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## **The Design of Density Functionals that are Broadly Accurate for Thermochemistry, Thermochemical Kinetics, and Nonbonded Interactions**

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### ***Abstract.***

This paper develops two new hybrid meta exchange-correlation functionals for thermochemistry, thermochemical kinetics, and nonbonded interactions. The new functionals are called PW6B95 (6-parameter functional based on Perdew-Wang-91 exchange and Becke-95 correlation) and PWB6K (6-parameter functional for kinetics based on Perdew-Wang-91 exchange and Becke-95 correlation). The resulting methods were comparatively assessed against the MGAE109/3 main group atomization energy database, against the IP13/3 ionization potential database, against the EA13/3 electron affinity database, against the HTBH38/4 and NHTBH38/04 hydrogen-transfer and non-hydrogen-transfer barrier height databases, against the HB6/04 hydrogen bonding database, against the CT7/04 charge transfer complex database, against the new DI6/04 dipole interaction database, against the WI7/05 weak interaction database, and against the PPS5/05  $\pi$ - $\pi$  stacking interaction database. From the assessment and comparison of methods, we draw the following conclusions, based on an analysis of mean unsigned error: (i) The PW6B95, MPW1B95, B98, B97-1 and TPSS1KCIS methods give the best results for a combination of thermochemistry and nonbonded interactions. (ii) PWB6K, MPWB1K, BB1K, MPW1K, and MPW1B95 give the best results for a combination of thermochemical kinetics and nonbonded interactions. (iii) PWB6K outperforms the MP2 method for nonbonded interactions. (iv) PW6B95 gives errors for main group covalent bond energies that are only 0.41 kcal (as measured by mean unsigned error per bond (MUEPB) for the MGAE109 database), as compared to 0.56 kcal/mol for the second best method and 0.92 kcal/mol for B3LYP.

## 1. Introduction

Development of exchange and correlation functionals for density functional theory (DFT) is an active research area in theoretical chemistry and physics.<sup>1-50</sup> There are two different philosophies for developing new functionals, namely nonempirical and semiempirical. The nonempirical approach is to construct functionals from first principles and subject to known exact constraints. DFT methods constructed this way may be called “ab initio” DFT methods. This approach has produced the successful PBE<sup>11</sup> and TPSS<sup>38,39,41</sup> functionals.

However, the most popular DFT method in chemistry, B3LYP,<sup>8,9</sup> has been constructed by the semiempirical approach. This involves choosing a flexible functional form depending on one or more parameters, and then fitting these parameters to a set of experimental data. B3LYP,<sup>8,9</sup> B97-2,<sup>30</sup> VSXC,<sup>16</sup> MPW1K,<sup>25</sup> MPWB1K<sup>44</sup> and MPW1B95<sup>44</sup> are examples of functionals determined by the semiempirical approach.

Both the nonempirical and semiempirical DFT methods can be assigned to various rungs of “Jacob’s ladder”,<sup>28</sup> according to the number and kind of the ingredients in the functional. The lowest rung is the local spin density approximation (LSDA, in which the density functional depends only on density), and the second rung is the generalized gradient approximation (GGA, in which the density functional depends on density and its reduced gradient). The third rung is meta GGA, in which the functional also depends kinetic energy density. The fourth rung is hyper GGA,<sup>28</sup> which employs exact HF exchange. Unfortunately, there is no nonempirical hyper-GGA thus far. However there are two kinds of DFT methods that belong to the fourth rung of the Jacob’s ladder, and they are called hybrid GGA (a combination of GGA with Hartree-Fock exchange, for example, B3LYP, PBE0, and MPW1K), and hybrid meta GGA (a combination of meta GGA with Hartree-Fock exchange, for example, MPWB1K, MPW1B95 and TPSSh). Both hybrid GGA and hybrid meta GGA are semiempirical, and they have been very successful for chemistry.

Recently we systematically tested a number of DFT methods against databases of atomization energies,<sup>42,44</sup> barrier heights,<sup>42,44,49</sup> and binding energies of nonbonded

complexes.<sup>44,50</sup> We found that MPW1B95 is one of best general-purpose DFT methods, and it gives excellent performance for non-bonded interactions. We also found that MPWB1K is the best DFT method for thermochemical kinetics and nonbonded interactions. Both MPW1B95 and MPWB1K are examples of hybrid meta GGAs, and both were parametrized within the past year.<sup>51</sup>

In the present study, we will further improve the MPW1B95 and MPWB1K methods by the semiempirical fitting approach. Since one of our goals is to develop a density functional that is simultaneously accurate for bond energies, barrier heights, and nonbonded interactions, including nonbonded interactions dominated by dispersion, and since DFT is often stated to be inappropriate for dispersion interactions, we distinguish two general approaches to improving DFT for dispersion interactions. In the first, which we will call empirical van der Waals correction methods,<sup>52,53</sup> one adds explicit  $r^{-6}$  terms to DFT (where  $r$  is an interatomic distance). In such methods, one needs to develop different parameters for different atoms and in some cases even for different hybridization states.<sup>52</sup> Furthermore, the performance of empirical van der Waals correction methods for covalent interactions and for other types of nonbonded interaction such as charge transfer interaction has not been evaluated. In the second general approach, one attempts to improve the performance of DFT for nonbonded interactions by improving the density functionals in the more traditional way. This, however, has proved to be difficult. For example, Walsh<sup>54</sup> has recently shown that two newly developed functionals, X3LYP<sup>40</sup> and xPBE,<sup>47</sup> are not capable of describing the interactions in methane dimers, benzene dimers, or nucleobase pair stacking, although both functionals were designed partly for nonbonded interactions. Walsh also showed that combining HF exchange with the Wilson-Levy correlation (HF + WL) approach<sup>54</sup> can give good predictions for van der Waals systems, but it would be expected that the HF + WL approach cannot give satisfactory results for covalent interactions because of the unbalanced exchange and correlation. Our goal here is to design some functionals which can perform equally well for both covalent interactions and for all types of nonbonded interactions. We optimize two new functionals, namely PW6B95 and PWB6K,

against a database of atomization energies, barrier heights, a hydrogen bond energy, and the dissociation energy of a nonpolar van der Waals complex. To test our functionals, we examine their performance for hydrogen bonding, charge transfer interactions, dipole interactions, weak interactions, and  $\pi$ - $\pi$  stacking interactions. We compare the performance of the newly developed functionals to that of LSDA, GGA, meta GGA, and hybrid GGA functionals and previous hybrid meta GGA methods.

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. Binding8.** The training set for the PW6B95 model is the Binding8 database, which includes the six atomization energies in the AE6 representative database presented previously<sup>55</sup> and the binding energies of (H<sub>2</sub>O)<sub>2</sub> dimer and (CH<sub>4</sub>)<sub>2</sub> dimer. The AE6 set of atomization energies consists of SiH<sub>4</sub>, S<sub>2</sub>, SiO, C<sub>3</sub>H<sub>4</sub> (propyne), C<sub>2</sub>H<sub>2</sub>O<sub>2</sub> (glyoxal) and C<sub>4</sub>H<sub>8</sub> (cyclobutane). We have previously used AE6 as a training set to optimize the MPW1B95,<sup>44</sup> TPSS1KCIS,<sup>48</sup> and MPW1KCIS<sup>49</sup> methods. The Binding8 database is given in the supporting information.

**2.2. Kinetics9.** To parametrize the PWB6K model, we also used (in addition to Binding8) a database of 3 forward barrier heights, 3 reverse barrier heights, and 3 energies of reaction for the three reactions in the BH6<sup>55</sup> database; this 9-component database is called Kinetics9. We have previously used this training set to optimize the BB1K,<sup>43</sup> MPWB1K<sup>44</sup> and MPWKCIS1K<sup>49</sup> methods. The Kinetics9 database is also given in the supporting information

**2.3. MGAE109 Test Set.** The MGAE109 test set consists of 109 atomization energies (AEs). This AE test set contains a diverse set of molecules including organic and inorganic compounds (but no transition metals; the MG in the name of this database denotes main group elements, and AE denotes atomization energies). All 109 data are pure electronic energies, i.e., zero-point energies and thermal vibrational-rotational energies have been removed by methods discussed previously.<sup>48,56,57</sup> The 109 zero-point-exclusive atomization energies are part of

Database/3<sup>57</sup> and have been updated<sup>48</sup> recently. The updates include NO, CCH, C2F4, and singlet and triplet CH2, the updated database is called MGAE109/05, and it is a subset of Database/4.

**2.4. 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.<sup>56</sup> 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<sup>58</sup> data set. These databases are called IP13/3 and EA13/3, respectively.

**2.5. HTBH38/04 Database.** The HTBH38/04 database consists of 38 transition state barrier heights for hydrogen transfer (HT) reactions, and it is taken from previous papers.<sup>48,49</sup> It consists of 38 transition state barrier heights of hydrogen transfer reactions, and the HTBH38/04 database is listed in the supporting information.

**2.6. NHTBH38/04 Database.** The HTBH38/04 database consists of 38 transition state barrier heights for non-hydrogen-transfer (NHT) reactions, and it is taken from a previous paper.<sup>49</sup> This test set consists of 12 barrier heights for heavy-atom transfer reactions, 16 barrier heights for nucleophilic substitution (NS) reactions, and 10 barrier heights for non-NS unimolecular and association reactions.

**2.7. HB6/04 Database.** The hydrogen bond database consists of the equilibrium binding energies of six hydrogen bonding dimers, namely (NH<sub>3</sub>)<sub>2</sub>, (HF)<sub>2</sub>, (H<sub>2</sub>O)<sub>2</sub>, NH<sub>3</sub>⋯H<sub>2</sub>O, (HCONH<sub>2</sub>)<sub>2</sub>, and (HCOOH)<sub>2</sub>. This database is taken from a previous paper,<sup>50</sup> and it is listed in the supporting information.

**2.8. CT7/04 Database.** The charge transfer (CT) database consists of binding energies of seven charge transfer complexes, in particular C<sub>2</sub>H<sub>4</sub>⋯F<sub>2</sub>, NH<sub>3</sub>⋯F<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>⋯ClF, HCN⋯ClF, NH<sub>3</sub>⋯Cl<sub>2</sub>, H<sub>2</sub>O⋯ClF, and NH<sub>3</sub>⋯ClF. This database is taken from a previous paper,<sup>50</sup> and it is also listed in the supporting information.

**2.9. DI6/04 Database.** The dipole interaction (DI) database consists of binding energies of six dipole interaction complexes: (H<sub>2</sub>S)<sub>2</sub>, (HCl)<sub>2</sub>, HCl⋯H<sub>2</sub>S, CH<sub>3</sub>Cl⋯HCl, CH<sub>3</sub>SH⋯HCN,

and  $\text{CH}_3\text{SH}\cdots\text{HCl}$ . This database is taken from a previous paper,<sup>50</sup> and it is also listed in the supporting information.

**2.10. WI7/05 Database.** The weak interaction database consists of binding energies of seven weak interaction complexes, namely HeNe, HeAr, Ne<sub>2</sub>, NeAr, CH<sub>4</sub>⋯Ne, C<sub>6</sub>H<sub>6</sub>⋯Ne, and (CH<sub>4</sub>)<sub>2</sub>, all of which are bound by dispersion interactions. The four rare gas dimers in the WI7/05 database represent dispersion interactions that are expected to be typical interaction of hydrogen–first row, first row –first row, hydrogen–second row, and first row – second row elements, respectively. This database is a subset of a previous WI9/04 database,<sup>50</sup> and it is also listed in the supporting information.

**2.11. PPS5/05 Database.** The  $\pi$ – $\pi$  stacking (PPS) database consists of binding energies of five  $\pi$ – $\pi$  stacking complexes, namely (C<sub>2</sub>H<sub>2</sub>)<sub>2</sub>, (C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>, sandwich (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>, T-shaped (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>, and parallel-displaced (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>. This database is listed in Table 1. The best estimate of the binding energies of (C<sub>2</sub>H<sub>2</sub>)<sub>2</sub> and (C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> are obtained by W1<sup>59</sup> calculations performed for the present article by methods explained in a previous paper.<sup>50</sup> The best estimate of binding energies of sandwich (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>, T-shaped (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>, and parallel-displaced (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub> are taken from the paper of Sinnokrot et al.<sup>60</sup>

**2.12. Database Availability.** All above mentioned databases are also available at the Truhlar group website.<sup>61</sup>

### 3. Computation Methods, Theory and Parametrization

**3.1. Geometries, Basis Sets, and Spin-Orbit Energy.** All calculations for the AE6, MGAE109, IP13/3, EA13/3, HTBH38/04 and NHTBH38/04 databases are single-point calculations at QCISD/MG3 geometries, where QCISD is quadratic configuration interaction with single and double excitations,<sup>62</sup> and MG3 is the modified<sup>63,64</sup> G3Large<sup>58</sup> basis set. The MG3 basis set,<sup>63</sup> also called G3LargeMP2,<sup>64</sup> is the same as 6-311++G(3d2f, 2df, 2p)<sup>65</sup> for H-Si, but improved<sup>58</sup> for P-Ar. The QCISD/MG3 geometries for molecules and saddle points in the MGAE109, IP13/3, EA13/3, HTBH38/04 and NHTBH38/04 databases can be obtained from the Truhlar group database website.<sup>61</sup>

Geometries for all molecules in the nonbonded database (HB6/04, CT7/04, DI6/04, and WI7/05) are optimized at the MC-QCISD/3 level, where MC-QCISD is the multi-coefficient QCISD method,<sup>57,66</sup> which is one of the most cost-efficient method of the set of multi-coefficient correlation methods (MCCMs). The geometries for the benzene dimers in the PPS5/05 database are taken from Sinnokrot and Sherrill.<sup>67</sup> The geometries for all monomers and complexes in the HB6/04, CT7/04, DI6/04, WI7/05, and PPS5/05 databases can be obtained from the Truhlar group database website.<sup>61</sup>

We tested all DFT methods with the MG3S basis sets. The MG3S basis<sup>56</sup> is the same as MG3 except it omits diffuse functions on hydrogens. However, the optimization of new parameters in density functionals are carried out with the 6-31+G(d,p)<sup>68</sup> basis set (also called DIDZ).

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.<sup>63</sup>

**3.2. Counterpoise Corrections and Software.** For nonbonded complexes, we perform calculations with and without the counterpoise corrections<sup>69,70</sup> for basis set superposition error (BSSE). All calculations were performed with the GAUSSIAN03 program<sup>71</sup> and use the ultrafine grid for evaluating integrals over density functionals.

### 3.3. Theory

**3.3.1. Exchange Functional.** The LSDA exchange energy can be written as:

$$E_X^{LSDA} = A_x \sum_{\sigma} \int \rho_{\sigma}(\mathbf{r})^{4/3} d\mathbf{r} \quad (1)$$

where  $\rho_{\sigma}$  is the density of electrons with spin  $\sigma$  (where  $\sigma = \alpha$  or  $\beta$ , and  $\rho_{\sigma}$  is also called spin density), and the constant  $A_x$  in Eq. 1 is defined as

$$A_x = -\frac{3}{2} \left( \frac{3}{4\pi} \right)^{1/3} \quad (2)$$

The GGA exchange energy can be expressed as

$$E_X^{GGA} = E_X^{LSDA} - \sum_{\sigma} \int F^{GCE}[x_{\sigma}] \rho_{\sigma}(\mathbf{r})^{4/3} d\mathbf{r} \quad (3)$$

where reduced gradient of the density with spin  $\sigma$  is

$$x_{\sigma} = \frac{|\nabla \rho_{\sigma}|}{(\rho_{\sigma})^{4/3}} \quad (4)$$

$F^{GCE}[x_{\sigma}]$  is the gradient-corrected enhancement factor. The gradient-corrected enhancement factor for the PW91<sup>5</sup> and mPW<sup>14</sup> exchange functional is

$$F^{GCE}[x_{\sigma}] = \frac{bx_{\sigma}^2 - (b - \beta)x_{\sigma}^2 \exp(-cx_{\sigma}^2) - 10^{-6}x_{\sigma}^d}{1 + 6bx_{\sigma} \sinh^{-1} x_{\sigma} - \frac{10^{-6}x_{\sigma}^d}{A_x}} \quad (5)$$

where  $\beta = 5(36\pi)^{-5/3}$  and  $c = 1.6455$  in both functionals. In the PW91 functional,  $b = 0.0042$  and  $d = 4$ , whereas in the mPW functional,  $b = 0.00426$  and  $d = 3.72$ . Note that in the original mPW paper,<sup>14</sup> the value of the parameters for  $b$  and  $d$  were incorrectly tabulated as 0.0046 and 3.73.

**3.3.2. Correlation Functional.** In the present study, we use Perdew and Wang's functional<sup>6</sup> for the correlation part of the LSDA. Then, following the analysis of Stoll, Pavlidou, and Preuss,<sup>72</sup> one can decompose the LSDA correlation energy into opposite-spin (*opp*) and parallel-spin ( $\sigma\sigma$ ) correlation energy components for the uniform electron gas (UEG):

$$E_{Copp}^{UEG}(\rho_{\alpha}, \rho_{\beta}) = E_C^{LSDA}(\rho_{\alpha}, \rho_{\beta}) - E_C^{LSDA}(\rho_{\alpha}, 0) - E_C^{LSDA}(0, \rho_{\beta}) \quad (6)$$

$$E_{C\sigma\sigma}^{UEG}(\rho_{\alpha}, \rho_{\beta}) = E_C^{LSDA}(\rho_{\alpha}, 0) \quad (7)$$

where  $E_C^{LSDA}(\rho_{\alpha}, \rho_{\beta})$  is the LSDA correlation energy.



Note that Eq. 7 does not vanish in the one-electron case, and this nonvanishing is a manifestation of self-interaction error. To correct this self-interaction error, Becke<sup>10</sup> used a quantity,  $D_\sigma$ , which is defined as:

$$D_\sigma = 2\tau_\sigma - \frac{1}{4} \frac{|\nabla\rho_\sigma|^2}{\rho_\sigma} \quad (8a)$$

and

$$\tau_\sigma = \frac{1}{2} \sum_i^{occup} |\nabla\Psi_{i\sigma}|^2 \quad (8b)$$

where  $\tau_\sigma$  is the kinetic energy density of electrons with spin  $\sigma$ , defined in terms of the occupied Kohn-Sham orbitals  $\Psi_{i\sigma}$ .  $D_\sigma$  can be also written as:

$$D_\sigma = 2(\tau_\sigma - \tau_\sigma^W) \quad (9a)$$

where

$$\tau_\sigma^W = \frac{1}{8} \frac{|\nabla\rho_\sigma|^2}{\rho_\sigma} \quad (9b)$$

and  $\tau_\sigma^W$  is the von Weizsäcker kinetic energy density.<sup>73</sup> In one-electron case,  $\tau_\sigma = \tau_\sigma^W$ , so  $D_\sigma$  vanishes in any one-electron system. Becke used  $D_\sigma$  as a self-interaction correction factor to the parallel spin case. Note that the uniform electron gas limit ( $\nabla\rho_\sigma \rightarrow 0$ ) of  $D_\sigma$  is:

$$D_\sigma^{UEG} = \frac{3}{5} (6\pi^2)^{2/3} \rho_\sigma^{5/3} \quad (10)$$

Now we can write down the B95 correlation functional<sup>10</sup> by incorporating the gradient correction factors for the opposite spin and parallel spin case, and incorporating the self-interaction correction factor for the parallel spin case.

The opposite-spins correlation energy by B95 functional can be expressed as:

$$E_C^{opp} = [1 + c_{opp} (x_\alpha^2 + x_\beta^2)]^{-1} E_{Copp}^{UEG} \quad (11)$$

and for parallel spins,

$$E_C^{\sigma\sigma} = [1 + c_{\sigma\sigma} x_\sigma^2]^{-2} \frac{D_\sigma}{D_\sigma^{UEG}} E_{C\sigma\sigma}^{UEG} \quad (12)$$

The total correlation energy is given by

$$E_C = E_C^{opp} + E_C^{\alpha\alpha} + E_C^{\beta\beta} \quad (13)$$

Becke fitted the parameters  $c_{opp}$  and  $c_{\sigma\sigma}$  in Eq. (11) and Eq. (12) to the correlation energies of the helium ( $c_{opp}$ ) and the neon ( $c_{\sigma\sigma}$ ) atoms. The values of these two parameters in the B95 functional are:

$$c_{opp} = 0.0031, \quad c_{\sigma\sigma} = 0.038 \quad (14)$$

**3.3.3. Hybrid Meta Functional.** The one-parameter hybrid Fock-Kohn-Sham operator can be written as follows:<sup>10,25</sup>

$$F = F^H + (X/100) F^{HFE} + [1 - (X/100)] (F^{SE} + F^{GCE}) + F^C \quad (15)$$

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 Slater local density functional (also called Dirac-Slater) for exchange,<sup>74,75</sup>  $F^{GCE}$  is the gradient correction for the exchange functional, and  $F^C$  is the total correlation functional including both local and gradient-corrected parts and a dependence on kinetic energy density. In the MPW1B95 and MPWB1K models,<sup>51</sup> we used the mPW exchange functional<sup>14</sup> (Eq. (5)) for  $F^{GCE}$  and the Becke95<sup>10</sup> functional (Eq. (11), (12), and (13)) for  $F^C$ .

**3.4. Optimization of the New Hybrid Meta Functionals.** All parameter optimizations were carried out with a genetic algorithm. We optimize two new methods using different training functions. In both new methods, we optimize the  $b$ ,  $c$ , and  $d$  parameters in PW exchange functional (Eq. (5)), the  $c_{opp}$  and  $c_{\sigma\sigma}$  parameters in the Becke95 correlation functional, and the percentage,  $X$ , of Hartree-Fock exchange. We minimize these parameters in a self-consistent way by solving the Fock-Kohn-Sham equation using the DIDZ basis set with

QCISD/MG3 geometries for the molecules in the AE6 database, and with MC-QCISD/3 geometries for  $(\text{H}_2\text{O})_2$  and  $(\text{CH}_4)_2$ . We also turned on counterpoise correction<sup>69</sup> (cp) to correct basis set superposition error (BSSE) during the optimization for  $(\text{H}_2\text{O})_2$  and  $(\text{CH}_4)_2$  dimers.

For the first new functional, we optimized the parameters against the Binding8 database to minimize the following training function:

$$F_3 = \text{MUEPB}(\text{AE6}) + 3 \times \text{MUE}(D_e[(\text{H}_2\text{O})_2], D_e[(\text{CH}_4)_2]) \quad (16)$$

where MUEPB is the mean unsigned error (MUE, same as mean absolute deviation (MAD)) per bond. In particular, MUEPB is obtained by dividing the MUE for AE6 database by the average number of bonds per molecule in this database. The second term of Eq. (16) is the MUE for the equilibrium binding energies of  $(\text{H}_2\text{O})_2$  and  $(\text{CH}_4)_2$  with a weight of 3, because these numbers are much smaller than the bond energies in AE6. The functional optimized in this way is called PW6B95, which denotes (in the usual way) a 6-parameters functional based on PW91 exchange and Becke95 correlation.

For the second new functional, the parameters were optimized in two stages. First we optimized all six parameters against the training function  $F_6$ , which is the same as  $F_3$ , except that the MUE in the  $(\text{H}_2\text{O})_2$  and  $(\text{CH}_4)_2$  binding energies is weighted by 6 instead of 3. Then we froze the  $b$ ,  $c$ ,  $d$ ,  $c_{opp}$ , and  $c_{\sigma\sigma}$  parameters, and we reoptimized  $X$  against the Kinetics9 database. In particular,  $X$  was adjusted to minimize the root-mean-square-error (RMSE) for the Kinetics9 database. This second functional is called PWB6K, which denotes a functional based on PW91 exchange and Becke95 correlation, with 6 parameters optimized to improve nonbonded interaction and kinetics (K).

All optimized parameters are listed in Table 2, where they are compared to the parameters in MPW1B95 and MPWB1K.

For plotting, we define a total GGA enhancement factor  $F^{GGA}$  as:

$$F^{GGA}[s] = F^{GCE}[s] + 1 \quad (17)$$

where  $F^{GCE}[s]$  is factor in Eq. 3. In addition, we use another definition of reduced gradient, in

particular:

$$s = \frac{|\nabla\rho|}{(24\pi^2)^{1/3}\rho^{4/3}} \quad (18)$$

Thus, for closed-shell system with  $\rho = 2\rho_\sigma$ , we have  $s = (48\pi^2)^{-1/3} x_\sigma$ . The total enhancement factors for the B, mPW, PW91, and X exchange and for the exchange parts of the PW6B95 and PWB6K methods are plotted in Figure 1. Interestingly, the shape of the exchange part of PWB6K is close to that for PW91 exchange, whereas the PW6B95 exchange lies between mPW and PW91 when  $s > 4$ . This may be surprising at first, but one should remember that one cannot evaluate exchange functionals separately from the correlation ones, to which they are added.

**3.5. Assessment of the New Hybrid Meta Functionals.** We fitted our new functionals against a very small data set (8 data in Binding8, 9 data in Kinetics9), but we assess the new functionals against a much larger data set that includes 109 atomization energies, 13 ionization potentials (IP13), 13 electron affinities (EA13), 76 barrier heights (HTBH38 and NHTBH38), 6 hydrogen dimers (HB6), 7 charge transfer complexes (CT7), 6 dipole interaction complexes (DI6), 7 weak interaction complexes (WI7), and 5  $\pi$ - $\pi$  stacking complexes (PPS5). We compare the new methods to a LSDA, namely Slater exchange<sup>76</sup> plus Perdew-Wang<sup>6</sup> local correlation (SPWL), and to a GGA: namely PBE.<sup>11</sup> We also compare the new methods to two meta-GGA methods: TPSS<sup>38,39</sup> and TPSSKCIS,<sup>20,21,34,38,39</sup> and to eight hybrid GGA methods: B3LYP,<sup>4,8,9</sup> B97-1,<sup>17</sup> B97-2,<sup>30</sup> mPW1PW91,<sup>14</sup> MPW1K,<sup>25</sup> MPW3LYP,<sup>4,14,51</sup> PBE1PBE,<sup>11</sup> and X3LYP.<sup>40</sup> We also compare the new functionals to nine hybrid meta GGA methods: B1B95,<sup>10</sup> BB1K,<sup>43</sup> MPW1B95,<sup>51</sup> MPWB1K,<sup>51</sup> MPW1KCIS,<sup>49</sup> MPWKCIS1K,<sup>49</sup> PBE1KCIS,<sup>50</sup> TPSS1KCIS,<sup>20,21,34,38,39,43</sup> and TPSSh,<sup>38,39</sup> and to an ab initio wave function method: MP2<sup>77</sup>. All DFT methods in the present paper are listed in the Table 3 in the chronological order of their invention.

## 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<sup>42,43</sup> more transferable comparison between databases with different average sizes of molecules. To make the trends more clear, in every table we will list the methods in increasing order of the values in the key (overall) error column, which is always the last column of a given table. The five smallest average errors for each of the individual databases and the ten smallest average errors overall (for each table) are in bold.

**4.1. Thermochemistry: AE, IP, and EA Results.** Table 4 summarizes the errors in AEs, IPs, and EAs for all tested methods. Table 4 shows that the PW6B95, B1B95, MPW1B95, MPW3LYP methods give the best results for AE calculations. PW6B95 is the only method which has MUEPB less than 0.5 kcal/mol. Note that the second best method for atomization energy has an error much larger, in fact 37% larger, than PW6B95, and the most popular method B3LYP has an error 124% larger than PW6B95.

MPWB1K, BB1K, MPW1B95, and B1B95 have the best performance for IP calculations, whereas PW6B95, B97-1, TPSSKCIS, and PBE give the best performance for EA calculations. The outstanding performance of PW6B95 for electron affinities is particularly noteworthy since no electron affinity data were used in the parametrization.

To compare their performance for thermochemistry, we defined the TMUE (total MUE) as follows:

$$TMUE = [MUEPB(AE) \times 109 + MUE(IP) \times 13 + MUE(EA) \times 13] / 135 \quad (19)$$

If we use TMUE as a criterion for thermochemistry, Table 4 shows that, PW6B95 is the best functional, followed by B1B95, MPW1B95, and B98. A final choice of method for many applications should probably be based on a broader assessment with more diverse data than on

small differences between the higher-quality methods in Table 4, and one of the goals of the rest of this paper is to present such an assessment.

Before moving on though, it is important to emphasize that PW6B95 is parametrized only against the Binding8 data set. Even though the new functional is parametrized on this small data set, it shows good performance for the much larger MGAE109/3 database and for the IP and EA databases.

Both new methods, and in fact most of the DFT methods tested, outperform MP2 in terms of TMUE.

If we compare the nonempirical functionals on the first three rungs of Perdew's nonempirical Jacob's ladder<sup>28,35,39</sup> for organizing DFT approximations, Table 3 shows that, as we climb the nonempirical ladder, the TMUE calculations improve significantly from LSDA (i.e., SPWL) to PBE (TMUE reduces from 14.7 to 3.0 kcal/mol) and also improve by more than a factor of two from PBE to TPSS (TMUE reduces from 3.0 to 1.4 kcal/mol).

**4.2. Thermochemical Kinetics: HTBH38/04 and NHTBH38/04 Results.** Table 5 gives the mean errors for the HTBH38/04 and NHTBH38/04 databases with the MG3S basis set. We also tabulated a value of mean MUE (called MMUE) that is defined as 1/4 times the MUE for heavy-atom transfer barrier heights plus 1/4 times the MUE for  $S_N2$  barrier heights plus 1/4 times the MUE for unimolecular and association barrier heights plus 1/4 times the MUE for hydrogen transfer barrier heights.

Table 5 shows that the BB1K, PWB6K, MPWB1K, and MPW1K methods give the best results for heavy-atom-transfer barrier height calculations. MP2, B1B95, PWB6K, and MPWKCIS1K have the best performance for nucleophilic substitution barrier height calculations. B1B95, MPW1B95, PW6B95, and BB1K give the best performance for non-NS unimolecular and association barrier height calculations. The BB1K, PWB6K, MPWB1K, and MPW1K methods give the best performance for hydrogen transfer barrier height calculations, and they also give the lowest values of MMUE, which means they give the best performance for overall barrier height calculation.

Another quantity, average MUE or AMUE, is defined as:

$$AMUE = [MUEPB(\Delta E, 38) + MMUE(BH76)]/2 \quad (20)$$

where MUE( $\Delta E$ ,38) is the mean unsigned error for the energy of reactions for the 38 reactions in the HTBH38 and NHTBH38 database. If we use AMUE as a criterion to justify the performance of a DFT method for thermochemical kinetics, Table 5 shows that BB1K, PWB6K, and MPWB1K are the best, followed by B1B95, MPW1K, and MPW1B95.

**4.3. Nonbonded Interactions.** The mean errors for nonbonded interaction are listed in Table 6 and Table 7. In both tables, 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. Table 6 summarizes MUEs, and Table 7 presents MSEs.

In Table 6, we only listed MUEs, and MSEs for these methods are given in the supporting information. We also defined a mean MUE:

$$MMUE = [MUE(\text{no-cp}) + MUE(\text{cp})]/2 \quad (21)$$

Although the cp correction has many advocates, it is often impractical to include this correction (for example, it is impractical for condensed-phase simulations). Since this is a paper about practical DFT and not about cp, we simply use the average in Eq. 21 without arguing one way or another about the merits of cp corrections. Those who prefer a different approach can find the separate cp and no-cp values in our tables.

Table 6 shows that PBE1PBE, PBE, PWB6K, and B97-1 give the best performance for calculating the binding energies for the hydrogen bonding dimers in the HB6/04 database.

In 1996, Ruiz, Salahub, and Vela<sup>78</sup> reported that some GGA methods seriously overestimate the binding energies and geometries of some charge transfer complexes. From Table 6 and Table 7, we can also see that the LSDA (SPWL), GGAs (BLYP, PBE), meta GGAs (TPSS, TPSSKICIS) give much larger MMUE and MSE than hybrid GGAs and hybrid meta GGAs. The wrong asymptotic behavior of the exchange and correlation functionals in DFT leads to a small energy gap between electron donor’s HOMO and the acceptor’s LUMO. The small gap leads to too much charge transfer and is the cause of the overestimation of the

strength of the charge transfer interaction. Inclusion of HF exchange in the DFT calculation can increase the HOMO-LUMO gap; hence hybrid functionals can give better performance,<sup>79</sup> as shown here by the low MMUE obtained by some hybrid and hybrid meta GGA methods such as PWB6K, MPWB1K, MPW1B95, and MPW1K. These methods give the best performance for calculating the binding energies of the charge transfer complexes, with the first three methods outperforming MP2. PW6B95 is only slightly worse than MPW1K.

Table 6 also shows that PWB6K, B97-1, MPW3LYP, and MP2 give the best performance for calculating the binding energies for the dipole interaction complexes in the DI6/04 database.

PWB6K, MP2, PW6B95, and B97-1 give the best performance for calculating the binding energies for the weak interaction complexes in the WI7/05 database. Note that PWB6K outperforms the MP2 method for all of the above four types of nonbonded interactions; this is encouraging because PWB6K is computationally much less expensive than MP2, and it therefore has broader applicability in biological and recognition systems where nonbonded interactions are important. It is well known that MP2 has the correct asymptotic  $R^{-6}$  binding behavior (where  $R$  is the internuclear distance for rare gas dimers), but DFT does not have this property. In Figure 2, we compared the calculated potential energy curve of the  $\text{Ar}_2$  dimer by PWB6K and MP2 with the basis set 6-311+G(2df,2p), and we also present the curve for  $-C_6 \times R^{-6}$ , where  $C_6$  was taken from a recent paper.<sup>80</sup> First observation of Figure 2 is that counterpoise correction has a stronger effect for MP2 than for PWB6K. The MP2-nocp curve deviates from the MP2-cp curve much more than the PWB6K method does. The  $D_e$  by MP2-cp is 0.11 kcal/mol which is 50% less than that by MP2-nocp, whereas the  $D_e$  by PWB6K-cp is 0.25 kcal/mol which is only 8% less than that by PWB6K-nocp. Note that the experimental  $D_e$  is 0.28 kcal/mol, so this is consistent with the conclusion we drew from Table 6 and Table 7 that PWB6K outperforms MP2 for the dispersion interactions. Figure 2 and Table S8 in the supporting information also shows that near the bottom of the van der Waals well, neither PWB6K nor MP2 gives the  $R^{-6}$  binding behavior. When intermolecular distance  $R$  increase to 6



Å, MP2 have correct asymptotic  $R^{-6}$  binding behavior, whereas the PWB6K method does not have this asymptotic behavior.

$\pi$ - $\pi$  stacking interactions play a dominant role in stabilizing various biopolymers, for example, the double helix structure of DNA. Table 6 and Table 7 show that the quality of PWB6K for describing  $\pi$ - $\pi$  stacking interaction is comparable to MP2, although they have different systematic error. PWB6K and most DFT methods underestimate the strength of  $\pi$ - $\pi$  stacking interaction, whereas MP2 overestimates the binding energies. Surprisingly and interestingly, the LSDA (SPWL) gives the best performance for  $\pi$ - $\pi$  stacking, but this is apparently due largely to error cancellation because LSDA seriously overestimates covalent interactions and other types of weak interactions.

We also define the mean MMUE as:

$$\begin{aligned} \text{MMMUE} = & [\text{MMUE}(\text{HB}) + \text{MMUE}(\text{CT}) + \text{MMUE}(\text{DI}) \\ & + \text{MMUE}(\text{WI}) + \text{MMUE}(\text{PPS})] / 5 \end{aligned} \quad (22)$$

If we use MMMUE as a criterion to evaluate the overall performance of DFT methods and MP2 for nonbonded interactions, we can see from Table 6 that the performance of PWB6K, MP2, MPWB1K, and PW6B95 are the best, followed by MPW1B95, PBE1PBE, B97-1, and MPW1K.

**4.4. Overall Results.** Table 8 is a summary of the performance of the tested methods for all quantities studied in this paper. The TCAE (Thermochemical Average Error) is defined as:

$$\text{TCAE} = (\text{TMUE} \times 2 + \text{MMMUE}) / 3 \quad (23)$$

where TMUE is from Table 4 and MMMUE is from Table 6, and this is the final measure that we use for the quality of a method for thermochemistry. The factor of two is included because we want to emphasize the performance for the database of thermochemistry. The TAKE (Thermochemical Kinetics Average Error) in Table 8 is defined as:

$$\text{TKAE} = (\text{AMUE} \times 2 + \text{MMMUE}) / 3 \quad (24)$$

where the AMUE is from Table 5, and again MMMUE is from Table 6. TKAE is the final measure that we use for the quality of a method for thermochemical kinetics. Clearly the exact position in Table 8 is not as meaningful as the general trends, but the table provides a way to

organize the discussion. As in other tables, the five smallest average errors for each of the individual quantities are in bold, except for the final column, where the ten best methods are bold.

Using Thermochemical Average Error (TCAE) in Table 8 as the overall, summarizing measure of quality of the tested methods for thermochemistry, we can see that PW6B95 is the best method, followed by MPW1B95, B98, B97-1, and TPSS1KCIS.

Using Thermochemical Kinetics Average Error (TKAE) in Table 8 as the overall, summarizing measure of quality of tested methods for thermochemical kinetics, we can see that PWB6K, MPWB1K, BB1K, MPW1K, and MPW1B95 are the best of all the tested methods for thermochemical kinetics.

Note that all the above conclusions were drawn on the calculations with the MG3S basis. We also did the calculations with the 6-31+G(d,p) basis set, the conclusions based on the calculations with this double zeta basis set are similar to the above conclusions.

**4.5. Concluding Remarks.** This paper developed two new hybrid meta exchange-correlation functionals for thermochemistry, thermochemical kinetics, and nonbonded interactions in main group atoms and molecules. The resulting methods were comparatively assessed against the MGAE109/3 main group atomization energy database, against the IP13/3 ionization potential database, against the EA13/3 electron affinity database, against the HTBH38/4 and NHTBH38/04 barrier height database, against the HB6/04 hydrogen bonding database, against the CT7/04 charge transfer database, against the DI6/04 dipole interaction database, against the WI7/05 weak interaction database and against the PPS5/05  $\pi$ - $\pi$  stacking database. From the above assessment and comparison, we draw the the following conclusions, based on an analysis of mean unsigned errors:

(1) The PW6B95, MPW1B95, B98, B97-1 and TPSS1KCIS methods give the best results for a combination of thermochemistry and nonbonded interactions.

(2) PWB6K, MPWB1K, BB1K, MPW1K, and MPW1B95 give the best results for a combination of thermochemical kinetics and nonbonded interactions.

(3) The new PWB6K functional is the first functional to outperform the MP2 method for nonbonded interactions.

(4) PW6B95 gives errors for main group covalent bond energies that are only 0.41 kcal (as measured by MUEPB for the MGAE109 database), as compared to 0.56 kcal/mol for the second best method and 0.92 kcal/mol for B3LYP.

From the present study, we recommend PW6B95, MPW1B95, B98, B97-1, and TPSS1KCIS for general purpose applications in thermochemistry and we recommend PWB6K, MPWB1K, BB1K, MPW1K, and MPW1B95 for kinetics. It is very encouraging that we succeeded in developing density functionals with very broad applicability. They should be especially useful for kinetics and for condensed-phase systems and molecular recognition problems (including supramolecular chemistry and protein assemblies) where nonbonded interactions are very important.

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**Supporting Information Available:** The training sets and all the databases are given in the supporting information. The mean signed errors for nonbonded interactions are also given in the supporting information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Table 1: Binding Energies (kcal/mol) in the  $\pi$ - $\pi$  Stacking Database (PPS5/05)

Complexes	Best estimate	Ref.
(C <sub>2</sub> H <sub>2</sub> ) <sub>2</sub>	1.34	50
(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	1.42	50
Sandwich (C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub>	1.81	60
T-Shaped (C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub>	2.74	60
Parallel-Displaced (C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub>	2.78	60
average	2.02	

Table 2: Parameters in the MPW1B95 and MPWB1K Methods and in the New Functionals

Method	Exchange			Correlation		$X$
	$b$	$c$	$d$	$c_{\text{opp}}$	$c_{\sigma\sigma}$	
MPW1B95	0.00426 <sup>a</sup>	1.6455 <sup>b</sup>	3.7200 <sup>a</sup>	0.00310 <sup>c</sup>	0.03800 <sup>c</sup>	31 <sup>d</sup>
MPWB1K	0.00426 <sup>a</sup>	1.6455 <sup>b</sup>	3.7200 <sup>a</sup>	0.00310 <sup>c</sup>	0.03800 <sup>c</sup>	44 <sup>d</sup>
PWB6K	0.00539	1.7077	4.0876	0.00353	0.04120	46 <sup>e</sup>
PW6B95	0.00538	1.7382	3.8901	0.00262	0.03668	28

<sup>a</sup>same as mPW (Ref. 14)

<sup>b</sup> same as PW91 (Ref. 5)

<sup>c</sup> same as Becke95 (Ref. 10)

<sup>d</sup> Ref. 51

<sup>e</sup> In the PWB6K functional,  $X = 31$  at the end of the first stage. Then all other parameters are frozen, and  $X$  is re-optimized for kinetics



Table 3: Summary of the DFT Methods Tested

Method	$X^a$	Year	Type	Ex. functional <sup>b</sup> Corr. functional <sup>c</sup>	Ref(s).
SPWL	0	1992	LSDA	Slater's local Ex. Perdew-Wang local	6, <sup>76</sup>
B3LYP	20	1994	hybrid GGA	Becke88 Lee-Yang-Parr	3, 4, 9
B1B95	25	1996	hybrid meta GGA	Becke88 Becke95	3, 10
PBE	0	1996	hybrid GGA	PBE Ex. PBE Corr.	11
PBE1PBE <sup>d</sup>	25	1996	hybrid GGA	PBE Ex. PBE Corr.	11
mPW1PW91 <sup>e</sup>	25	1998	hybrid GGA	modified PW91 Perdew-Wang91	5, 14
B97-1	21	1998	hybrid GGA	B97-1 Ex. B97-1 Corr.	17
B98	21.98	1998	hybrid GGA	B98 Ex. B98 Corr.	15
MPW1K	42.8	2000	hybrid GGA	modified PW91 Perdew-Wang91	14, 24
B97-2	21	2001	hybrid GGA	B97-2 Ex. B97-2 Corr.	17
TPSS	0	2003	meta GGA	TPSS Ex. TPSS Corr.	38,39
TPSSh	10	2003	hybrid meta GGA	TPSS Ex. TPSS Corr.	38,39
X3LYP	21.8	2004	hybrid GGA	Becke88+PW91 Lee-Yang-Parr	3, 4, 5, 40
MPW3LYP	21	1998	hybrid GGA	modified PW91 Lee-Yang-Parr	4, 14, <sup>51</sup>
TPSSKCIS	0	2004	hybrid meta GGA	TPSS Ex. KCIS Corr.	20,21,34,38,39

BB1K	42	2004	hybrid meta GGA	Becke88 Becke95	3, 10, 43
MPW1B95	31	2004	hybrid meta GGA	modified PW91 Becke95	10, 14, <sup>51</sup>
MPWB1K	44	2004	hybrid meta GGA	modified PW91 Becke95	10, 14, <sup>51</sup>
TPSS1KCIS	13	2004	hybrid meta GGA	TPSS Ex. KCIS Corr.	20,21,34,38,39,43
MPW1KCIS	15	2004	hybrid meta GGA	modified PW91 KCIS Corr.	10, 20,21,34, <sup>49</sup>
MPWKCIS1K	41	2004	hybrid meta GGA	modified PW91 KCIS Corr.	10, 20,21,34, <sup>49</sup>
PBE1KCIS	22	2005	hybrid meta GGA	PBE Ex. KCIS Corr.	11,20,21,34, <sup>50</sup>
PW6B95	28	2005	hybrid meta GGA	PW6B95 Ex. PW6B95 Corr.	This work
PWB6K	46	2005	hybrid meta GGA	PWB6K Ex. PWB6K Corr.	This work

<sup>a</sup>  $X$  denotes the percentage of HF exchange in the functional.

<sup>b</sup> Upper entry

<sup>c</sup> Lower entry

<sup>d</sup> also called PBE0

<sup>e</sup> also called mPW1PW, mPW0, and MPW25

Table 4: Mean Errors<sup>a</sup> (kcal/mol for Ionization Potentials (IP) and Electron Affinities (EA) and kcal/mol per Bond for Atomization Energies (AE))<sup>b</sup>

Method	MGAE109		IP13		EA13		TMUE
	MSEPB	MUEPB	MSE	MUE	MSE	MUE	
PW6B95	-0.03	<b>0.41</b>	2.24	3.24	0.72	<b>1.78</b>	<b>0.81</b>
B1B95	-0.24	<b>0.56</b>	-0.13	<b>2.18</b>	3.02	3.16	<b>0.96</b>
MPW1B95	0.30	<b>0.63</b>	0.36	<b>2.14</b>	2.72	2.91	<b>0.99</b>
B98	-0.51	<b>0.65</b>	1.99	3.21	0.30	<b>1.84</b>	<b>1.01</b>
B97-2	-0.22	0.66	0.46	<b>2.21</b>	2.41	2.89	<b>1.02</b>
TPSS1KCIS	-0.06	0.67	0.91	2.63	1.84	2.81	<b>1.06</b>
B97-1	-0.40	0.76	0.99	2.84	1.09	<b>2.02</b>	<b>1.08</b>
MPW3LYP	-0.20	<b>0.64</b>	2.72	4.32	-0.70	<b>2.14</b>	<b>1.14</b>
PBE1PBE	0.10	0.92	2.44	3.23	1.50	2.76	<b>1.32</b>
mPW1PW91	-0.74	0.89	3.17	3.72	1.09	2.62	<b>1.33</b>
TPSS	0.62	1.03	1.80	3.11	0.51	2.31	1.35
MPW1KCIS	-0.25	0.69	5.04	5.46	-2.59	2.76	1.35
PBE1KCIS	-0.05	0.79	4.77	5.08	-1.84	2.39	1.36
TPSSh	-0.13	0.98	1.96	3.17	1.40	2.81	1.37
MPWB1K	-0.85	0.98	0.51	<b>2.05</b>	3.99	4.11	1.39
TPSSKCIS	0.90	1.12	0.72	2.78	0.64	<b>2.21</b>	1.39
B3LYP	-0.70	0.92	3.58	4.72	-1.51	2.29	1.42
BB1K	-1.33	1.35	0.13	<b>2.09</b>	4.28	4.36	1.71
PWB6K	-1.42	1.44	1.57	2.28	3.23	3.59	1.73

X3LYP	-1.28	1.43	2.58	4.73	-0.41	3.04	1.90
MP2	-1.12	2.05	-3.57	3.57	2.92	2.99	2.29
MPW1K	-2.34	2.35	3.41	3.53	2.79	3.71	2.60
MPWKCIS1K	-2.65	2.68	5.32	5.32	0.05	2.61	2.93
PBE	2.79	3.03	2.11	3.58	-1.20	2.22	3.01
BLYP	-2.27	7.07	-0.41	4.87	-0.11	2.63	6.43
SPWL	16.88	16.88	4.34	5.18	-5.77	5.80	14.69

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<sup>a</sup> 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:  $TMUE = [MUEPB \times 109 + MUE(IP) \times 13 + MUE(AE) \times 13] / 135$ .

<sup>b</sup> QCISD/MG3 geometries and the MG3S basis set are used for calculations in this table.

Table 5: Mean Errors for HTBH38 and NHTBH38 Database <sup>a b c</sup>

Methods	Heavy Atom Transfer (12)		NS <sup>d</sup> (16)		Uni. and Ass. <sup>e</sup> (10)		Hydrogen Transfer (38)		MMUE	AMUE
	MSE	MUE	MSE	MUE	MSE	MUE	MSE	MUE		
BB1K	-0.69	<b>1.58</b>	1.23	1.30	0.53	<b>1.44</b>	-0.57	<b>1.16</b>	<b>1.37</b>	<b>1.50</b>
PWB6K	-0.24	<b>1.61</b>	0.94	<b>1.10</b>	0.65	<b>1.53</b>	-0.50	<b>1.28</b>	<b>1.38</b>	<b>1.59</b>
MPWB1K	-0.77	<b>1.69</b>	1.08	<b>1.19</b>	0.52	1.61	-0.85	<b>1.29</b>	<b>1.45</b>	<b>1.60</b>
B1B95	-4.73	4.73	-0.95	<b>1.08</b>	-0.58	<b>1.21</b>	-2.80	2.80	2.45	<b>1.78</b>
MPW1K	-0.83	<b>1.89</b>	1.12	1.28	0.96	2.42	-0.60	<b>1.32</b>	<b>1.73</b>	<b>1.82</b>
MPW1B95	-4.62	4.62	-0.81	1.21	-0.52	<b>1.31</b>	-3.02	3.02	2.54	<b>1.92</b>
MPWKCIS1K	-0.77	<b>1.97</b>	0.92	<b>1.17</b>	0.91	2.05	0.14	<b>1.71</b>	<b>1.73</b>	<b>1.94</b>
B97-2	-3.13	3.52	-1.43	1.47	0.62	1.91	-3.09	3.24	2.54	<b>1.96</b>
PW6B95	-5.36	5.36	-2.05	2.05	-0.76	<b>1.43</b>	-3.14	3.14	2.99	<b>2.04</b>
B98	-5.18	5.18	-2.96	2.96	-0.31	1.97	-4.16	4.16	3.57	<b>2.41</b>
mPW1PW91	-5.99	5.99	-1.81	1.94	-0.38	2.00	-3.54	3.55	3.37	2.44
PBE1KCIS	-7.07	7.07	-2.41	2.41	-0.78	1.91	-3.68	3.72	3.78	2.62
B97-1	-5.18	5.18	-3.21	3.21	-0.23	1.83	-4.40	4.40	3.65	2.63
PBE1PBE	-6.62	6.62	-1.87	2.05	-0.58	2.16	-4.22	4.22	3.76	2.75
B3LYP	-8.49	8.49	-3.25	3.25	-1.42	2.02	-4.13	4.23	4.50	3.08
MPW1KCIS	-8.64	8.64	-3.55	3.55	-1.21	1.96	-4.39	4.41	4.64	3.16
X3LYP	-8.48	8.48	-2.89	2.90	-1.43	2.06	-3.98	4.09	4.38	3.29
MPW3LYP	-9.29	9.29	-4.29	4.29	-1.61	2.21	-4.66	4.71	5.13	3.38
TPSS1KCIS	-9.26	9.26	-4.88	4.88	-1.39	2.12	-4.69	4.69	5.24	3.52
MP2	11.76	11.76	0.74	<b>0.74</b>	4.71	5.44	3.69	4.14	5.52	3.99
TPSSh	-11.51	11.51	-5.78	5.78	-2.94	3.23	-5.97	5.97	6.62	4.54

TPSSKCIS	-13.37	13.37	-7.64	7.64	-2.56	2.98	-7.01	7.01	7.75	5.00
BLYP	-14.66	14.66	-8.40	8.40	-3.38	3.51	-7.52	7.52	8.52	5.53
TPSS	-14.65	14.65	-7.75	7.75	-3.84	4.04	-7.71	7.71	8.54	5.68
PBE	-14.93	14.93	-6.97	6.97	-2.94	3.35	-9.32	9.32	8.64	5.89
SPWL	-23.48	23.48	-8.50	8.50	-5.17	5.90	-17.72	17.72	13.90	10.17

<sup>a</sup> MUE denotes mean unsigned error (kcal/mol). MSE denotes mean signed error (kcal/mol). MMUE in this table is calculated by averaging the numbers in column 2, 4, 6, and 8.

<sup>b</sup> AMUE is defined in as:  $AMUE = [MUE(\Delta E, 38) + MMUE]/2$ , where  $MUE(\Delta E, 38)$  is the mean unsigned error for the energy of reactions for the 38 reactions involved in this table. AMUE is a measure of the quality of a method for kinetics.

<sup>c</sup> The QCISD/MG3 geometries and MG3S basis set are used for calculations in this table.

<sup>d</sup> NS denote nucleophilic substitution reactions.

<sup>e</sup> This denote unimolecular and association reactions.

Table 6: Mean Errors for Nonbonded Databases (kcal/mol)<sup>a b c</sup>

Method	HB6/04			CT7/04			DI6/04			WI7/05			PPS5/05			MMMUE
	MUE		MMUE	MUE		MMUE	MUE		MMUE	MUE		MMUE	MUE		MMUE	
	no-cp	cp		no-cp	cp		no-cp	cp		no-cp	cp		no-cp	cp		
PWB6K	0.44	0.34	<b>0.39</b>	0.25	0.16	<b>0.21</b>	0.24	0.32	<b>0.28</b>	0.15	0.07	<b>0.11</b>	0.79	1.00	<b>0.90</b>	<b>0.38</b>
MP2	0.26	0.93	0.60	0.73	0.26	<b>0.49</b>	0.45	0.25	<b>0.35</b>	0.07	0.18	<b>0.13</b>	1.26	0.50	<b>0.88</b>	<b>0.49</b>
MPWB1K	0.41	0.70	0.56	0.24	0.45	<b>0.34</b>	0.50	0.65	0.57	0.08	0.16	<b>0.12</b>	1.32	1.57	<b>1.45</b>	<b>0.61</b>
PW6B95	0.53	0.78	0.65	0.69	0.47	0.58	0.40	0.49	0.45	0.11	0.09	<b>0.10</b>	1.21	1.44	<b>1.32</b>	<b>0.62</b>
MPW1B95	0.50	0.86	0.68	0.47	0.31	<b>0.39</b>	0.50	0.63	0.56	0.10	0.16	<b>0.13</b>	1.46	1.70	1.58	<b>0.67</b>
B97-1	0.45	0.45	<b>0.45</b>	1.17	0.89	1.03	0.28	0.30	<b>0.29</b>	0.10	0.11	<b>0.10</b>	1.57	1.78	1.68	<b>0.71</b>
PBE1PBE	0.40	0.28	<b>0.34</b>	1.04	0.75	0.90	0.35	0.38	0.37	0.12	0.18	0.15	1.84	2.09	1.96	<b>0.74</b>
PBE1KCIS	0.49	0.59	0.54	0.89	0.63	0.76	0.32	0.38	<b>0.35</b>	0.12	0.14	0.13	1.92	2.13	2.02	<b>0.76</b>
B98	0.45	0.66	0.55	0.91	0.66	0.79	0.34	0.40	0.37	0.12	0.16	0.14	1.91	2.13	2.02	<b>0.78</b>
MPW1K	0.33	0.61	0.47	0.44	0.66	<b>0.55</b>	0.52	0.67	0.60	0.20	0.29	0.25	2.25	2.53	2.39	<b>0.85</b>
MPW3LYP	0.51	0.41	<b>0.46</b>	1.39	1.06	1.22	0.31	0.36	<b>0.34</b>	0.19	0.16	0.18	2.11	2.34	2.22	0.88
X3LYP	0.45	0.48	0.47	0.96	0.68	0.82	0.45	0.59	0.52	0.16	0.22	0.19	2.49	2.71	2.60	0.92
mPW1PW91	0.39	0.79	0.59	0.65	0.51	0.58	0.53	0.63	0.58	0.58	0.30	0.44	2.43	2.71	2.57	0.95
TPSS1KCIS	0.49	0.86	0.67	1.22	0.95	1.08	0.46	0.55	0.50	0.17	0.21	0.19	2.39	2.62	2.50	0.99
MPWKCIS1K	0.59	1.00	0.80	0.52	0.85	0.69	0.75	0.90	0.83	0.18	0.25	0.22	2.56	2.80	2.68	1.04
TPSSh	0.41	0.80	0.60	1.44	1.16	1.30	0.49	0.58	0.54	0.18	0.26	0.22	2.46	2.72	2.59	1.05
MPW1KCIS	0.87	1.28	1.07	0.85	0.68	0.77	0.66	0.82	0.74	0.20	0.27	0.24	2.65	2.88	2.76	1.12
B3LYP	0.60	0.93	0.76	0.71	0.54	0.63	0.78	0.94	0.86	0.31	0.39	0.35	2.95	3.17	3.06	1.13
BB1K	0.99	1.37	1.18	0.68	1.00	0.84	1.02	1.16	1.09	0.34	0.44	0.39	2.03	2.27	2.15	1.13
PBE	0.45	0.32	<b>0.39</b>	2.95	2.63	2.79	0.46	0.40	0.43	0.13	0.15	0.14	1.86	2.09	1.97	1.14

TPSSKCIS	0.55	0.89	0.72	2.17	1.84	2.01	0.49	0.52	0.50	0.18	0.22	0.20	2.48	2.70	2.59	1.20
TPSS	0.45	0.82	0.63	2.20	1.86	2.03	0.52	0.56	0.54	0.19	0.26	0.22	2.53	2.78	2.66	1.22
B97-2	1.22	1.64	1.43	0.56	0.67	0.61	0.87	1.02	0.94	0.25	0.35	0.30	2.73	2.96	2.84	1.23
B1B95	1.31	1.69	1.50	0.53	0.72	0.62	1.11	1.26	1.19	0.42	0.51	0.47	2.34	2.58	2.46	1.25
BLYP	1.18	1.56	1.37	1.67	1.42	1.54	1.00	1.18	1.09	0.45	0.53	0.49	3.58	3.79	3.69	1.63
SPWL	4.64	4.20	4.42	6.78	6.41	6.59	2.93	2.73	2.83	0.30	0.20	0.25	0.35	0.43	0.39	2.90

<sup>a</sup> MUE denotes mean unsigned error (MUE). MMUE= [MUE(cp) +MUE(no-cp)]/2, and MMMUE= [MMUE(HB) + MMUE(CT) + MMUE(DI) + MMUE(WI)+ MMUE(PPS)]/5; HB: hydrogen bonding; CT: charge transfer; DI: dipole interaction; WI: weak interaction; PPS:  $\pi$ - $\pi$  stacking

<sup>b</sup> 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

<sup>c</sup> MC-QCISD/3 geometries and the MG3S basis set are used for calculations in this table.



Table 7: Mean Signed Errors for the Nonbonded Database <sup>a</sup>

Method	HB6/04		CT7/04		DI6/04		WI7/05		PPS5/05	
	MSE		MSE		MSE		MSE		MSE	
	no-cp	cp	no-cp	cp	no-cp	cp	no-cp	cp	no-cp	cp
PWB6K	0.17	-0.23	0.23	-0.09	-0.12	-0.26	0.15	0.07	-0.77	-0.78
MP2	0.24	-0.93	0.73	-0.21	0.45	-0.08	0.04	-0.18	1.26	1.22
MPWB1K	-0.31	-0.70	-0.12	-0.45	-0.50	-0.65	-0.06	-0.16	-1.32	-1.33
PW6B95	-0.39	-0.78	0.65	0.29	-0.34	-0.49	0.06	-0.03	-1.21	-1.22
MPW1B95	-0.46	-0.86	0.36	0.04	-0.48	-0.63	-0.06	-0.16	-1.46	-1.47
B97-1	-0.04	-0.43	1.17	0.86	0.09	-0.06	-0.01	-0.09	-1.57	-1.58
PBE1PBE	0.19	-0.23	1.04	0.71	0.03	-0.13	-0.09	-0.18	-1.84	-1.85
PBE1KCIS	-0.20	-0.59	0.87	0.56	-0.17	-0.32	-0.04	-0.12	-1.92	-1.92
B98	-0.26	-0.66	0.87	0.55	-0.17	-0.32	-0.07	-0.16	-1.91	-1.92
MPW1K	-0.17	-0.61	-0.21	-0.56	-0.51	-0.67	-0.19	-0.29	-2.25	-2.26
MPW3LYP	0.26	-0.14	1.39	1.06	-0.14	-0.30	0.05	-0.03	-2.11	-2.12
X3LYP	-0.05	-0.44	0.96	0.65	-0.43	-0.59	-0.14	-0.22	-2.49	-2.50
mPW1PW91	-0.36	-0.79	0.53	0.18	-0.46	-0.63	0.18	-0.30	-2.43	-2.44
TPSS1KCIS	-0.43	-0.86	1.18	0.85	-0.37	-0.53	-0.11	-0.21	-2.39	-2.40
MPWKCIS1K	-0.59	-1.00	-0.52	-0.85	-0.75	-0.90	-0.15	-0.25	-2.56	-2.57
TPSSh	-0.36	-0.80	1.43	1.09	-0.38	-0.54	-0.16	-0.26	-2.46	-2.47
MPW1KCIS	-0.87	-1.28	0.70	0.37	-0.66	-0.82	-0.17	-0.26	-2.65	-2.65
B3LYP	-0.55	-0.93	0.61	0.30	-0.78	-0.94	-0.31	-0.39	-2.95	-2.96
BB1K	-0.99	-1.37	-0.68	-1.00	-1.02	-1.16	-0.34	-0.44	-2.03	-2.04
PBE	0.22	-0.19	2.95	2.63	0.38	0.20	-0.04	-0.12	-1.86	-1.86
TPSSKCIS	-0.46	-0.89	2.17	1.84	-0.26	-0.43	-0.10	-0.20	-2.48	-2.49
TPSS	-0.37	-0.82	2.20	1.86	-0.29	-0.46	-0.15	-0.25	-2.53	-2.54
B97-2	-1.22	-1.64	-0.10	-0.43	-0.87	-1.02	-0.25	-0.35	-2.73	-2.73
B1B95	-1.31	-1.69	-0.27	-0.59	-1.11	-1.26	-0.42	-0.51	-2.34	-2.35
BLYP	-1.18	-1.56	1.63	1.32	-1.00	-1.18	-0.45	-0.53	-3.58	-3.59
SPWL	3.13	2.67	5.61	5.23	2.16	1.95	0.30	0.20	0.23	0.22

<sup>a</sup> MC-QCISD/3 geometries and the MG3S basis set are used for calculations in this table.

<sup>b</sup> The order of the methods in this table is the same as that in Table 6.

<sup>c</sup> MSE denotes mean signed error (MSE).

<sup>d</sup> 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

Table 8: Overall Results <sup>a b</sup>

Method	Thermochemistry	Kinetics	Nonbonded Interaction	TCAE <sup>b</sup>	TKAE <sup>c</sup>
	TMUE	AMUE	MMMUE		
PWB6K	1.73	<b>1.59</b>	<b>0.38</b>	1.28	<b>1.18</b>
MPWB1K	1.39	<b>1.60</b>	<b>0.61</b>	1.13	<b>1.27</b>
BB1K	1.71	<b>1.50</b>	1.13	1.52	<b>1.38</b>
MPW1K	2.60	<b>1.82</b>	0.85	2.02	<b>1.49</b>
MPW1B95	<b>0.99</b>	1.92	<b>0.67</b>	<b>0.88</b>	<b>1.50</b>
PW6B95	<b>0.81</b>	2.04	<b>0.62</b>	<b>0.75</b>	<b>1.57</b>
B1B95	<b>0.96</b>	<b>1.78</b>	1.25	1.06	<b>1.60</b>
MPWKCIS1K	2.93	1.94	1.04	2.30	<b>1.64</b>
B97-2	<b>1.02</b>	1.96	1.23	1.09	<b>1.72</b>
B98	<b>1.01</b>	2.41	0.78	<b>0.93</b>	<b>1.87</b>
mPW1PW91	1.33	2.44	0.95	1.20	1.94
B97-1	1.08	2.63	0.71	<b>0.96</b>	1.99
PBE1KCIS	1.36	2.62	0.76	1.16	2.00
PBE1PBE	1.32	2.75	0.74	1.13	2.08
B3LYP	1.42	3.08	1.13	1.32	2.43
MPW1KCIS	1.35	3.16	1.12	1.27	2.48
X3LYP	1.90	3.29	0.92	1.57	2.50
MPW3LYP	1.14	3.38	0.88	1.06	2.55
TPSS1KCIS	1.06	3.52	0.99	<b>1.04</b>	2.68
MP2	2.29	3.99	<b>0.49</b>	1.69	2.82
TPSSh	1.37	4.54	1.05	1.26	3.38
TPSSKCIS	1.39	5.00	1.20	1.33	3.73
TPSS	1.35	5.68	1.22	1.30	4.19
BLYP	6.43	5.53	1.63	4.83	4.23
PBE	3.01	5.89	1.14	2.38	4.31
SPWL	14.69	10.17	2.90	10.76	7.75

<sup>a</sup> TMUE for thermochemistry is from Table 4, AMUE for kinetics is from Table 5, and the MMMUE for nonbonded interaction is from Table 6.

<sup>b</sup> TCAE = (TMUE×2 + MMMUE)/3

<sup>c</sup> TKAE = (AMUE×2 + MMMUE)/3.

**Figure caption**

Figure 1 The GGA enhancement factors for the Becke88, mPW, PW91, PW6B95, PWB6K, and X exchange functionals.

Figure 2 Potential energy curves for the Ar<sub>2</sub> dimer. C<sub>6</sub> represents the curve for  $-C_6 \times R^{-6}$ , and the C<sub>6</sub> coefficient for Ar<sub>2</sub> was taken from literature.<sup>80</sup> “no-cp” denotes the calculation without the counterpoise correction for the BSSE, and “cp” denotes the calculation with the counterpoise correction. Basis set used for MP2 and PWB6K calculations is 6-311+G(2df,2p).  $D_e$  (kcal/mol): 0.19 (MP2-nocp); 0.11 (MP2-cp); 0.27 (PWB6K-nocp); 0.25 (PWB6K-cp); 0.28 (Experiments<sup>81</sup>).  $R_e$  (Å): 3.960 (MP2-nocp); 4.073 (MP2-cp); 3.877 (PWB6K-nocp); 3.881 (PWB6K-cp); 3.757 (Experiments<sup>81</sup>).

Figure 1

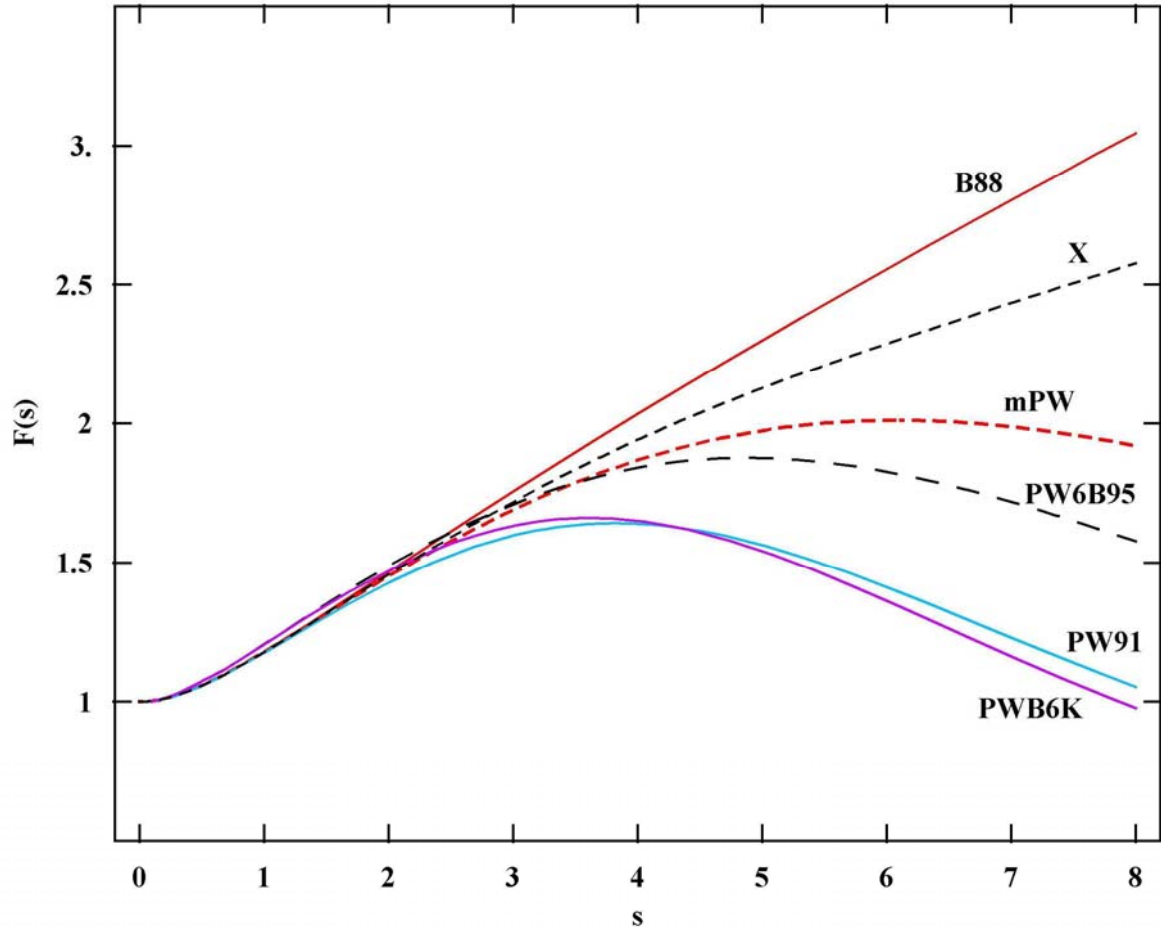


Figure 2

