-0.57	0.55	0.57	0.56	-0.55	-0.58	0.55	0.59	0.57	-0.48	-0.57	0.50	0.57	0.53	0.56
XLYP	-0.41	-0.58	0.55	0.58	0.56	-0.55	-0.58	0.55	0.58	0.57	-0.50	-0.57	0.51	0.57	0.54	0.56
BLYP	-0.67	-0.84	0.75	0.84	0.80	-0.81	-0.84	0.81	0.84	0.83	-0.77	-0.84	0.77	0.84	0.80	0.81
OLYP	-0.72	-0.91	0.94	0.95	0.94	-0.90	-0.93	0.92	0.95	0.93	-0.83	-0.92	0.88	0.94	0.91	0.93
BP86	-0.83	-0.98	0.84	0.98	0.91	-0.94	-0.97	0.94	0.97	0.95	-0.90	-0.98	0.90	0.98	0.94	0.93
BPW91	-0.98	-1.13	0.99	1.13	1.06	-1.11	-1.15	1.11	1.15	1.13	-1.05	-1.14	1.05	1.14	1.09	1.09
BPBE	-1.00	-1.15	1.01	1.15	1.08	-1.12	-1.16	1.12	1.16	1.14	-1.06	-1.15	1.06	1.15	1.11	1.11
G96LYP	-1.78	-1.94	1.78	1.94	1.86	-1.90	-1.94	1.90	1.94	1.92	-1.86	-1.95	1.86	1.95	1.90	1.89
meta GGA																
PBEKCIS	-0.06	-0.21	0.30	0.27	0.29	-0.18	-0.21	0.26	0.27	0.26	-0.15	-0.22	0.26	0.27	0.27	0.27
mPWB95	-0.17	-0.33	0.35	0.35	0.35	-0.29	-0.32	0.31	0.34	0.33	-0.23	-0.31	0.27	0.32	0.30	0.32
TPSSKCIS	-0.28	-0.42	0.42	0.43	0.43	-0.39	-0.42	0.41	0.43	0.42	-0.33	-0.42	0.39	0.43	0.41	0.42
TPSS	-0.35	-0.48	0.46	0.48	0.47	-0.45	-0.49	0.46	0.49	0.48	-0.39	-0.48	0.42	0.48	0.45	0.47
mPWKCIS	-0.37	-0.52	0.53	0.54	0.53	-0.50	-0.53	0.51	0.54	0.53	-0.44	-0.52	0.48	0.53	0.50	0.52
BB95	-0.76	-0.91	0.79	0.91	0.85	-0.87	-0.91	0.87	0.91	0.89	-0.82	-0.90	0.82	0.90	0.86	0.87
VSXC	1.52	1.37	1.62	1.49	1.55	1.66	1.63	1.73	1.71	1.72	1.55	1.48	1.65	1.61	1.63	1.64

hybrid GGA																
B97-1	-0.06	-0.19	0.20	0.20	0.20	-0.15	-0.18	0.18	0.20	0.19	-0.11	-0.18	0.18	0.20	0.19	0.19
B98	-0.17	-0.30	0.28	0.30	0.29	-0.26	-0.29	0.27	0.30	0.29	-0.22	-0.29	0.25	0.30	0.28	0.28
PBE1PBE	-0.18	-0.31	0.28	0.31	0.30	-0.27	-0.30	0.28	0.31	0.29	-0.22	-0.30	0.25	0.30	0.28	0.29
MPW3LYP	-0.07	-0.21	0.36	0.32	0.34	-0.18	-0.21	0.29	0.30	0.30	-0.12	-0.20	0.31	0.30	0.31	0.32
X3LYP	-0.28	-0.42	0.40	0.42	0.41	-0.39	-0.42	0.39	0.42	0.41	-0.34	-0.41	0.36	0.41	0.38	0.40
BHandHLYP	-0.32	-0.44	0.38	0.44	0.41	-0.40	-0.43	0.40	0.43	0.42	-0.34	-0.42	0.35	0.42	0.39	0.41
MPW1K	-0.35	-0.47	0.41	0.47	0.44	-0.44	-0.48	0.44	0.48	0.46	-0.37	-0.47	0.38	0.47	0.42	0.44
mPW1PW91	-0.37	-0.50	0.47	0.51	0.49	-0.48	-0.52	0.48	0.52	0.50	-0.12	-0.50	0.71	0.50	0.61	0.53
B97-2	-0.46	-0.58	0.53	0.58	0.56	-0.56	-0.60	0.56	0.60	0.58	-0.50	-0.59	0.50	0.59	0.54	0.56
B3LYP	-0.49	-0.63	0.56	0.63	0.60	-0.60	-0.63	0.60	0.63	0.62	-0.55	-0.62	0.55	0.62	0.59	0.60
B3P86	-0.60	-0.72	0.60	0.72	0.66	-0.67	-0.71	0.67	0.71	0.69	-0.63	-0.72	0.63	0.72	0.67	0.68
O3LYP	-0.61	-0.77	0.79	0.80	0.80	-0.77	-0.79	0.78	0.80	0.79	-0.70	-0.78	0.74	0.80	0.77	0.79
B3PW91	-0.76	-0.89	0.77	0.89	0.83	-0.86	-0.89	0.86	0.89	0.88	-0.80	-0.89	0.80	0.89	0.84	0.85
hybrid meta GGA																
MPWB1K	-0.13	-0.25	0.22	0.25	0.23	-0.21	-0.24	0.22	0.25	0.23	-0.14	-0.23	0.16	0.23	0.20	0.22
MPW1B95	-0.15	-0.27	0.26	0.28	0.27	-0.24	-0.27	0.25	0.28	0.26	-0.17	-0.25	0.20	0.26	0.23	0.25
PBE1KCIS	-0.13	-0.26	0.28	0.27	0.28	-0.22	-0.25	0.25	0.27	0.26	-0.18	-0.25	0.25	0.27	0.26	0.27
TPSS1KCIS	-0.28	-0.41	0.40	0.42	0.41	-0.38	-0.41	0.40	0.42	0.41	-0.33	-0.41	0.37	0.41	0.39	0.40
MPWKCIS1K	-0.33	-0.44	0.41	0.45	0.43	-0.41	-0.45	0.42	0.45	0.43	-0.35	-0.44	0.37	0.44	0.41	0.42
TPSSh	-0.35	-0.48	0.44	0.48	0.46	-0.45	-0.48	0.45	0.48	0.47	-0.39	-0.48	0.40	0.48	0.44	0.45
MPW1KCIS	-0.36	-0.49	0.48	0.50	0.49	-0.47	-0.50	0.48	0.51	0.49	-0.41	-0.49	0.44	0.50	0.47	0.48
BB1K	-0.47	-0.59	0.48	0.59	0.54	-0.55	-0.58	0.55	0.58	0.57	-0.49	-0.57	0.49	0.57	0.53	0.54
B1B95	-0.57	-0.70	0.59	0.70	0.64	-0.66	-0.69	0.66	0.69	0.68	-0.60	-0.68	0.60	0.68	0.64	0.65
ab initio WFT																
MP2	-0.02	-0.38	0.12	0.38	0.25	0.12	-0.03	0.12	0.07	0.10	0.07	-0.17	0.09	0.17	0.13	0.16

[a] MUE denotes mean unsigned error (also called mean absolute deviation). MSE denotes mean signed error. MMUE=[MUE(no-cp) + MUE(cp)]/2. MMMUE= [MMUE(DIDZ) + MMUE(aug-cc-pVTZ) + MMUE(MG3S)]/3

[b] We use "no-cp" to denote the calculation without the counterpoise correction for the BSSE, and use "cp" to denote the calculation with the counterpoise correction for the BSSE. DIDZ denotes 6-31+G(d,p) basis.

Table 8 Overall results (kcal/mol) [a]

rank	Method	HB MMMUE	CT MMMUE	DI MMMUE	WI MMMUE	MMMMUE [b]
1	MPWB1K	0.61	**0.50**	0.52	**0.22**	**0.46**
2	MP2	0.66	**0.60**	0.55	**0.16**	**0.49**
3	MPW1B95	0.71	**0.56**	0.53	**0.25**	**0.51**
4	PBE1KCIS	0.60	0.93	**0.36**	**0.27**	**0.54**
5	MPW1K	**0.53**	**0.68**	0.55	0.44	**0.55**
6	PBE1PBE	**0.47**	1.05	**0.39**	0.29	**0.55**
7	B98	0.61	0.95	**0.38**	0.28	**0.55**
8	B97-1	**0.53**	1.20	**0.33**	**0.19**	**0.56**
9	BHandHLYP	**0.52**	**0.63**	0.73	0.41	**0.57**
10	X3LYP	0.55	0.98	0.49	0.40	**0.60**
11	mPW1PW91	0.63	0.75	0.55	0.53	0.62
12	MPW3LYP	0.57	1.38	**0.34**	0.32	0.65
13	MPWKCIS1K	0.79	0.74	0.74	0.42	0.67
14	B3P86	**0.46**	1.10	0.53	0.68	0.69
15	TPSS1KCIS	0.71	1.22	0.50	0.40	0.71
16	B3LYP	0.77	0.80	0.78	0.60	0.74
17	TPSSh	0.63	1.43	0.53	0.45	0.76
18	MPW1KCIS	1.04	0.93	0.69	0.48	0.79
19	B97-2	1.32	0.75	0.86	0.56	0.87
20	BB1K	1.11	0.86	1.01	0.54	0.88
21	B3PW91	1.13	0.82	0.97	0.85	0.94
22	TPSS	0.66	2.15	0.54	0.47	0.95
23	TPSSKCIS	0.75	2.13	0.51	0.42	0.95
24	B1B95	1.37	0.73	1.11	0.65	0.96
25	PBEKCIS	0.70	2.60	0.41	0.27	1.00
26	mPWPBE	0.82	2.17	0.60	0.56	1.03
27	mPWB95	0.94	2.36	0.53	0.32	1.04
28	HCTH	1.76	1.45	0.59	0.36	1.04
29	mPWPW91	0.77	2.28	0.58	0.53	1.04
30	mPWKCIS	1.15	1.87	0.62	0.52	1.04
31	PBE	**0.50**	2.94	0.49	0.28	1.05

32	mPWLYP	0.72	2.71	0.41	0.40	1.06
33	XLYP	0.92	2.15	0.64	0.56	1.06
34	BP86	0.88	2.03	0.71	0.93	1.14
35	BLYP	1.29	1.72	1.00	0.81	1.21
36	BPW91	1.70	1.47	1.18	1.09	1.36
37	BB95	1.87	1.56	1.19	0.87	1.37
38	BPBE	1.74	1.45	1.20	1.11	1.38
39	VSXC	0.61	2.84	1.10	1.64	1.55
40	O3LYP	2.76	1.32	2.00	0.79	1.72
41	OLYP	3.60	1.60	2.40	0.93	2.13
42	G96LYP	2.95	1.33	2.56	1.89	2.18
43	SPWL	4.62	6.73	2.93	0.40	2.75
44	SVWN5	4.63	6.73	2.93	0.40	3.67
45	SVWN3	4.87	6.94	3.08	0.44	3.83
	average	1.28	1.78	0.92	0.56	1.14

[a] MMMUE= [MMUE(DIDZ) + MMUE(aug-cc-pVTZ) + MMUE(MG3S)]/3, and MMUE defined in the text and also in the footnote of Table 4, 5, 6, 7. MMMMUE is defined as:

MMMMUE= [MMMUE(HB) + MMMUE(CT) + MMMUE(DI) + MMMUE(WI)]/4

[b] All mean errors are computed from unrounded results and the ranking is determined prior to rounding.

Table 9 Comparison of mean errors by different geometries. [a,b]

Methods	MC-QCISD geometries					Consistently optimized geometries					Max. Error [c]		
	MSE		MUE		MMUE	MSE		MUE		MMUE			
	no-cp	cp	no-cp	cp		no-cp	cp	no-cp	cp		Error [d]	Complex [e]	BSSE [f]
HB6/04													
B3LYP	-0.55	-0.93	0.60	0.93	0.76	-0.52	-0.90	0.58	0.90	0.74	-2.22	$(HCONH_2)_2$	cp
B97-1	-0.04	-0.43	0.45	0.45	0.45	-0.02	-0.41	0.44	0.44	0.44	-1.45	$(HCONH_2)_2$	cp
B97-2	-1.22	-1.64	1.22	1.64	1.43	-1.22	-1.63	1.22	1.63	1.43	-3.29	$(HCONH_2)_2$	cp
B98	-0.26	-0.66	0.45	0.66	0.55	-0.24	-0.64	0.45	0.64	0.54	-1.83	$(HCONH_2)_2$	cp
BLYP	-1.18	-1.56	1.18	1.56	1.37	-1.08	-1.46	1.08	1.46	1.27	-3.15	$(HCONH_2)_2$	cp
HCTH	-1.68	-2.12	1.68	2.12	1.90	-1.56	-1.95	1.56	1.95	1.76	-4.60	$(HCOOH)_2$	cp
MP2	0.24	-0.93	0.26	0.93	0.60	0.24	-0.91	0.27	0.91	0.59	-2.04	$(HCOOH)_2$	cp
MPW1B95	-0.46	-0.86	0.50	0.86	0.68	-0.47	-0.86	0.51	0.86	0.69	-2.12	$(HCONH_2)_2$	cp
MPW1K	-0.17	-0.61	0.33	0.61	0.47	-0.18	-0.63	0.33	0.63	0.48	-1.68	$(HCONH_2)_2$	cp
MPW3LYP	0.26	-0.14	0.51	0.41	0.46	0.30	-0.11	0.55	0.41	0.48	-1.13	$(HCONH_2)_2$	cp
MPWB1K	-0.31	-0.70	0.41	0.70	0.56	-0.33	-0.72	0.43	0.72	0.57	-1.88	$(HCONH_2)_2$	cp
PBE	0.22	-0.19	0.45	0.32	0.39	0.41	-0.03	0.59	0.28	0.44	-0.95	$(HCONH_2)_2$	cp
PBE1KCIS	-0.20	-0.59	0.49	0.59	0.54	-0.19	-0.58	0.49	0.58	0.53	-1.74	$(HCONH_2)_2$	cp
PBE1PBE	0.19	-0.23	0.40	0.28	0.34	0.24	-0.19	0.46	0.26	0.36	-1.06	$(HCONH_2)_2$	cp
SPWL	4.64	4.20	4.64	4.20	4.42	6.27	5.47	6.27	5.47	5.87	13.03	$(HCOOH)_2$	no-cp
TPSS	-0.37	-0.82	0.45	0.82	0.63	-0.22	-0.69	0.38	0.69	0.54	-1.91	$(HCONH_2)_2$	cp
TPSS1KCIS	-0.43	-0.86	0.49	0.86	0.67	-0.37	-0.81	0.48	0.81	0.65	-2.09	$(HCONH_2)_2$	cp
TPSSh	-0.36	-0.80	0.41	0.80	0.60	-0.26	-0.72	0.37	0.72	0.55	-1.91	$(HCONH_2)_2$	cp
X3LYP	-0.05	-0.44	0.45	0.48	0.47	-0.02	-0.42	0.45	0.47	0.46	-1.53	$(HCONH_2)_2$	cp
XLYP	-0.65	-1.04	0.74	1.04	0.89	-0.55	-0.94	0.70	0.94	0.82	-2.42	$(HCONH_2)_2$	cp

CT7/04													
B3LYP	0.61	0.30	0.71	0.54	0.63	1.22	0.85	1.29	1.01	1.15	3.46	NH_3-F_2	no-cp
B97-1	1.17	0.86	1.17	0.89	1.03	1.52	1.15	1.52	1.17	1.34	3.14	NH_3-ClF	no-cp
B97-2	-0.10	-0.43	0.56	0.67	0.61	-0.06	-0.43	0.62	0.69	0.65	-1.44	HCN-ClF	cp
B98	0.87	0.55	0.91	0.66	0.79	1.13	0.76	1.16	0.86	1.01	2.76	NH_3-ClF	no-cp
BLYP	1.63	1.32	1.67	1.42	1.54	5.03	4.62	5.03	4.62	4.83	13.06	NH_3-F_2	no-cp
HCTH	0.94	0.63	1.31	1.22	1.26	2.25	1.84	2.56	2.32	2.44	8.05	NH_3-F_2	no-cp
MP2	0.73	-0.21	0.73	0.26	0.49	0.76	-0.22	0.76	0.26	0.51	1.30	NH_3-ClF	no-cp
MPW1B95	0.36	0.04	0.47	0.31	0.39	0.37	0.02	0.48	0.30	0.39	1.49	NH_3-ClF	no-cp
MPW1K	-0.21	-0.56	0.44	0.66	0.55	-0.24	-0.61	0.46	0.68	0.57	-0.96	HCN-ClF	cp
MPW3LYP	1.39	1.06	1.39	1.06	1.22	2.11	1.72	2.11	1.72	1.91	4.46	NH_3-F_2	no-cp
MPWB1K	-0.12	-0.45	0.24	0.45	0.34	-0.19	-0.52	0.27	0.52	0.40	-0.78	HCN-ClF	cp
PBE	2.95	2.63	2.95	2.63	2.79	6.34	5.85	6.34	5.85	6.10	12.59	NH_3-F_2	no-cp
PBE1KCIS	0.87	0.56	0.89	0.63	0.76	1.13	0.78	1.15	0.85	1.00	2.49	NH_3-ClF	no-cp
PBE1PBE	1.04	0.71	1.04	0.75	0.90	1.28	0.88	1.28	0.90	1.09	3.36	NH_3-ClF	no-cp
SPWL	6.78	6.41	6.78	6.41	6.59	12.79	12.15	12.79	12.15	12.47	18.43	NH_3-F_2	no-cp
TPSS	2.20	1.86	2.20	1.86	2.03	5.21	4.69	5.21	4.69	4.95	10.65	NH_3-F_2	no-cp
TPSS1KCIS	1.18	0.85	1.22	0.95	1.08	2.23	1.78	2.23	1.82	2.02	4.88	NH_3-F_2	no-cp
TPSSh	1.43	1.09	1.44	1.16	1.30	2.88	2.39	2.88	2.39	2.64	5.73	NH_3-F_2	no-cp
X3LYP	0.96	0.65	0.96	0.68	0.82	1.50	1.12	1.50	1.13	1.31	3.35	NH_3-F_2	no-cp
XLYP	2.14	1.82	2.14	1.82	1.98	5.65	5.23	5.65	5.23	5.44	13.73	NH_3-F_2	no-cp
DI6/04													
B3LYP	-0.78	-0.94	0.78	0.94	0.86	-0.59	-0.75	0.59	0.75	0.67	-1.34	(CH_3Cl-HCl)	cp
B97-1	0.09	-0.06	0.28	0.30	0.29	0.19	0.04	0.30	0.30	0.30	0.99	(CH_3SH-HCl)	no-cp
B97-2	-0.87	-1.02	0.87	1.02	0.94	-0.67	-0.82	0.67	0.82	0.74	-1.55	(CH_3Cl-HCl)	cp

B98	-0.17	-0.32	0.34	0.40	0.37	-0.04	-0.20	0.33	0.36	0.35	-0.76	(CH_3Cl-HCl)	cp
BLYP	-1.00	-1.18	1.00	1.18	1.09	-0.72	-0.90	0.72	0.90	0.81	-1.53	(CH_3Cl-HCl)	cp
HCTH	-0.55	-0.71	0.55	0.71	0.63	-0.22	-0.37	0.30	0.37	0.33	-1.00	(CH_3Cl-HCl)	cp
MP2	0.45	-0.08	0.45	0.25	0.35	0.46	-0.05	0.46	0.23	0.35	1.30	(CH_3SH-HCl)	no-cp
MPW1B95	-0.48	-0.63	0.50	0.63	0.56	-0.42	-0.58	0.45	0.58	0.52	-1.06	(CH_3Cl-HCl)	cp
MPW1K	-0.51	-0.67	0.52	0.67	0.60	-0.40	-0.56	0.47	0.56	0.51	-1.21	(CH_3Cl-HCl)	cp
MPW3LYP	-0.14	-0.30	0.31	0.36	0.34	-0.02	-0.18	0.29	0.32	0.31	-0.66	(CH_3Cl-HCl)	cp
MPWB1K	-0.50	-0.65	0.50	0.65	0.57	-0.45	-0.60	0.45	0.60	0.53	-1.05	(CH_3Cl-HCl)	cp
PBE	0.38	0.20	0.46	0.40	0.43	0.60	0.41	0.60	0.48	0.54	1.99	(CH_3SH-HCl)	no-cp
PBE1KCIS	-0.17	-0.32	0.32	0.38	0.35	-0.06	-0.21	0.30	0.34	0.32	-0.77	(CH_3Cl-HCl)	cp
PBE1PBE	0.03	-0.13	0.35	0.38	0.37	0.15	-0.02	0.35	0.38	0.37	1.08	(CH_3SH-HCl)	no-cp
SPWL	2.93	2.73	2.93	2.73	2.83	4.20	3.92	4.20	3.92	4.06	7.11	(CH_3SH-HCl)	no-cp
TPSS	-0.29	-0.46	0.52	0.56	0.54	-0.07	-0.26	0.52	0.54	0.53	0.97	(CH_3SH-HCl)	no-cp
TPSS1KCIS	-0.37	-0.53	0.46	0.55	0.50	-0.20	-0.36	0.43	0.48	0.46	-1.02	(CH_3Cl-HCl)	cp
TPSSh	-0.38	-0.54	0.49	0.58	0.54	-0.19	-0.37	0.47	0.52	0.49	-1.03	(CH_3Cl-HCl)	cp
X3LYP	-0.43	-0.59	0.45	0.59	0.52	-0.29	-0.45	0.39	0.48	0.44	-0.97	(CH_3Cl-HCl)	cp
XLYP	-0.58	-0.76	0.58	0.76	0.67	-0.34	-0.53	0.50	0.60	0.55	-1.11	(CH_3Cl-HCl)	cp
						WI9/04							
B3LYP	-0.55	-0.62	0.55	0.62	0.59	-0.41	-0.43	0.41	0.43	0.42	-1.47	$(C_2H_4)_2$	cp
B97-1	-0.11	-0.18	0.18	0.20	0.19	-0.08	-0.15	0.16	0.17	0.17	-0.67	$(C_2H_4)_2$	cp
B97-2	-0.50	-0.59	0.50	0.59	0.54	-0.31	-0.36	0.31	0.36	0.34	-1.25	$(C_2H_4)_2$	cp
B98	-0.22	-0.29	0.25	0.30	0.28	-0.16	-0.23	0.21	0.24	0.22	-0.90	$(C_2H_4)_2$	cp
BLYP	-0.77	-0.84	0.77	0.84	0.80	-0.45	-0.45	0.45	0.45	0.45	-1.43	$(C_2H_4)_2$	cp
HCTH	0.02	-0.05	0.39	0.34	0.36	0.23	0.16	0.29	0.23	0.26	0.40	CH_4-Ne	no-cp
MP2	0.07	-0.17	0.09	0.17	0.13	0.07	-0.14	0.09	0.14	0.11	-0.33	C_6H_6-Ne	cp
MPW1B95	-0.17	-0.25	0.20	0.26	0.23	-0.10	-0.18	0.22	0.19	0.20	-0.70	$(C_2H_4)_2$	cp

MPW1K	-0.37	-0.47	0.38	0.47	0.42	-0.28	-0.34	0.29	0.34	0.31	-1.23	$(C_2H_4)_2$	cp
MPW3LYP	-0.12	-0.20	0.31	0.30	0.31	-0.05	-0.13	0.30	0.26	0.28	-0.92	$(C_2H_4)_2$	cp
MPWB1K	-0.14	-0.23	0.16	0.23	0.20	-0.06	-0.14	0.20	0.17	0.19	-0.54	$(C_2H_4)_2$	cp
PBE	-0.19	-0.26	0.26	0.28	0.27	-0.14	-0.20	0.22	0.23	0.22	-0.88	$(C_2H_4)_2$	cp
PBE1KCIS	-0.18	-0.25	0.25	0.27	0.26	-0.13	-0.20	0.21	0.22	0.21	-0.84	$(C_2H_4)_2$	cp
PBE1PBE	-0.22	-0.30	0.25	0.30	0.28	-0.19	-0.25	0.22	0.25	0.24	-0.93	$(C_2H_4)_2$	cp
SPWL	0.44	0.36	0.44	0.36	0.40	0.78	0.47	0.78	0.47	0.63	1.68	$(C_2H_4)_2$	no-cp
TPSS	-0.39	-0.48	0.42	0.48	0.45	-0.24	-0.38	0.27	0.38	0.33	-1.76	$(C_2H_4)_2$	cp
TPSS1KCIS	-0.33	-0.41	0.37	0.41	0.39	-0.21	-0.28	0.25	0.28	0.27	-1.06	$(C_2H_4)_2$	cp
TPSSh	-0.39	-0.48	0.40	0.48	0.44	-0.25	-0.32	0.28	0.32	0.30	-1.16	$(C_2H_4)_2$	cp
X3LYP	-0.34	-0.41	0.36	0.41	0.38	-0.27	-0.35	0.30	0.35	0.33	-1.33	$(C_2H_4)_2$	cp
XLYP	-0.50	-0.57	0.51	0.57	0.54	-0.35	-0.41	0.36	0.41	0.38	-1.40	$(C_2H_4)_2$	cp
Overall Results g													
B3LYP	-0.32	-0.55	0.66	0.76	0.71	-0.07	-0.31	0.72	0.77	0.75	3.46	NH_3-F_2	no-cp
B97-1	0.28	0.05	0.52	0.46	0.49	0.40	0.16	0.61	0.52	0.56	3.14	NH_3-ClF	no-cp
B97-2	-0.67	-0.92	0.79	0.98	0.88	-0.57	-0.81	0.71	0.88	0.79	-3.29	$(HCONH_2)_2$	cp
B98	0.06	-0.18	0.49	0.50	0.50	0.17	-0.08	0.54	0.52	0.53	2.76	NH_3-ClF	no-cp
BLYP	-0.33	-0.56	1.15	1.25	1.20	0.70	0.45	1.82	1.86	1.84	13.06	NH_3-F_2	no-cp
HCTH	-0.32	-0.56	0.98	1.10	1.04	0.17	-0.08	1.18	1.22	1.20	8.05	NH_3-F_2	no-cp
MP2	0.37	-0.35	0.38	0.40	0.39	0.38	-0.33	0.39	0.39	0.39	-2.04	$(HCOOH)_2$	cp
MPW1B95	-0.19	-0.43	0.42	0.51	0.47	-0.16	-0.40	0.41	0.48	0.45	-2.12	$(HCONH_2)_2$	cp
MPW1K	-0.32	-0.58	0.42	0.60	0.51	-0.27	-0.53	0.39	0.55	0.47	-1.68	$(HCONH_2)_2$	cp
MPW3LYP	0.35	0.11	0.63	0.53	0.58	0.58	0.32	0.81	0.68	0.74	4.46	NH_3-F_2	no-cp
MPWB1K	-0.27	-0.51	0.33	0.51	0.42	-0.26	-0.50	0.34	0.50	0.42	-1.88	$(HCONH_2)_2$	cp
PBE	0.84	0.59	1.03	0.91	0.97	1.81	1.51	1.94	1.71	1.82	12.59	NH_3-F_2	no-cp
PBE1KCIS	0.08	-0.15	0.49	0.47	0.48	0.19	-0.05	0.54	0.50	0.52	2.49	NH_3-ClF	no-cp

PBE1PBE	0.26	0.01	0.51	0.43	0.47	0.37	0.10	0.58	0.45	0.51	3.36	NH_3-ClF	no-cp
SPWL	3.70	3.43	3.70	3.43	3.56	6.01	5.50	6.01	5.50	5.76	18.43	NH_3-F_2	no-cp
TPSS	0.29	0.03	0.90	0.93	0.91	1.17	0.84	1.60	1.58	1.59	10.65	NH_3-F_2	no-cp
TPSS1KCIS	0.02	-0.24	0.64	0.69	0.66	0.36	0.08	0.85	0.85	0.85	4.88	NH_3-F_2	no-cp
TPSSh	0.08	-0.18	0.68	0.75	0.72	0.54	0.25	1.00	0.99	0.99	5.73	NH_3-F_2	no-cp
X3LYP	0.04	-0.20	0.56	0.54	0.55	0.23	-0.02	0.66	0.61	0.63	3.35	NH_3-F_2	no-cp
XLYP	0.10	-0.14	0.99	1.05	1.02	1.10	0.84	1.80	1.79	1.80	13.73	NH_3-F_2	no-cp

[a] MUE denotes mean unsigned error (also called mean absolute deviation). MSE denotes mean signed error. MMUE=[MUE(no-cp) + MUE(cp)]/2

[b] The MG3S basis set is used for all calculations in this table.

[c] Maximum errors are taken from the results for the consistently optimized geometries. Although we tabulate the error that has the largest absolute value, we tabulate it as a signed quantity.

[d] Error = Calculation – Best Estimate

[e] This is the complex that gives the maximum error.

[f] This column specify whether the maximum error occurs in the calculation with counterpoise corrections (cp) turned on during the optimization or without counterpoise corrections (no-cp).

[g] The results in this section are 0.25×HB + 0.25×CT7+ 0.25×DI6+ 0.25×WI9, except for maximum error with the maximum over the whole nonbonded data set.

Figure caption

Figure 1. Geometries of the dimers in the HB6/04 database

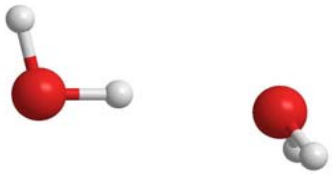
Figure 2. Geometries of the complexes in the CT7/04 database

Figure 3. Geometries of the dimers in the DI6/04 database

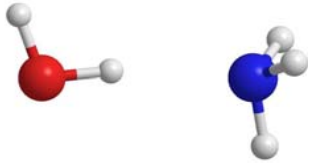
Figure 4. Geometries of the dimers in the WI9/04 database

$(NH_3)_2$

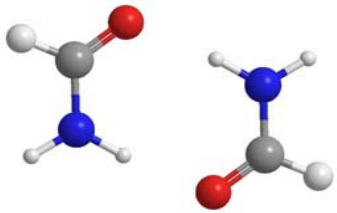
$(HF)_2$



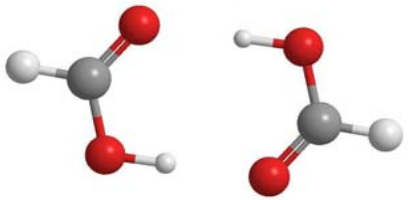
$(H_2O)_2$



$NH_3 \cdots H_2O$



$(HCONH_2)_2$



$(HCOOH)_2$

Figure 1

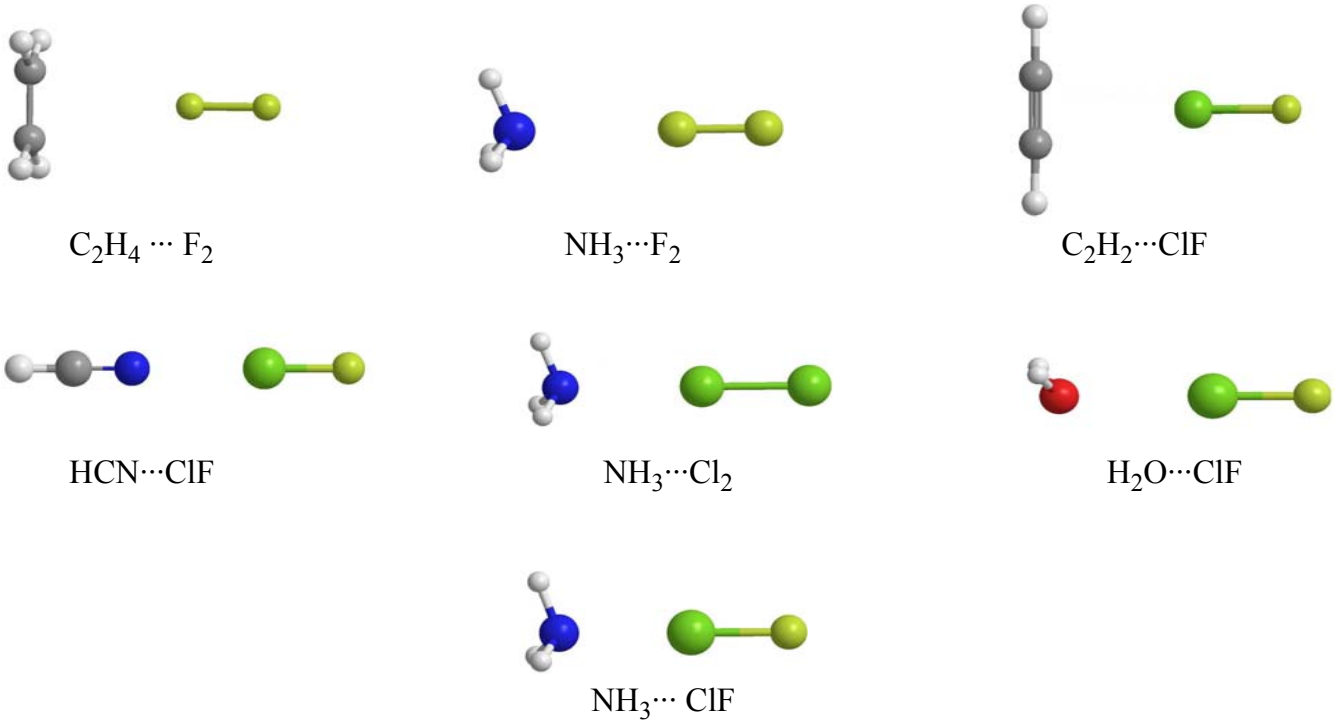
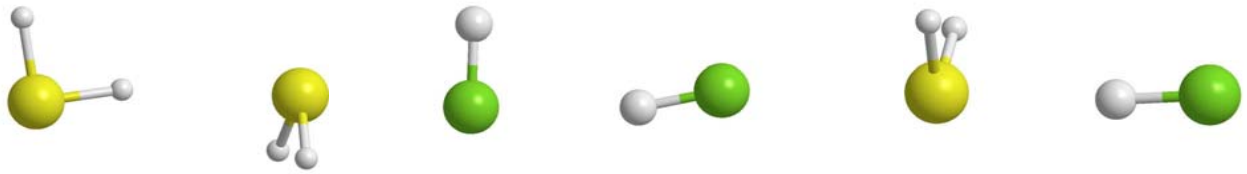
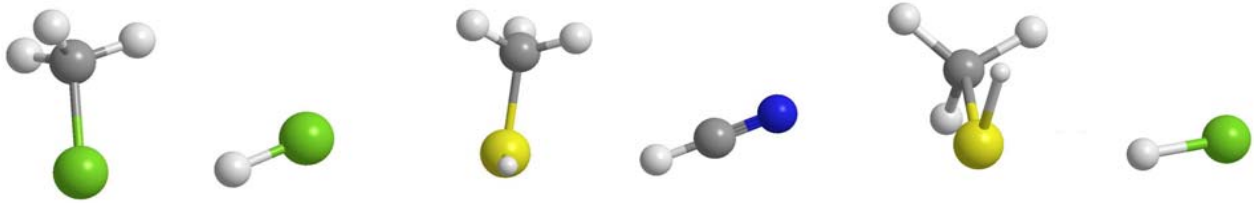

$C_2H_4 \cdots F_2$
$NH_3 \cdots F_2$
$C_2H_2 \cdots ClF$
$HCN \cdots ClF$
$NH_3 \cdots Cl_2$
$H_2O \cdots ClF$
$NH_3 \cdots ClF$

Figure 2



$(H_2S)_2$ $(HCl)_2$ $H_2S \cdots HCl$



$CH_3Cl \cdots HCl$ $CH_3SH \cdots HCN$ $CH_3SH \cdots HCl$

Figure 3

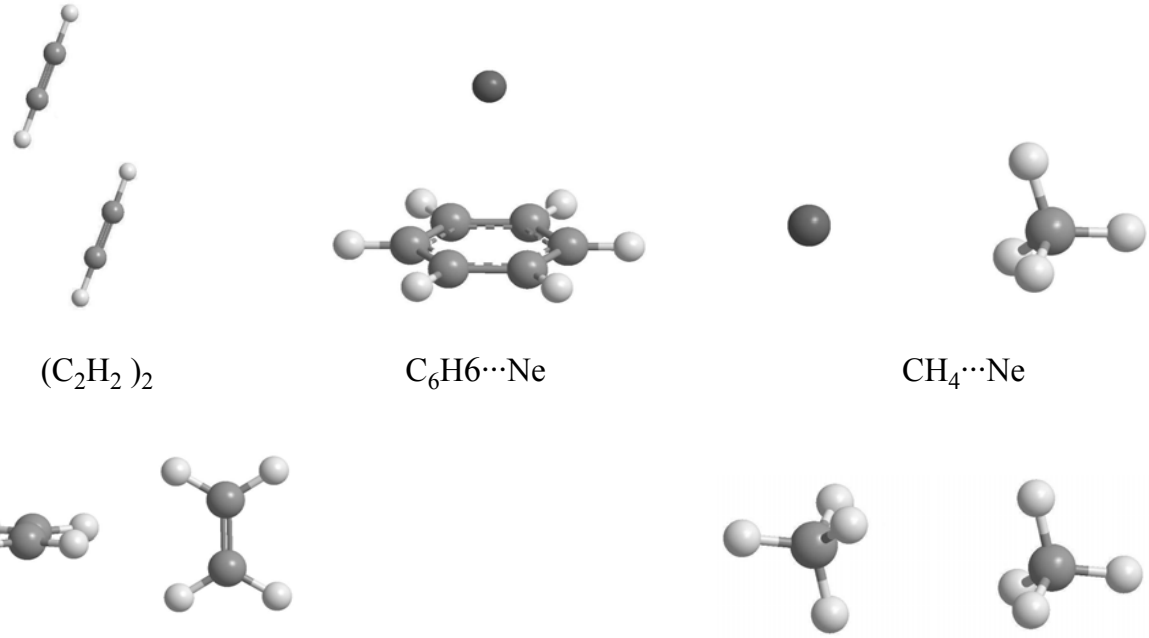


Figure 4