Final Author version Jan. 5, 2005
Revised for *J. Chem. Theory Comput.*

Design of Density Functionals by Combining the Method of Constraint Satisfaction with Parametrization for Thermochemistry, Thermochemical Kinetics, and Noncovalent Interactions

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Abstract.

We present a new hybrid meta exchange-correlation functional, called M05-2X, for thermochemistry, thermochemical kinetics, and noncovalent interactions. We also provide a full discussion of the new M05 functional, previously presented in a short communication. The M05 functional was parametrized including both metals and nonmetals, whereas M05-2X is a high-nonlocality functional with double the amount of nonlocal exchange (2X) and it is parametrized only for nonmetals. In particular, M05 was parametrized against 35 data, and M05-2X is parametrized against 34 data. Both functionals, along with 28 other functionals, have been comparatively assessed against 234 data: the MGAE109/3 main group atomization energy database, the IP13/3 ionization potential database, the EA13/3 electron affinity database, the HTBH38/4 database of barrier height for hydrogen transfer reactions, five noncovalent databases, two databases involving metal-metal and metal-ligand bond energies, a dipole moment database, a database of four alkyl bond dissociation energies of alkanes and ethers, and three total energies of one-electron systems. We also tested the new functionals and 12 others for eight hydrogen bonding and stacking interaction energies in nucleobase pairs, and we tested M05 and M05-2X and 19 other functionals for the geometry, dipole moment, and binding energy of $HCN–BF_3$, which has recently been shown to be a very difficult case for density functional theory. We tested 8 functionals for four more alkyl bond dissociation energies, and we tested 12 functionals for several additional bond energies with varying amounts of multireference character. Based on all the results for 256 data in 18 databases in the present study, we recommend M05-2X, M05, PW6B95, PWB6K, and MPWB1K for general-purpose applications in thermochemistry, kinetics, and noncovalent interactions involving nonmetals, and we recommend M05 for studies involving both metallic and nonmetallic elements. The M05 functional, essentially uniquely among the functionals with broad applicability to chemistry, also performs well not only for main-group thermochemistry and radical reaction barrier heights but also for transition metal–transition metal interactions. The M05-2X functional has best performance for thermochemical kinetics, noncovalent interactions (especially weak interaction, hydrogen bonding, π···π stacking and interactions energies of nucleobases), and alkyl bond dissociation energies and best composite results for energetics, excluding metals.

1. Introduction

Kohn-Sham density functional theory (DFT) is now one of the most popular tools in computational and theoretical chemistry community, and much progress has been made in the last decade in the development and validation of exchange and correlation functionals.[1-67] The line of research developing functionals by requiring them to satisfy constraints has led to the PW91,[4] PBE,[12] PKZB,[23] and TPSS[41] functionals on the second and third rungs of "Jacob's ladder".[30] Although the PKZB functional proved disappointing,[23,26,44] the PBE and TPSS functionals have had some notable success in solid-state physics and some areas of chemistry.[42,44] However, as pointed out in a prescriptive paper by Perdew et al.,[61] PBE and TPSS are not suitable for kinetics (i.e., barrier heights) because both functionals seriously underestimate barrier heights; for example, they were found[55] to underestimate barrier height by an average of 8.5 kcal/mol for 76 barrier heights. The successful DFT methods for kinetics have been developed in a semiempirical way. This involves choosing a flexible functional form depending on one or more parameters, and then fitting these parameters to a set of experimental or accurate data. MPW1K,[27] BB1K,[49] BMK,[50] MPWB1K,[51] and PWB6K[58] are examples of functionals for kinetics determined by the semiempirical approach. The semiempirical approach has also been used to obtain improved functionals for main-group thermochemistry, and a sequence of closely related papers leading successively to functionals called B97,[13] B98,[16] HCTH,[19] B97-1,[19] B97-2,[32] τ-HCTH,[34] τ-HCTHh,[34] BMK,[50] and B97-3[64] provides a good example of this approach. The successive functionals, however, may be improved for one kind of prediction but worsened for another, depending on changes in the functional form, optimization strategy, and training data. A common misconception is that the choice of training data is of over-riding importance; actually the choice of functional form is more critical in that, if the functional form is inadequate, one will not be able to fit a diverse set of data even if it is used for training. Nevertheless, the choice of data is sometimes critical as well. For example, BMK[50] is a functional using the same functional form as τ-HCTHh,[34] but it was reparametrized against a data set not only for thermochemistry but also for kinetics; the functional form and training set were well enough chosen that BMK performs

equally well for kinetics and thermochemistry. However BMK's performance for noncovalent interactions is inferior to, for example, PWB6K. PWB6K[58] has been shown to be a good functional for weak interactions, and it can describe stacking interactions in small organic clusters[59] and nucleobase pairs,[60] but its performance for thermochemistry is inferior to BMK. It has proved very challenging to develop a functional which can perform well for kinetics, main-group thermochemistry, and noncovalent interactions, including those in nonpolar weakly interacting systems and charge transfer complexes.

It has been stated[42] that "sophisticated nonempirical functional should provide a uniformly accurate description of diverse systems and properties, putting to rest the 'different functionals for different tasks' philosophy." Unfortunately, if one simultaneously considers metallic chemistry and barrier heights in open-shell systems, such a functional did not exist until, in a recent communication,[65] we reported a new functional, called M05, which was designed for very general purposes. The M05 functional performs well for all three of the properties mentioned at the end of the previous paragraph and also for transition metal bond energies, ionization potentials, and electron affinities. One purpose of the present full article is to give a more complete account of this new functional. Another purpose is to present an alternative parametrization in which transition metals are not included in the training set. The new functional, to be called M05-2X, performs even better for kinetics, thermochemistry, and noncovalent interactions. Since a large number of important applications in chemistry and biochemistry do not involve transition metals, M05-2X may be very useful for such practical work. In contrast the original M05 functional should be useful for problem involving bonds between two transition metals or metal–ligand bonds where one must treat general metals and organic or inorganic ligands accurately in the same system. In addition, the M05 functional has fundamental importance in demonstrating the ability of a sufficiently flexible functional form containing kinetic energy density in both the exchange and correlation functionals and parametrized against a purposefully assembled and diverse data set to predict all the data reasonably well.

The M05 and M05-2X functionals belong to the fourth rung of Jacob's ladder (which is explained elsewhere[30,41]), and they, like the earlier B1B95,[10] τ-HCTHh,[34] TPSSh,[42] BB1K,[68] BMK,[50] MPW1B95,[51] MPWB1K,[51] PWB6K,[58] PW6B95,[58] and TPSS1KCIS functionals,[54] can be called hybrid meta-generalized gradient approximations (hybrid meta-GGAs), because they incorporate electron spin density, density gradient, kinetic energy density, and HF exchange. Spin density, density gradient, and kinetic energy density are local properties of the density, although the later two are sometimes called semilocal (in the early literature they were sometimes incorrectly called nonlocal), whereas Hartree-Fock exchange is nonlocal. Including Hartree-Fock exchange is sometimes regarded as a temporary expedient that is necessary only because the local exchange–correlation functionals are insufficiently developed, but that is a misimpression. Perdew et al.[61] pointed out that since the exact exchange energy of a fully spin-polarized one-electron system (like a hydrogen atom or H_2^+) is nonlocal, no local exchange–correlation functional can possibly be correct for this in general (of course one could force any finite number of one-electron systems to be correct, but this is not the same as getting the effect exactly correct). Thus the inclusion of Hartree-Fock exchange is a permanent feature of accurate exchange-correlation functionals, not a temporary expedient. The recent post-Hartree-Fock model[38,62,63] proposed by Becke employs 100% percent Hartree-Fock exchange. One line of argument would be that the ability to tolerate a high percentage of HF exchange and still give good results is the mark a high-quality density functional.

For the present development effort, we combined the semiempirical approach with the incorporation of constraints in the new functionals. The constraints employed are:

1) The new functionals are correct in the uniform electron gas (UEG) limit.

2) The correlation functional should be free of self-interaction.

The first condition is of fundamental importance, and any functional that violates the UEG limit cannot possibly be a universal functional. (Of course any functional gets the ionization potential of carbon wrong or the atomization energy of SiH_4 wrong also cannot be universal, but in the present article, the errors in ionization potential and atomization energies are minimized with

respect to parameter variations, whereas the UEG limit is actually constrained to be exact.) The second constraint is also important even though it does not remove the self-interaction error for the exchange part. Because we use both semiempirical parameter optimization and the method of constraint satisfaction, our approach may be considered to partake of key elements in both of the previously successful lines of functional development. Some workers make a distinction between fitting to analytic results such as fits to the artificial limit of a uniform electron gas or the analytic energy of a hydrogen atom and fitting to numerical results such as the energy of a helium atom, the ionization potential of carbon, or the hydrogen bond strength of water dimer. Our own philosophy is to use both kinds of information for functional design. Another distinction sometimes made is between using parameters for fitting data and using parameters for shaping a functional. In designing a functional for broad applicability by not only incorporating constraints but also using training data, this distinction becomes arbitrary, and we will not be concerned with it.

Section 2 presents our training sets and test sets. Section 3 gives computational details. Section 4 discusses the theory and parametrization of the new functionals. Section 5 presents results and discusses them. Because the M05 functional was already discussed briefly in a preliminary communication,[65] we will discuss the M05-2X functional first.

2. Databases

2.1. M05-2X Training Set. The training set for the M05-2X models includes the six atomization energies in the AE6 representative database presented previously,[69] the binding energies of three dimers,[56] $(H_2O)_2$, $(CH_4)_2$, and $(C_2H_4)_2$, the binding energy[56] of the $C_2H_4\cdots F_2$ charge transfer complex, the total atomic energies[70] of the H, C, O, S, and Si atoms, the ionization potentials[66] of C, O, OH, Cu, and Cr, the electron affinities[71] of C, O, and OH, the carbon-carbon bond dissociation energies[72] of the CH_3 bond with CH_3 and the isopropyl bond to CH_3, and the Kinetics9 database,[49,58] which is a database of of 3 forward barrier heights, 3 reverse barrier heights, and 3 energies of reaction for the three reactions in the BH6[69] database. We have

previously used this Kinetics9 to optimize the BB1K,[49] MPWB1K,[51] and PWB6K[58] methods. Note that we used this small data set to parametrize the new methods, but we assess the new methods with several much large data sets described below.

2.2. MGAE109/05 Test Set. The MGAE109/05 test set consists of 109 atomization energies (AEs) for main group compound. All 109 data are pure electronic energies, i.e., zero-point energies and thermal vibrational-rotational energies have been removed by methods discussed previously.[54,71,73] The 109 molecules are part of Database/3,[73] and the atomization energies of NO, CCH, C_2F_4, and singlet and triplet CH_2 have been updated[54] recently. The updated data is a subset of Database/4.[74]

2.3. Ionization Potential and Electron Affinity Test Set. The zero-point-exclusive ionization potential (IP) and electron affinity (EA) test sets are called IP13/3 and EA13/3, respectively, and they are taken from a previous paper.[71] These data for six atoms and seven molecules are part of Database/3.

2.4. HTBH38/04 Database. The HTBH38/04 database contains 38 transition state barrier heights for 19 hydrogen transfer (HT) reactions, eighteen of which involve radicals as reactant and product. They are taken from previous papers,[54,55] and they are also listed in the supporting information.

2.5. Noncovalent Interaction Databases. Recently we developed several databases in particular, HB6/04,[56] CT7/04,[56] DI6/04,[56] WI7/05,[58] and PPS5/05,[58] for various kinds of noncovalent interactions. HB6/04 is a hydrogen bond database that consists of the equilibrium 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 CT7/04 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 DI6/04 database contains the binding energies of six dipole interaction complexes: $(H_2S)_2$, $(HCl)_2$, $HCl\cdots H_2S$, $CH_3Cl\cdots HCl$, $CH_3SH\cdots HCN$, and $CH_3SH\cdots HCl$. The WI7/05 database consists of the binding energies of seven weak interaction complexes, namely HeNe, HeAr, Ne_2, NeAr, $CH_4\cdots Ne$, $C_6H_6\cdots Ne$, and $(CH_4)_2$, all of which are

bound by dispersion interactions. The PPS5/05 database consists of binding energies of five π–π stacking complexes, namely $(C_2H_2)_2$, $(C_2H_4)_2$, sandwich $(C_6H_6)_2$, T-shaped $(C_6H_6)_2$, and parallel-displaced $(C_6H_6)_2$.

2.6. Transition Metal–Transition-Metal and Metal–Ligand Databases. We employ two databases involving metals. One[57] is for atomization energies of transition metal–transition metal dimers, and it is called the TMAE4/05 database; it contains the bond energies of Cr_2, Cu_2, V_2, and Zr_2. The other,[66] called MLBE4/05, is for the metal–ligand bond energies in organometallic and inorganometallic complexes, and it contains the Cr–C, Ni–C, Fe–C, and V–S bond energies of $CrCH_3^+$, $NiCH_2^+$, $Fe(CO)_5$, and VS. These databases are reprentative subset of the larger and more diverse TMAE9/05[57] and MLBE21/05[66] databases. In the present paper we also use these databases to illustrate the performance of the M05 and M05-2X functionals for the energies of bonds involving metal atoms.

2.7. Alkyl Bond Dissociation Energy (ABDE) Database. This database contains four R-X bond dissociation energies D_e (R = Me and ; X = CH_3 and OCH_3). This is called the ABDE4/05 database. The reference D_0 are taken from a recent paper by Izgorodina et al,[72] and we used the B3LYP/6-31G(d) zero-point vibrational energies scaled with a scale factor of 0.9806[75] to obtain D_e.

2.8. Dipole Moment Database. This database consists the fixed-geometry dipole moments for six molecules, namely N6, H_2CO, CuH, BF, LiCl, and H_2O, where N6 is α-amino,ω-nitro dodecahexaene, which has the formula $H_2N(CH{=}CH)_6NO_2$. This database is called the DM6/05 database. We use the MP2/6-31G geometry[76] for the N6 molecule, and the reference dipole moment is computed at the MP2/ 6-311+G(2df,2p) level of theory since previous work[77] showed good agreement between the MP2 and CCSD(T) level of theory for a smaller basis set. For the CuH molecule, we use the geometry from the modified coupled pair functional (MCPF) calculations of Langhoff and Bauschlicher.[78] The reference dipole moment for CuH is an average of the values (2.95 D and 2.98 D, respectively) obtained by their MCPF calculation[78] and our own[65] CCSD(T)/ANO calculation, where ANO denotes the triple zeta atomic natural orbital basis

set of Widmark et al.[79,80] The geometries and accurate dipole moments for H_2CO, BF, LiCl, and H_2O are calculated at the CCSD(T)/aug-cc-pVTZ level of theory.

2.9. IPEA8 Database. The IPEA8 database contains the ionization potentials of C, O, OH, Cr, and Cu and the electron affinities of C, O, and OH.

2.10. AAE5 and AAE4 Databases. The AAE5 database consists of the total atomic energies[70] of H, C, O, S, and Si, and the AAE4 database is the same as AAE5 except that it excludes the atomic energy of H.

3. Computational methods

3.1. Geometries, Basis Sets, and Spin-Orbit Energy. All calculations for the AE6, MGAE109/05, IP13/3, EA13/3, and HTBH38/04 databases are single-point calculations at QCISD/MG3 geometries, where QCISD is quadratic configuration interaction with single and double excitations,[81] and MG3 is the modified[82,83] G3Large[84] basis set. The MG3 basis set,[82] also called G3LargeMP2,[83] is the same as 6-311++G(3d2f, 2df, 2p)[85,86] for H-Si, but improved[84] for P-Ar.

Geometries for all molecules in the HB6/04, CT7/04, DI6/04, and WI7/05 noncovalent databases and the $(C_2H_4)_2$ and $(C_2H_2)_2$ dimers in the PPS5/05 database are optimized at the MC-QCISD/3 level, where MC-QCISD is the multi-coefficient QCISD method.[73,87] The geometries for the benzene dimers in the PPS5/05 database are taken from Sinnokrot and Sherrill.[88]

Geometries for all molecules in the ABDE4/05 database are optimized at the B3LYP/6-31G(d) level, and they are taken from the supporting information of a previous paper.[72] The 6-311+G(3df,2p) basis set is used for the calculations of ABDEs for the purpose of comparison with the previous results.

Geometries for the molecules in the transition metal–metal (TMAE4/05) and metal–ligand (MLBE4/05) databases are optimized consistently with each level of theory. We used the double-zeta-quality DZQ basis set[57] for the calculations on the molecules in these two databases. The DZQ basis set uses the relativistic effective core potential method of Stevens et al.[89] for both the

3d and 4d transition metals, and it uses the 6-31+G(d,p) basis set for main group atoms. In these cases (i.e., for the metal-compound calculations) the *d* functions are spherical harmonic 5D sets. Although one require triple-zeta quality or better basis sets for quantitative results on transition metals, DZQ is good enough for a broad survey of many functionals to ascertain which ones gives relatively good results for bonds involving metal atoms.

Geometries for the stacked and hydrogen bonded nucleobase pairs are optimized at the PWB6K/6-31+G(d,p) level. All DFT calculation for the base pairs use the 6-31+G(d,p) basis set.

To test the functionals for the one–electron systems, we employed the cc-pVQZ basis set for the hydrogen atom, H_2^+ (r_e = 1.4 bohr), and H_2^+ (r_e = 2.0 bohr). For the DM6/05 dipole moment database, we used the TZQ basis set which is described in our previous paper.[57,66] For the MGAE109, HTBH38/04, IP13/3, EA13/3, and all five noncovalent databases, we used the MG3S basis sets for single-point energy calculations. The MG3S basis[71] is the same as MG3 except it omits diffuse functions on hydrogens.

Note that all basis sets mentioned above use pure *d* and/or *f* functions except the 6-31+G(d,p) basis set employed in the calculations for nucleobase pairs, which uses Cartesian basis function.

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.[57,66,82]

3.2. Counterpoise Correction. For noncovalent complexes, we perform calculations with and without the counterpoise corrections[90,91] for basis set superposition error (BSSE).

3.3. Software. All calculations were performed with a locally modified version of the GAUSSIAN03 program[92] except that the benchmark CCSD(T) calculation of the dipole moment for CuH were calculated with MOLPRO.[93]

4. Theory and Parametrization

4.1. Meta-GGA Exchange Functional. The functional form adopted for the meta-GGA exchange functional is

$$E_{\mathrm{X}}^{(0)} = \sum_{\sigma} \int d\mathrm{r}\, F_{\mathrm{X}\sigma}^{\mathrm{PBE}}\left(\rho_\sigma, \nabla\rho_\sigma\right) f(w_\sigma) \qquad (1)$$

where $F_{\mathrm{X}\sigma}^{\mathrm{PBE}}\left(\rho_\sigma, \nabla\rho_\sigma\right)$ is the exchange energy density of the PBE[11] exchange model (which has the same functional form as the earlier exchange functional of Becke,[1] but with different values for the two parameters) and $f(w_\sigma)$ is the kinetic-energy-density enhancement factor

$$f(w_\sigma) = \sum_{i=0}^{m} a_i w_\sigma^i \qquad (2)$$

where the variable w_σ is a function of t_σ, and t_σ is a function of the kinetic energy density τ_σ of electrons with spin σ.

$$w_\sigma = (t_\sigma - 1)/(t_\sigma + 1) \qquad (3)$$

$$t_\sigma = \tau_\sigma^{\mathrm{LSDA}} / \tau_\sigma \qquad (4)$$

$$\tau_\sigma = \frac{1}{2} \sum_{i}^{occup} \left|\nabla\Psi_{i\sigma}\right|^2 \qquad (5)$$

where

$$\tau_\sigma^{\mathrm{LSDA}} \equiv \frac{3}{10}(6\pi^2)^{2/3}\rho_\sigma^{5/3} \qquad (6)$$

The motivation for the functional form in eqs 1-6 is explained in our previous paper,[65] and here we simply emphasize the key elements, namely that it allows us to combine the correct uniform-electron-gas (UEG) limit with reasonable behavior for large reduced density gradient and with Becke's strategy[18,25] for simulating delocalized exchange by local density functionals by using local functionals to detect delocalization and inhomogeneity.

4.2. Meta-GGA Correlation Functional. In the correlation functional, we treat the opposite-spin and parallel-spin correlation differently. We begin with Perdew and Wang's functional[5] for the correlation part of the LSDA. Then, following the analysis of Stoll et al.,[94] one can decompose the LSDA correlation energy into opposite-spin (denoted $\alpha\beta$) and parallel-spin (denoted $\sigma\sigma$,$\alpha\alpha$, and $\beta\beta$, depending on the content) correlation energy components for the uniform electron gas (UEG):

$$E_{\mathrm{C}\alpha\beta}^{\mathrm{UEG}}(\rho_\alpha, \rho_\beta) = E_{\mathrm{C}}^{\mathrm{LSDA}}(\rho_\alpha, \rho_\beta) - E_{\mathrm{C}}^{\mathrm{LSDA}}(\rho_\alpha, 0) - E_{\mathrm{C}}^{\mathrm{LSDA}}(0, \rho_\beta)$$

(7)

$$E_{C\sigma\sigma}^{UEG}(\rho_\alpha) = E_C^{LSDA}(\rho_\alpha, 0) \quad (8)$$

where $E_C^{LSDA}(\rho_\alpha, \rho_\beta)$ is the LSDA correlation energy. Recently Gori-Giorgi et al.[95] showed that the spin resolution of the uniform electron gas correlation energy by eqs 7 and 8 is not accurate for spin-unpolaried ($\rho_\alpha = \rho_\beta$) systems. More recently, Gori-Giorgi and Perdew proposed a better formula.[96]

Note that Eq. 8 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[10] used a quantity, D_σ, which is defined as:

$$D_\sigma = 2\tau_\sigma - \frac{1}{4}\frac{|\nabla\rho_\sigma|^2}{\rho_\sigma} \quad (9)$$

where τ_σ is the kinetic energy density of electrons with spin σ, defined in Eq. 10. The function D_σ can also be written as:

$$D_\sigma = 2(\tau_\sigma - \tau_\sigma^W) \quad (10)$$

where τ_σ^W is the von Weizsäcker kinetic energy density[97] given by

$$\tau_\sigma^W = \frac{1}{8}\frac{|\nabla\rho_\sigma|^2}{\rho_\sigma} \quad (11)$$

In a one-electron case, $\tau_\sigma = \tau_\sigma^W$, so D_σ vanishes in any one-electron system. Note that the uniform electron gas limit ($\nabla\rho_\sigma \to 0$) of D_σ is:

$$D_\sigma^{UEG} = \frac{3}{5}(6\pi^2)^{2/3}\rho_\sigma^{5/3} \quad (12)$$

Becke used $D_\sigma / D_\sigma^{\mathrm{UEG}}$ as a self-interaction correction factor to the parallel–spin case for the B95 correlation functional.[10] We have pointed out previously[56] that the function D_σ^{UEG} in the denominator causes some SCF convergence problems that can be eliminated by using a different cutoff criterion. The D_σ^{UEG} in the denominator also cause some integration grid problem as pointed by Johnson and co-workers.[53] To avoid these numerical problems, we used a different self-interaction correction factor, $D_\sigma/2\tau_\sigma$ (also proposed by Becke[18]), which gives the right UEG limit but does not have the above mentioned numerical instability.

The opposite-spins correlation energy of our new functional is expressed as:

$$E_{\mathrm{C}}^{\alpha\beta} = \int e_{\alpha\beta}^{\mathrm{UEG}} g_{\alpha\beta}(x_\alpha, x_\beta) dr \tag{13}$$

where $g_{\alpha\beta}(x_\alpha, x_\beta)$ is defined as:

$$g_{\alpha\beta}(x_\alpha, x_\beta) = \sum_{i=0}^{n} c_{\mathrm{C}\alpha\beta,i} \left(\frac{\gamma_{\mathrm{C}\alpha\beta}(x_\alpha^2 + x_\beta^2)}{1 + \gamma_{\mathrm{C}\alpha\beta}(x_\alpha^2 + x_\beta^2)} \right)^i \tag{14a}$$

where

$$x_\sigma = \frac{|\nabla \rho_\sigma|}{\rho_\sigma^{4/3}} \qquad \sigma = \alpha,\ \beta \tag{14b}$$

For parallel spins,

$$E_{\mathrm{C}}^{\sigma\sigma} = \int e_{\sigma\sigma}^{\mathrm{UEG}} g_{\sigma\sigma}(x_\sigma) \frac{D_\sigma}{2\tau_\sigma} dr \tag{15}$$

where $D_\sigma/2\tau_\sigma$ is the self-interaction correction factor, and

$$g_{\sigma\sigma}(x_\sigma) = \sum_{i=0}^{n} c_{\mathrm{C}\sigma\sigma,i} \left(\frac{\gamma_{\mathrm{C}\sigma\sigma} x_\alpha^2}{1 + \gamma_{\mathrm{C}\sigma\sigma} x_\alpha^2} \right)^i \tag{16}$$

Note that $e_{\alpha\beta}^{\mathrm{UEG}}$ and $e_{\sigma\sigma}^{\mathrm{UEG}}$ in Eq. 13 and Eq. 15 are the UEG correlation energy density for the anti-parallel-spin and parallel spin cases, and they can be extracted from the total UEG correlation energy density in the same way as shown in eqs 7 and 8. The total correlation energy of the new correlation functional is given by

$$E_{\mathrm{C}} = E_{\mathrm{C}}^{\alpha\beta} + E_{\mathrm{C}}^{\alpha\alpha} + E_{\mathrm{C}}^{\beta\beta} \tag{17}$$

Note that our new correlation functional is similar to the correlation functional in the BMK[50] method; the difference is that BMK does not have the self-interaction correction factor $D_\sigma/2\tau_\sigma$ for the parallel spin case.

We require $c_{\mathrm{C}\alpha\beta,0} = c_{\mathrm{C}\sigma\sigma,0} = 1$ in eqs 14a and 16. In agreement with the philosophy of the B95 functional,[10] this forces the correlation functionals to have the correct UEG limit, which is not enforced in a considerable body of work[16,19,34,50] using similar correlation functionals. One can easily confirm that our new correlation functional gives the right UEG limit (with $x_\sigma \to 0$, $D_\sigma \to 2\tau_\sigma \to D_\sigma^{\mathrm{UEG}}$)

Following Becke,[18] we pre-optimized the γ parameters to the correlation energies of He and Ne in a preliminary fit. The values of these two non-linear parameters in the new functionals are:

$$\gamma_{\mathrm{C}\alpha\beta} = 0.0031\,, \qquad \gamma_{\mathrm{C}\sigma\sigma} = 0.06 \tag{18}$$

4.3. Hybrid Meta Functional. The hybrid exchange-correlation energy can be written as follows:

$$E_{\mathrm{XC}}^{\mathrm{hyb}} = \frac{X}{100} E_{\mathrm{X}}^{\mathrm{HF}} + (1 - \frac{X}{100}) E_{\mathrm{X}}^{\mathrm{DFT}} + E_{\mathrm{C}}^{\mathrm{DFT}} \tag{19}$$

where $E_{\mathrm{X}}^{\mathrm{HF}}$ is the nonlocal Hartree-Fock exchange energy, X is the percentage of Hartree-Fock exchange in the hybrid functional, $E_{\mathrm{X}}^{\mathrm{DFT}}$ is the local DFT exchange energy, and $E_{\mathrm{C}}^{\mathrm{DFT}}$ is the local DFT correlation energy. Equation 19 can be re-written as

$$E_{\mathrm{XC}}^{\mathrm{hyb}} = E_{\mathrm{X}}^{\mathrm{HF}} + (1 - \frac{X}{100})(E_{\mathrm{X}}^{\mathrm{DFT}} - E_{\mathrm{X}}^{\mathrm{HF}}) + E_{\mathrm{C}}^{\mathrm{DFT}} \tag{20}$$

From eq 20, one can see that the total correlation energy for a DFT calculation is modeled as the sum of the dynamic correlation energy given by E_C^{DFT} and the nondynamical correlation energy[29] contained in $(1-\frac{X}{100})(E_X^{DFT}-E_X^{HF})$.

We optimize X along with the parameters in the new meta exchange and correlation functionals; the optimization procedure is given in the next section.

4.4. Optimization of the New Hybrid Meta-GGA. All parameter optimizations were carried out with a genetic algorithm.[98] The parameters a_i in eq 2 are determined by fitting to the data in the training set with a constraint that $a_0 = 1$, which enforces the UEG limit. This limit corresponds to $t_\sigma = 1$, $w_\sigma = 0$, and $x_\sigma = 0$, and $f(w_\sigma)$ should tend to unity in this limit because the PBE exchange functional satisfies the UEG limit. Therefore we constrained a_0 to unity to enforce this limit. Simultaneously we optimized the $c_{C\alpha\beta,i}$ and $c_{C\sigma\sigma,i}$ parameters in eqs 14a and 16 to the data in the training set.

The M05 and M05-2X functionals were optimized using different training sets. In both new methods, we optimize the a_i parameters in the exchange functional, the $c_{C\alpha\beta,i}$ and $c_{C\sigma\sigma,i}$ parameters in the correlation functional, and the percentage, X, of Hartree-Fock exchange. We minimize the training function with respect to these parameters in a self-consistent way by solving the Fock-Kohn-Sham equation using the basis set and geometries described in section 3.1.

We optimized the parameters in M05-2X against the data in the training set to minimize the following training function

$$F = \text{RMSEPB(AE6)} + \text{RMSE(IPEA8)} + \text{RMSE(Kinetics9)} + 10\times\text{RMSE(NB4)} + \text{RMSE(ABDE2)} + 0.2\times\text{RMSE(AAE4)} + 2\times\text{UE(AEH)} \quad (21)$$

where RMSEPB is the root-mean-sqared error (RMSE) per bond. In particular, RMSEPB is obtained by dividing the RMSE for the AE6 database by the average number of bonds per molecule in this database. The second term is the RMSE for the IPEA8 database which is defined in Section 2. The third term is the RMSE for the Kinetics9 database. RMSE(NCCE4) is the RMSE for four noncovalent complexation energies, namely the equilibrium binding energies of

$(H_2O)_2$, $(CH_4)_2$, and $(C_2H_4)_2$ dimers and that of the $C_2H_4\cdots F_2$ charge transfer complex, RMSE(ABDE2) is the root-mean square error in the bond dissociation energies of CH_3–CH_3 and isopropyl–CH_3, RMSE(AAE4) is the RMSE for the total atomic energies of C, O, S, and Si, and UE(AEH) is the unsigned error in the atomic energy of hydrogen atom. Our preliminary fitting showed that, for the training function F, unphysical parameters are produced when $m > 11$ or $n > 4$, so we used $m = 11$ in eq 2, and we used $n = 4$ in eqs 14a and 16. Thus we optimized 20 parameters (11 in a_i, 4 in $c_{C\alpha\beta,i}$, 4 in $c_{C\sigma\sigma,i}$ and X) for the M05-2X method.

All optimized parameters for M05-2X are listed in Table 2 along with the parameters for the M05 functional. In the optimization of the M05 functional,[65] the RMSE(ABDE2) is replaced by the RMSE for the bond dissociation energies of Cr_2 and V_2 and the Cr–C bond of $CrCH_3^+$, and the weight we used for the error for the atomic energy of hydrogen is 0.2 instead of 2.

In the original work on the M05 functional, we found that we could obtain very similar results (the mean unsigned error for nonmetals was about 1% smaller and that for metals was about 13% larger) by employing the same strategy with the PBE exchange functional replaced by mPW[15] one. Thus the treatment of kinetic energy density and correlation energy, along with the consistency between the exchange and correlation functionals, are the key ingredients in the M05 functionals, not the precise form of $F_{x\sigma}$.

The optimized functions of eq 2 for the final M05 and M05-2X functionals are shown in Fig. 1.

A useful way to visualize the meta-GGA non-locality is to write the meta-GGA exchange-correlation energy as

$$E_{XC}[\rho_\alpha,\rho_\beta] = \int d^3r \rho \varepsilon_X^{UEG}(\rho) F_{XC}(\rho_\alpha,\rho_\beta,\nabla\rho_\alpha,\nabla\rho_\beta,\tau_\alpha,\tau_\beta) \quad (22)$$

where $\rho = \rho_\alpha + \rho_\beta$ is the total density and $\varepsilon_X^{UEG} = -(3/4\pi)(3\pi^2\rho)$ is the exchange energy per electron of a spin-unpolarized ($\rho_\alpha = \rho_\beta$) uniform electron gas; the enhancement factor F_{XC} shows the effects of correlation and inhomogeneity.[45] In order to visualize F_{XC} for the meta-GGA part

of the M05 and M05-2X functionals, we define three quantities, namely, s, r_s and α_τ

$$s = \frac{|\nabla\rho|}{(24\pi^2)^{1/3}\rho^{4/3}} \tag{23}$$

$$r_s = \left(\frac{3}{4\pi\rho}\right)^{1/3} \tag{24}$$

$$\alpha_\tau = \frac{\tau_\sigma - \tau_\sigma^W}{\tau_\sigma^{LSDA}} \tag{25}$$

By using eqs 6, 11, 23, 24, and 25, we can transform the kinetic energy density into a function of s, r_s, and α_τ Figure 2, 3, 4, and 5 show the enhancement factors for the meta-GGA part of the M05 and M05-2X functionals. Figures 2, 3, 4, and 5 show that both functionals violate the scaling inequality:[99]

$$F_{\mathrm{XC}}(r_s', s) > F_{\mathrm{XC}}(r_s, s); \qquad r_s' > r_s \tag{26}$$

and they also violate the Lieb-Oxford bound[100]

$$F_{\mathrm{XC}}(r_s, s) \le 2.273 \tag{27}$$

We note, though that these figures only show the behavior of the meta-GGA part of the functional, and we do not recommend users to use the pure meta-GGA part of M05 of M05-2X method, because the parameters both functionals are optimized with the mixing of certain amount of the Hartree-Fock exchange. We are working on the optimization of a pure local meta-GGA without the Hartree-Fock exchange using the same functional form.

5. Results and Discussion

5.1. Assessment of the New Hybrid Meta Functionals. We fitted our new functionals against a small and diverse data set (6 data in AE6, 9 data in Kinetics9, 4 data for noncovalent complexation, 8 data for ionization energies and electron affinities, and 3 data for transition metal–transition metal and metal–ligand interactions), but we assess the new functionals against a much larger data set that includes 109 main-group atomization energies, 13 ionization potentials

(IP13), 13 electron affinities (EA13), 38 barrier heights (HTBH38), 19 energies of reaction, 6 hydrogen bonding energies (HB6), 7 charge transfer complexation energies (CT7), 6 complexation energies of complexes dominated by dipole interaction (DI6), 7 weak interaction energies (WI7), 5 π–π stacking interaction energies (PPS5), 4 transition metal-metal bond energies (TMAE4), 4 metal-ligand bond energies (MLBE4), 6 dipole moments, 4 alkyl bond dissociation energies (R–CH_3, and R–OCH_3), and 8 nucleobase pairs interaction energies.

We compare the results obtained by the new methods to those for 28 other functionals. Table 2 lists all 30 density functionals considered in this work. In each case we specify the year it was first published, the functional forms used for dependence on $\nabla\rho$, whether or not the functional includes τ in the exchange and correlation functional, and whether the correlation functional is self-correlation-free (SCorF). Table 2 also contains two columns (one for the exchange functional and one for the correlation functional) that tell whether or not the functional reduces to the correct uniform electron gas limit when $\nabla\rho_\sigma \to 0$ and $\tau_\sigma \to \tau_\sigma^{LSDA}$.

In most of comparisons 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 reference values, and by mean signed errors (MSEs), 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[49,101] more transferable comparison between databases with different average sizes of molecules. Because the dipole moments considered in the dipole moment database vary widely in magnitude, we also consider mean signed percentage error (MS%E) and mean unsigned percentage error (MU%E). We also use MU%E in one later table because the quantities considered in that table do not all have units of energy. 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 five smallest average errors overall (for each table) are in bold.

5.2. Thermochemistry: AE, IP, and EA Results Table 3 summarizes the errors in atomization energies (AEs), ionization potentials (IPs), and electron affinities (EAs) for all tested methods. Table 3 shows that the PW6B95, M05-2X and BMK methods give the best results for AE calculations, and they give an MUEPB less than 0.5 kcal/mol.

MPWB1K, BB1K, and MPW1B95 have the best performance for IP calculations, whereas BMK, PW6B95, and τ-HCTHh give the best performance for EA calculations.

To compare their performance for thermochemistry, we defined the TMUE (total MUE) as the mean signed error over all 135 data in this table:

$$\mathrm{TMUE} = [\mathrm{MUEPB(AE)}\times 109 + \mathrm{MUE(IP)}\times 13 + \mathrm{MUE(EA)}\times 13]/135 \quad (28)$$

If we use TMUE as a criterion of practical usefulness for thermochemistry, Table 3 shows that, M05-2X is the best functional, followed by PW6B95 and BMK.

5.3. Thermochemical Kinetics. Table 4 gives the mean errors for the HTBH38/04 database. Eighteen of the 19 reactions in this database involve radicals as reactants or products, and sixteen of those involve an odd number of electrons. Systems with an odd number of electrons and stretched bonds are well known to provide a critical test case for density functional theory. Furthermore, we have shown elsewhere[55] that functionals that perform well for hydrogen transfer barrier heights also perform well for barrier heights of more general classes of reaction, so we believe that good performance on this database is critical if a functional is to be judged as broadly applicable. Table 4 shows that BB1K gives the best results for barrier heights, with PWB6K, MPWB1K, MPW1K, BMK and M05-2X less accurate on average by 0.12-0.18 kcal/mol. M05 and the very new B97-3 are less accurate than these six functionals by 0.59-0.77 and 0.93-1.11 kcal/mol, respectively; whereas the other 22 functionals in the table are less accurate than these six by 1.46-15.56 kcal/mol. The mean unsigned error in the energies of reaction for the 19 reactions is called MUE(ΔE19) and is given in the second last column of Table 4. M05-2X gives the best performance for these energies of reaction, followed by B1B95, PW6B95, MPW1B95, BMK, and M05. Right behind these six are B98, τ-HCTHh, B3PW91, B97-2, and

mPW1PW91, with the other 19 functionals significantly less accurate. We also tabulated an average MUE (called AMUE) that is defined as:

$$\text{AMUE} = [\text{MUE}(\Delta E19) + \text{MMUE}(BH38)]/2 \qquad (29)$$

where MUE(ΔE19) is the mean unsigned error for the energy of reactions for the 19 reactions in the HTBH38 database. If we use AMUE as a criterion to judge the performance of a DFT method for thermochemical kinetics, Table 4 shows that M05-2X, BMK, BB1K, MPW1K, MPWB1K, and M05 are the best methods for kinetics. Table 4 is particularly encouraging in that M05-2X has a mean unsigned error for hydrogen transfer barrier height on the order of 1.3 kcal/mol, a level of accuracy that is significantly exceeded only by the BB1K density functional, which is much less broadly applicable and by large-basis CCSD(T) or some equally expensive wave function theory. Furthermore, both M05-2X and M05 are in the top seven for each of these three mean unsigned error column in Table 4. The only other functional that appears in the top-seven list for all three of these columns is BMK.

5.4. Noncovalent Interactions. The mean errors for noncovalent interaction are listed in Table 5. In Table 5, 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. In Table 5, we also defined a mean MUE:

$$\text{MMUE} = [\text{MUE(no-cp)} + \text{MUE(cp)}]/2 \qquad (30)$$

This is a reasonable error criterion because the cp correction is sometimes an overestimate of BSSE, and because in practical work some calculations are carried out with cp corrections and some without.

Table 5 shows that PBE1PBE, M05-2X, PWB6K, and PBE give the best performance for calculating the binding energies of the hydrogen bonding dimers in the HB6/04 database. Table 5 also shows that M05-2X, PWB6K, and M05 give very good performance for calculating the binding energies for the complexes in the CT7/04 and DI6/04 databases. M05-2X, M05, and PW6B95 give the best performance for calculating the binding energies of the weak interaction complexes in the WI7/05 database.

We note that π–π stacking interactions play a dominant role in stabilizing various biopolymers, for example, the double helix structure of DNA, and such interactions are also important for supramolecular design. Table 5 shows that the quality of M05-2X for describing π–π stacking interactions is better than PWB6K. This is encouraging because we have already shown[59,60] that PWB6K performs unusually well for the stacking interactions in the small organic clusters and nucleobase pairs.

The overall performance for noncovalent interactions can be judged by the mean MMUE, which is defined as:

$$\mathrm{MMMUE} = [\mathrm{MMUE(HB)} + \mathrm{MMUE(CT)} + \mathrm{MMUE(DI)} + \mathrm{MMUE(WI)} + \mathrm{MMUE(PPS)}]/5 \quad (31)$$

Notice that the five component in eq 31 place different requirements on a density functional. For example, high accuracy for charge transfer complexes is not well correlated with high accuracy for weak interactions. If we use MMMUE as a criterion to evaluate the overall performance of DFT methods a for noncovalent interactions, we can see from Table 5 that M05-2X, PWB6K, M05, MPWB1K, and PW6B95 are the best functionals.

5.5. Composite Results for Main Group Energetic Databases. Table 6 is a summary of the performance of the tested methods for thermochemistry, kinetics, and noncovalent interactions. The second last column of Table 6 is an average of the three mean unsigned errors. The M05-2X functional has an average error 1.4 times smaller than the second best performing method (M05), followed by BMK, MPWB1K, and PW6B95.

We also computed a weighted average where each error is divided by the average error of all 30 functionals for that quantity; this is shown in the last column. With this scaled average, the M05-2X functional performs 1.4 times better than the second best performing functional M05, followed by PW6B95, PWB6K, and MPWB1K.

5.6. Trends in Alkyl Bond Dissociation Energies. Recently Izgorodina et al. reported a study of the performance of several DFT, for the prediction of absolute and relative R-X bond dissociation energies (BDEs) where R is an alkyl group (R = Me, Et, *i*-Pr and *t*-Bu) and X is a

substituent (X = H, CH_3, OCH_3, OH and F) , and they found that all of the tested DFT methods overestimate the stabilizing effect on BDEs in going from R = Me to R = *t*-Bu, leading in some cases to incorrect qualitative behavior. Note that their results are consistent with the trends for the reaction energies in Table 3 of a earlier paper by Dybala-Defratyka et al.[102] Some earlier studies by Curtiss et al.[103] had also shown that conventional DFT methods perform much worse for the enthalpies of formation of the larger molecules, and they concluded that this is due to a cumulative effect in the error for the larger molecules.

Table 7 summarizes the results for the trends in R–X BDEs (R = Me and *i*-Pr; X = CH_3 and OCH_3). Table 7 shows that M05-2X gives surprisingly good results for these BDEs; it gives better performance than the expensive G3-RAD[104] method for the ABDE4/05 database, and it gives an MUE of only 0.6 kcal/mol, whereas BMK (the second best DFT method) gives an MUE of 1.7 kcal/mol.

Eight functionals were tested against more data of this type, and the results are in Figures 6 and 7 and supporting information; the additional tests include larger alkyl groups than those present in ABDE4/05, but they yields similar conclusions to those drawn from Table 7. Figures 6 and 7 present the trends for eight relative R–X BDEs (R = Me, Et, *i*-Pr, and *t*-Bu; X = CH_3 and OCH_3), and both figures shows that M05-2X, like other DFT methods but to a much lesser extent, tends to overestimate the BDE-lowering effect accompanying increasing size of the alkyl group. In contrast, the wavefunction based method G3-RAD slightly underestimate the stabilizing effect on R–X BDEs of going from R = Me to *t*-Bu. Since Table 7 shows smaller mean unsigned errors for M05-2X than for G3-RAD, it is no longer appropriate to consider this kind of error as a failure of DFT, although is a failure of some functionals.

The results in Table 7 and Figures 6 and 7 are encouraging because M05-2X shows small errors for the *absolute* and *relative* BDEs, and M05-2X offers promise as a reliable for larger systems.

5.7. Transition Metal–Transition Metal and Metal–Ligand Bond Energies. Metal–metal and metal-ligand bonding is very important in many application areas.[105-117] Table 8 summarizes

the results for the TMAE4/05 and MLBE4/05 databases. For the TMAE4/05 database of bond energies of transition metal dimers, BLYP, G96LYP, PBE, mPWPW91, and M05 give the best results. Note that M05-2X, PWB6K, MPWB1K, BB1K, and BMK are among the worst methods for transition metal dimers because these DFT methods contain a large amount of HF exchange, and this makes the functionals less valid for systems with significant nondynamical correlation energy; hence methods with correlation functionals that primarily account for dynamical (not static) correlation (this includes all 30 functionals tested in this article) and with more than 30% HF exchange are not recommended for studies of interactions of transition metal atoms with other transition metal atoms where nondynamical correlation plays an important role; we will come back to this point in section 5.12.

For the MLBE4/05 database of metal–ligand compounds, TPSS1KCIS, TPSSh, M05, B97-2, and PBE1PBE give the best performance. In Table 8, MMUE is the average of the MUE for the TMAE4/05 and MLBE4/05 databases, and BLYP, M05, G96LYP, TPSS, and B97-2 give the smallest MMUE. Notice that, of the 11 functionals with smallest MMUEs thatn B97-1, only M05 (X = 28) and B97-2 (X = 21) have X larger than 15; six of these functionals have X = 0, and three (TPSSh, τ-HCTHh, and TPSS1KCIS) have X in the range 10-15. The ability to obtain good results for bonds to metal atoms with an X value as large as 28 is one of the characteristics that allows M05 to have a broader range of applicability than any other functional.

5.8. Tests for Dipole Moments. Table 9 presents the performance for the DM6/05 database of dipole moments. $NH_2(CH{=}CH)_6NO_2$ (denoted as N6) is a push-pull π-conjugated systems, and accurate evaluation of electric dipole properties for this type of molecule is a difficult problem for density-functional theory.[76,77] Among the tested DFT methods, M05-2X give the best results for the dipole moment of N6, and in general the DFT methods with higher percentages of Hartree-Fock exchange perform better than the DFT methods with lower (or zero) percentages of Hartree-Fock exchange. Overall, PWB6K gives the lowest MUE, followed by M05-2X, MPWB1K, BB1K, and BMK. If we consider the mean unsigned percentage error (MU%E), MPW1B95 give the lowest MU%E, followed by PWB6K, M05, MPWB1K, and BB1K.

5.9. Tests for Noncovalent Interactions in Nucleobase Pairs. Table 10 summarizes the results for the stacking and hydrogen bonding interactions in nucleobase pairs. All structures have been detailed in a previous paper,[60] and they are also given in Supporting Information. For stacking interactions, SPWL and M05-2X give the best performance. However the good performance of SPWL for stacking interactions is not matched by good accuracy for hydrogen bonding. Table 9 shows that SPWL give the largest errors for the hydrogen bonding interactions, while M05-2X give the best performance for the interaction energies of the two Watson-Crick hydrogen bonded base pairs.

The average MUE in Table 10 is defined as:

$$\text{AMUE} = \text{MUE(stacking)} + \text{MUE(hydrogen bonding)} \qquad (32)$$

M05-2X give the lowest AMUE, followed by PWB6K and MPWB1K.

5.10. Tests for One-Electron Systems. Table 11 presents the results for three one-electron systems, namely hydrogen atom, H_2^+ with a bond distance of 1.4 bohr, and H_2^+ with a bond distance of 2.0 bohr. In Table 11, PWB6K gives the lowest MUE, and followed by BB1K and BMK. All the mean errors are disconcertingly large, but it is encouraging that the better functionals have errors 1.5 to 3 times smaller than the popular B3LYP. Again the DFT methods with higher percentages of Hartree-Fock exchange generally (but not always) perform better than the DFT methods with lower (or zero) percentages of Hartree-Fock exchange.

It is interesting to note that five of the six best functionals for thermochemical kinetics (Table 4) are also among the six best density functionals in Table 11. B1B95 and MPW1B95 also rank in the top ten of both tables. However, one cannot generalize this result because there are also cases where performance in these two tables does not correlate. For example, MPW1K and B97-3 rank much higher in Table 4 than in Table 11, and X3LYP and PBE rank much higher in Table 11 than in Table 4.

5.11. Tests for a Donor-Acceptor System: HCN–BF3. Recently Philips and Cramer[118] reported a study of a boron-nitrogen complex, namely, HCN–BF3.[119,120] This is an example of a Lewis acid-base complex, also called a dative bond or a coordinate covalent bond. They

employed 12 GGA and hybrid GGA functionals as well as some wave function based methods, and their conclusion is that "all DFT methods fail to predict a binding energy that compares favorably to the MCG3//MC-QCISD result of -5.7 kcal/mol." In particular, all DFT methods tested gave bond energies in the range 1.8-4.3 kcal/mol, except MPW1K and BLYP which respectively yielded 4.7 and 7.4 kcal/mol. Table 12 shows the results for the 14 DFT methods tested in Table 10; of these 13 were not tested in Philips and Cramer's paper. Table 12 also includes the B3PW91 method, which was judged[118] overall best for structures and frequencies, MPW1K, which was best (of those functionals tested[118]) for complexation energy, and PBE, TPSS, BB95, B1B95, and BB1K, which are added for their fundamental interest and to illustrate the dependence on the fraction of Hartree-Fock exchange. Table 12 shows that the binding energies calculated by the PWB6K, MPWB1K, and M05-2X methods agree well with the best estimate (MCG3//MC-QCISD/3 calculation), and M05-2X even predicts more attraction than MCG3//MC-QCISD/3. It is encouraging that M05 is the most successful functional for this system, and that Table 12 shows that almost all of the functionals in Table 10 are better on average than B3PW91; M05 and PW6B95 are more accurate, on average, by factor of 2.9 and 2.5, respectively, as well as being more accurate than MP2. M05-2X reduces the error in B3PW91, on average, by 33%.

5.12. Multireference Character. A simple and useful way to describe the optimum domains of applicability of the M05 and M05-2X functionals is that the former is recommended for systems containing metals or transition metals (especially those in groups 2-10), and the latter is recommended for systems containing only nonmetallic or only main group elements (although M05 is also very good for such systems, as shown in Tables 6, 8, and 10). This way of classifying systems, though, does not really capture the essence of the issue at a higher level of sophistication. We believe that the essential distinction is multireference character. Systems with significant multireference character are not well described by most density functionals that have more than 5–15% of Hartree-Fock exchange. A system with large multireference character is one for which no single configuration-state function provides a good zero-order description;[121,122] such a system

is said to contain significant amounts of static, near-degeneracy, or nondynamical correlation energy, often associated with multi-center systems, but also found in atoms.[123] Having made this distinction, one might summarize the situation as follows: M05 is recommended for applications where the systems studied involve both multireference and single-reference behavior, whereas if only single-reference behavior is to be encountered one can obtain higher quantitative accuracy by switching to M05-2X. This is more satisfactory than the formulation at the start of this paragraph, but only partly more satisfactory because "multireference character" is not completely unambiguous.

One can characterize multireference character by analyzing a configuration interaction[124] or coupled cluster calculation,[125] but this is often impractical. In a recent paper,[66] we proposed a simpler criterion for the multireference character of a bond. We called this the B_1 diagnostic and defined it as:

$$B_1 = [D_e(\mathrm{BLYP}) - D_e(\mathrm{B1LYP//BLYP})]/n \qquad (33)$$

where D_e is the energy to break n bonds, and B1LYP//BLYP denotes a B1LYP calculation of the same quantity using the BLYP equilibrium geometries for the molecule and the fragments. For B1LYP, the percentage of Hartree-Fock exchange is 25. The B_1 diagnostic measures multireference character because the Hartree-Fock exchange approximation fails badly for multireference systems, whereas GGAs can usually handle these systems almost as well as they handle single-reference systems. We previously concluded that bonds with $B_1 \lesssim 10$ kcal/mol are reasonably classified as single-reference cases whereas those with $B_1 \gtrsim 10$ kcal/mol should be classified as multireference. This criterion is clearly not sophisticated enough to supplant system-specific discussions of metallic and multireference character,[78,122,123,126-135] and it does not fully supersede characterizing bonds in chemical terms,[66] but its ease of use is appealing.

In Tables 13 and 14, we present results for 8 systems, four of which have B_1 less than 10 kcal/mol (single reference), and 4 of which have B_1 greater than 10 kcal/mol (multireference). Ozone (O_3) is a well studied multireference system,[124] and its B_1 is about 22 kcal/mol. The cases in Table 13 were chosen so that two of the single-reference cases involve transition metals, one

involves a main-group metal, and one has no metals. Similarly, two of the multireference cases involve metallic elements, and two involve only non-metals. Table 14 shows that the quality of the predictions depends more on multireference character than on the metallic character. For prediction of the bond energies in systems with a low B_1 value, M05 and M05-2X perform equally well, but for the systems with high B_1 value, M05-2X performs much worse than M05.

Note that eq 33 does not apply to transition states, but the reader should be aware that transition states, even those for radical reactions, are not all multireference systems, although it is a common misconception that they are. For example, a multireference plus single and double excitation calculation lowers the barrier height of the H + H_2 reactions only 0.3 kcal/mol as compared to a single-reference calculation with single and double excitations.[136] Similarly, single-reference-plus-dynamical-correlation-energy treatments give reasonable descriptions of the F-H-H and H-F-H transition states.[137] These conclusions based on wave function theory are consistent with our DFT findings that several methods fail that quite badly for multireference systems with $B_1 > 10$ kcal/mol are nevertheless quite accurate for transition states, even radical transition states. Example would be MPW1K, BB1K, and PWB6K. In this light the good performance of the M05 functional both for $B_1 > 10$ kcal/mol systems and for barrier heights is even more dramatic.

A final comment on transition-metal systems is warranted. In particular it should be noted that complexes in which a transition metal is saturated with ligands or one ligand short of saturation may have far less multireference character than highly unsaturated systems like metal-containing diatomic molecules. Thus the cases in our metallic training sets are more difficult than the kinds of transition-metal complexes that occur in many areas of organometallic chemistry and metalloenzyme chemistry.[112,113] Nevertheless there are many other important applications where the valence state, magnetic state, or oxidation state of the metal is unknown or changes during a reaction, and the results in Table 18 and the high-B_1 section of Table 14 provide an indication of the ability of various density functionals to treat this important class of problems.

5.13. Self-exchange. One of the key sources of error in density functional theory is self-exchange.[138-140] For example, self-exchange is responsible for the poor performance of time-

dependent DFT for charge transfer excited states.[141] One direction of some current research in DFT is to try to obtain correlation functionals that perform well even with 100% Hartree exchange,[38,62,63] which eliminates the self-exchange problem. The present functional does not achieve this goal, but it does perform well with 56% Hartree-Fock exchange, which is much higher than the fraction of Hartree-Fock exchange, 20-28%[7,8,10,15,16,19,22,32,47,56,58,64,65] or, in one case, 31%,[51] of previous functionals with good general-purpose performance and is even higher than the fraction of Hartree-Fock exchange, 42-46%,[27,50,51,58,68] of functionals designed especially for chemical kinetics. And yet the M05-2X functional gives better performance than any of the functionals for thermochemical kinetics and alkyl bond energies. Thus the M05-2X functional should ameliorate some of the problems caused by spurious self-exchange. Furthermore, both M05-2X and M05 are completely free of self-correlation error.

5.14. Comment on Functional Development. A lesson reinforced by the present work is that a good training set is very helpful in parametrizing density functionals, but it is not sufficient. The previous functional forms, prior to M05, did not take full advantage of kinetic energy density and its combination with constraint satisfaction, and they are unable to provide the kind of performance we achieved with M05 and M05-2X. Designing the dependence of the exchange-correlation functional on kinetic energy density was the key to the improved performance achieved here, as compared (for example) to our previous PW6B95 and PWB6K functionals. In designing the new functional form, we built on several key insights in the work of Becke,[10,18,25] but we combined them in new ways and extended them to allow greater flexibility while satisfying the uniform-electron-gas limit and self-correlation-free limits. In addition we simultaneously optimized the correlation functional, the exchange functional, and the fraction of Hartree-Fock exchange. It is well known that it is important for the exchange and correlation functionals to be well matched. This is partly because they separately have the wrong form at long range and also because exchange density functionals include not only exchange but also near-degeneracy correlation,[7,25,29,142-145] whereas the correlation functional includes only dynamical correlation. It is important to balance the inclusion of near-degeneracy correlation, which is

neceeary to treat multireference character, with Hartree-Fock exchange, which eliminates (or partially eliminates, when X <100 in eq 20) spurious self-exchange interactions.

6. Concluding Remarks

This paper presents a new hybrid meta exchange-correlation functional, M05-2X, for thermochemistry, thermochemical kinetics, and noncovalent interactions. It also presents a more complete picture of the original M05 functional that was originally defined in a preliminary communication. These two functionals incorporate kinetic energy density in a balanced way in the exchange and correlation functionals, they satisfy the uniform electron gas limit, and they are self-correlation-free. They were comparatively assessed against the MGAE109/3 main group atomization energy database, the IP13/3 ionization potential database, the EA13/3 electron affinity database, the HTBH38/4 database of barrier heights for hydrogen transfer reactions, the HB6/04 hydrogen bonding database, the CT7/04 charge transfer database, the DI6/04 dipole interaction database, the WI7/05 weak interaction database, the PPS5/05 π–π stacking database, the ABDE4/05 alkyl bond dissociation energy database, the TMAE4/05 database for transition metal dimers, the MLBE4/05 database for metal-ligand compounds, a dipole moment database DM6/05, and accurate results for nucleobase interaction energies, the absolute energies of one-electron systems, and the properties of a Lewis acid-base complex, HCN-BF_3. From these assessments and from comparison to results for 28 functionals in the literature, we draw the following conclusions, based on an analysis of mean unsigned errors:

(1) The M05-2X, M05, PW6B95, PWB6K and MPWB1K functionals give the best results for a combination of nonmetallic thermochemical kinetics thermochemistry, and noncovalent interactions.

(2) The M05-2X method gives the best performance for the calculation of absolute and relative bond dissociation energies for single-reference systems and for calculations of noncovalent interactions between nucleobases.

(3) The M05 functional gives, in addition, good performance for multireference systems, including metals.

From the present study, we recommend M05-2X, M05, PW6B95, PWB6K, and MPWB1K for general purpose applications in thermochemistry and kinetics, and we especially recommend M05-2X for calculating bond dissociation energies. For systems involving transition metal bonding and other multireference systems, we recommend the M05 functional. It is very encouraging that we succeeded in developing density functionals with very broad applicability. They should be especially useful for many applications in chemistry and for condensed-phase systems and molecular recognition problems (including supramolecular chemistry and protein assemblies) where noncovalent interactions are very important.

Acknowledgment. We are grateful to Jan Martin and Mark Iron for assistance with the BMK functional and to Benoit Champagne for supplying the N6 geometry. This work was supported in part by the U. S. Department of Energy, Office of Basic Energy Sciences and by the Office of Naval Research.

Supporting Information Available: All the databases are given in the supporting information. The geometries of the nucleobase pairs, of the DM6/05 database and of the noncovalent interactions are also given in the supporting information. This material is available free of charge via the Internet at http://pubs.acs.org.

(1) Becke, A. D. *J. Chem. Phys.* **1986**, *84*, 4524.
(2) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
(3) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(4) Perdew, J. P. In *Electronic Structure of Solids '91*; Ziesche, P., Eschig, H., Eds.; Akademie Verlag: Berlin, 1991; p. 11.
(5) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.
(6) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.
(7) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(8) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.
(9) Gill, P. M. W. *Mol. Phys.* **1996**, *89*, 433.
(10) Becke, A. D. *J. Chem. Phys.* **1996**, *104*, 1040.
(11) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett* **1996**, *77*, 3865.
(12) Perdew, J. P.; Ernzerhof, M.; Burke, K. *J. Chem. Phys.* **1996**, *105*, 9982.
(13) Becke, A. D. *J. Chem. Phys.* **1997**, *107*, 8554.
(14) Adamo, C.; Barone, V. *Chem. Phys. Lett.* **1997**, *274*, 242.
(15) Adamo, C.; Barone, V. *J. Chem. Phys.* **1998**, *108*, 664.
(16) Schmider, H. L.; Becke, A. D. *J. Chem. Phys.* **1998**, *108*, 9624.
(17) Rey, J.; Savin, A. *Int. J. Quantum Chem.* **1998**, *69*, 581.
(18) Becke, A. D. *J. Chem. Phys.* **1998**, *109*, 2092.
(19) Hamprecht, F. A.; Cohen, A. J.; Tozer, D. J.; Handy, N. C. *J. Chem. Phys.* **1998**, *109*, 6264.
(20) Handy, N. C.; Tozer, D. J. *Mol. Phys.* **1998**, *94*, 707.
(21) Krieger, J. B.; Chen, J.; Iafrate, G. J.; Savin, A. In *Electron Correlations and Materials Properties*; Gonis, A., Kioussis, N., Eds.; Plenum: New York, 1999; p. 463.
(22) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158.
(23) Perdew, J. P.; Kurth, S.; Zupan, A.; Blaha, P. *Phys. Rev. Lett* **1999**, *82*, 2544.
(24) Adamo, C.; Ernzerhof, M.; Scuseria, G. E. *J. Chem. Phys.* **2000**, *112*, 2643.
(25) Becke, A. D. *J. Chem. Phys.* **2000**, *112*, 4020.
(26) Rabuck, A. D.; Scuseria, G. E. *Theor. Chem. Acc.* **2000**, *104*, 439.
(27) Lynch, B. J.; Fast, P. L.; Harris, M.; Truhlar, D. G. *J. Phys. Chem. A* **2000**, *104*, 4811.
(28) Proynov, E.; Chermette, H.; Salahub, D. R. *J. Chem. Phys.* **2000**, *113*, 10013.
(29) Handy, N. C.; Cohen, A. J. *Mol. Phys.* **2001**, *99*, 403.
(30) Perdew, J. P.; Schmidt, K. In *Density Functional Theory and Its Applications to Materials*; Van-Doren, V., Alsenoy, C. V., Geerlings., P., Eds.; American Institute of Physics: New York, 2001; p. 1.
(31) Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2001**, *105*, 2936.
(32) Wilson, P. J.; Bradley, T. J.; Tozer, D. J. *J. Chem. Phys.* **2001**, *115*, 9233.
(33) Parthiban, S.; de Oliveira, G.; Martin, J. M. L. *J. Phys. Chem. A* **2001**, *105*, 895.
(34) Boese, A. D.; Handy, N. C. *J. Chem. Phys.* **2002**, *116*, 9559.
(35) Baker, J.; Pulay, P. *J. Chem. Phys.* **2002**, *117*, 1441.
(36) Toulouse, J.; Savin, A.; Adamo, C. *J. Chem. Phys.* **2002**, *117*, 10465.
(37) Boese, A. D.; Martin, J. M. L.; Handy, N. C. *J. Chem. Phys.* **2003**, *119*, 3005.
(38) Becke, A. D. *J. Chem. Phys.* **2003**, *119*, 2972.

(39) Boese, A. D.; Chandra, A.; Martin, J. M. L.; Marx, D. *J. Chem. Phys.* **2003**, *119*, 5965.

(40) Guner, V.; Khuong, K. S.; Leach, A. G.; Lee, P. S.; Bartberger, M. D.; Houk, K. N. *J. Phys. Chem. A* **2003**, *107*, 11445.

(41) Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. *Phys. Rev. Lett.* **2003**, *91*, 146401.

(42) Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P. *J. Chem. Phys.* **2003**, *119*, 12129.

(43) Li, Q. S.; Xu, X. D.; Zhang, S. *Chem. Phys. Lett.* **2004**, *384*, 20.

(44) Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P. *Phys. Rev. B* **2004**, *69*, 75102.

(45) Perdew, J. P.; Tao, J.; Staroverov, V. N.; Scuseria, G. E. *J. Chem. Phys.* **2004**, *120*, 6898.

(46) Zhao, Y.; Pu, J.; Lynch, B. J.; Truhlar, D. G. *Phys. Chem. Chem. Phys.* **2004**, *6*, 673.

(47) Xu, X.; Goddard, W. A. *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 2673.

(48) Coote, M. L. *J. Phys. Chem.* **2004**, *108*, 3865.

(49) Zhao, Y.; Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2004**, *108*, 2715.

(50) Boese, A. D.; Martin, J. M. L. *J. Chem. Phys.* **2004**, *121*, 3405.

(51) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2004**, *108*, 6908.

(52) Andersson, S.; Gruning, M. *J. Phys. Chem. A* **2004**, *108*, 7621.

(53) Johnson, E. R.; Wolkow, R. A.; DiLabio, G. A. *Chem. Phys. Lett.* **2004**, *394*, 334.

(54) Zhao, Y.; Lynch, B. J.; Truhlar, D. G. *Phys. Chem. Chem. Phys.* **2005**, *7*, 43.

(55) Zhao, Y.; González-García, N.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 2012.

(56) Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2005**, *1*, 415.

(57) Schultz, N.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A.* **2005**, *109*, 4388.

(58) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 5656.

(59) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 6624.

(60) Zhao, Y.; Truhlar, D. G. *Phys. Chem. Chem. Phys.* **2005**, *7*, 2701.

(61) Perdew, J. P.; Ruzsinszky, A.; Tao, J.; Staroverov, V. N.; Scuseria, G. E.; Csonka, G. I. *J. Chem. Phys.* **2005**, *123*, 62201.

(62) Becke, A. D. *J. Chem. Phys.* **2005**, *122*, 64101.

(63) Dickson, R. M.; Becke, A. D. *J. Chem. Phys.* **2005**, *123*, 111101.

(64) Keal, T. W.; Tozer, D. J. *J. Chem. Phys.* **2005**, *123*, 121103.

(65) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Phys.* **2005**, *123*, 161103; Note that in this communication we interchanged $c_{C\alpha\beta,i}$ and $c_{C\sigma\sigma,i}$ in Table 1. In addition, "reduced density x_σ" before eq. (1) should read "reduced density gradient x_σ".

(66) Schultz, N.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A.* **2005**, *109*, 11127.

(67) Quintal, M. M.; Karton, A.; Iron, M. A.; Boese, A. D.; Martin, J. M. L. *J. Phys. Chem. A* **2006**, *110*, 709.

(68) Zhao, Y.; Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2004**, *108*, 2715.

(69) Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2003**, *107*, 8996.

(70) Chakravorty, S. J.; Gwaltney, S. R.; Davidson, E. R.; Parpia, F. A.; Fischer, C. F. F. *Phys. Rev. A* **1993**, *47*, 3649.

(71) Lynch, B. J.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2003**, *107*, 1384.

(72) Izgorodina, E. I.; Coote, M. L.; Radom, L. *J. Phys. Chem. A* **2005**, *109*, 7558.

(73) Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2003**, *107*, 3898.
(74) Lynch, B. J.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 1643.
(75) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.
(76) Champagne, B.; Perpete, E. A.; Jacquemin, D.; Gisbergen, S. J. A. V.; Baerends, E.-J.; Soubra-Ghaoui, C.; Robins, K. A.; Kirtman, B. *J. Phys. Chem. A* **2000**, *104*, 4755.
(77) Bulat, F. A.; Toro-Labbé, A.; Champagne, B.; Kirtman, B.; Yang, W. *J. Chem. Phys.* **2005**, *123*, 14319.
(78) Langhoff, S. R.; Bauschlicher, C. W. *Annu. Rev. Phys. Chem.* **1988**, *39*, 181.
(79) Widmark, O.; Malmqvist, P. A.; Roos, B. *Theor. Chim. Acta* **1990**, *77*, 291.
(80) Pou-Amerigo, R.; Merchan, M.; Nebot-Gil, I.; Widmark, P. O.; Roos, B. *Theor. Chim. Acta* **1995**, *92*, 149.
(81) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.
(82) Fast, P. L.; Sanchez, M. L.; Truhlar, D. G. *Chem. Phys. Lett.* **1999**, *306*, 407.
(83) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1999**, *110*, 4703.
(84) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.
(85) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.
(86) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.
(87) Fast, P. L.; Truhlar, D. G. *J. Phys. Chem. A* **2000**, *104*, 6111.
(88) Sinnokrot, M. O.; Sherrill, C. D. *J. Phys. Chem. A* **2004**, *108*, 10200.
(89) Stevens, W.; Basch, H.; Krauss, J. *J. Chem. Phys.* **1984**, *81*, 6026.
(90) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
(91) Schwenke, D. W.; Truhlar, D. G. *J. Chem. Phys.* **1985**, *82*, 2418; **1987**, *86*, 3760 (E).
(92) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Jr., T. V.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision C.01; Gaussian, Inc.: Pittsburgh PA, 2003.
(93) Werner, H.-J.; Knowles, P. J.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Celani, P.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Korona, T.; Lindh, R.; Lloyd, A. W.; McNicholas, S. J.; Manby, F. R.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R.; Rauhut, G.; Schütz, M.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T. *MOLPRO*, 2002.6; University of Birmingham: Birmingham, 2002.
(94) Stoll, H.; Pavkidou, C. M. E.; Preuss, H. *Theor. Chim. Acta* **1978**, *49*, 143.
(95) Gori-Giorgi, P.; Sacchetti, F.; Bachelet, G. G. *Phys. Rev. B* **2000**, *61*, 7353.

(96) Gori-Giorgi, P.; Perdew, J. P. *Phys. Rev. B* **2004**, *69*, 041103.
(97) von-Weizsäcker, C. F. *Z. Phys.* **1935**, *96*, 431.
(98) Yang, G.; Reinstein, L. E.; Pai, S.; Xu, Z.; Carroll, D. L. *Medical Physics* **1998**, *25*, 2308.
(99) Levy, M.; Perdew, J. P. *Phys. Rev. A* **1985**, *32*, 2010.
(100) Lieb, E. H.; Oxford, S. *Int. J. Quantum Chem.* **1981**, *19*, 427.
(101) Zhao, Y.; Pu, J.; Lynch, B. J.; Truhlar, D. G. *Phys. Chem. Chem. Phys.* **2004**, *6*, 673.
(102) Dybala-Defratyka, A.; Paneth, P.; Pu, J.; Truhlar, D. G. *J. Phys. Chem. A* **2004**, *108*, 2475.
(103) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **2000**, *112*, 7374.
(104) Henry, D. J.; Sullivan, M. B.; Radom, L. *J. Phys. Chem. A* **2003**, *118*, 4849.
(105) Hautman, J.; Klein, M. L. *NATO ASI Ser. E* **1991**, *205*, 395.
(106) Karlin, K. D. *Science* **1993**, *261*, 701.
(107) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 2nd ed.; Wiley: New York, 1994.
(108) George, S. M. *Chem. Rev.* **1995**, *95*, 475.
(109) Somorjai, G. A. *Chem. Rev.* **1995**, *96*, 1223.
(110) Ratner, M. A.; Davis, B.; Kemp, M.; Mujica, V.; Roitberg, A.; YalirakiI, S. *Ann. N. Y. Acad. Sci.* **1998**, *852*, 22.
(111) *Transition State Modeling for Catalysis*; Truhlar, D. G.; Morokuma, K., Eds.;ACS Symposium Series 721; American Chemical Sociaty: Washington, DC, 1999.
(112) Davidson, E. R. *Chem. Rev.* **2000**, *100*, 351.
(113) Siegbahn, P. E. M.; Blomberg, M. R. A. *Chem. Rev.* **2000**, *100*, 421.
(114) Gladysz, J. A. *Chem. Rev.* **2000**, *100*, 1167.
(115) *Handbook on Metalloproteins*; Bertini, I.; Sigel, A.; Sigel, H., Eds.; Dekker: New York, 2001.
(116) Rappe, A. K.; Skiff, W. M.; Casewit, C. J. *Chem. Rev.* **2000**, *100*, 1435.
(117) Coperat, C.; Chabonas, M.; Saint-Arromon, R. P.; Basset, J.-M. *Angew. Chemie Int. Ed.* **2003**, *42*, 156.
(118) Phillips, J. A.; Cramer, C. J. *J. Chem. Theory Comput.* **2005**, *1*, 827.
(119) Reeve, S. W.; Burns, W. A.; Lovas, F. J.; Suenram, R. D.; Leopold, K. R. *J. Phys. Chem. A* **1993**, *97*, 10630.
(120) Fiacco, D. L.; Mo, Y.; Hunt, S. W.; Ott, M. E.; Roberts, A.; Leopold, K. R. *J. Phys. Chem. A* **2001**, *105*, 484.
(121) Hartree, D. R.; Hartree, W.; Swirles, B. *Phil. Trans. Roy. Soc. Ser. A* **1939**, *238*, 229.
(122) Anderson, W. B.; Burdett, J. K.; Czech, P. T. *J. Am. Chem. Soc.* **1994**, *116*, 8808.
(123) McKoy, V.; Sinanoglu, V. *J. Chem. Phys.* **1964**, *41*, 2689.
(124) Laidig, W. D.; Schaefer, H. F. *J. Chem. Phys.* **1981**, *74*, 3411.
(125) Lee, T. J.; Taylor, P. R. *Int. J. Quantum Chem. Symp.* **1989**, *23*, 199.
(126) Das, G.; Wahl, A. C. *J. Chem. Phys.* **1967**, *47*, 2934.
(127) Botch, B. H.; Dunning, T. H.; Harrison, J. F. *J. Chem. Phys.* **1981**, *47*, 2934.
(128) Walch, S. P.; Bauschlicher, C. W. *Chem. Phys. Lett.* **1982**, *86*, 66.
(129) Chong, D. P.; Langhoff, S. R. *J. Chem. Phys.* **1986**, *84*, 5606.

(130) Carter, E. A.; Goddard, W. A. *J. Chem. Phys.* **1988**, *88*, 1752.
(131) Murthy, R. B.; Messemer, R. P. *J. Chem. Phys.* **1992**, *97*, 4974.
(132) Schmidt, M. W.; Gordon, M. S. *Annu. Rev. Phys. Chem.* **1998**, *49*, 233.
(133) Staroverov, V. N.; Davidson, E. R. *J. Am. Chem. Soc.* **2000**, *122*, 186.
(134) Gräfenstein, J.; Cremer, D. *Chem. Phys. Lett.* **2000**, *316*, 569.
(135) Pollet, R.; Savin, A.; Leininger, T.; Stoll, H. *J. Chem. Phys.* **2002**, *116*, 1250.
(136) Dunning, T. H.; Harding, L. B. In *Theory of Chemical Reaction Dynamics*; Baer, M., Ed.; CRC press: Boca Raton, 1985; p. 1.
(137) Brown, F. B.; Steckler, R.; Schwenke, D. W.; Truhlar, D. G.; Garrett, B. C. *J. Chem. Phys.* **1985**, *82*, 188.
(138) Perdew, J. P.; Zunger, A. *Phys. Rev. B* **1981**, *23*, 5048.
(139) Kryachko, E. S.; Ludeña , E. V. Energy Density Functional Theory of Many-Electron Systems; Kluwer Academic: Dordrecht, 1990; p. 637.
(140) Ciofini, I.; Adamo, C.; Chermette, H. *J. Chem. Phys.* **2005**, *123*, 121102.
(141) Dreuw, A.; Head-Gordon, M. *Chem. Rev.* **2005**, *105*, 4009.
(142) Slater, J. C. *Phys. Rev.* **1954**, 528.
(143) Tschinke, V.; Ziegler, T. A. *J. Chem. Phys.* **1990**, *93*, 8051.
(144) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651.
(145) Gritsenko, O. V.; Schipper, P. R. T.; Baerends, E. J. *J. Chem. Phys.* **1997**, *107*, 5007.
(146) Slater, J. C. *Quantum Theory of Molecular and Solids. Vol. 4: The Self-Consistent Field for Molecular and Solids*; McGraw-Hill: New York, 1974.

Table 1: Optimized parameters in the M05-2X and M05 Methods.

parameters	M05-2X			M05		
	a_i	$c_{C\alpha\beta,i}$	$c_{C\sigma\sigma,i}$	a_i	$c_{C\alpha\beta,i}$	$c_{C\sigma\sigma,i}$
0	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
1	-0.56833	1.09297	-3.05430	0.08151	3.78569	3.77344
2	-1.30057	-3.79171	7.61854	-0.43956	-14.15261	-26.04463
3	5.50070	2.82810	1.47665	-3.22422	-7.46589	30.69913
4	9.06402	-10.58909	-11.92365	2.01819	17.94491	-9.22695
5	-32.21075			8.79431		
6	-23.73298			-0.00295		
7	70.22996			9.82029		
8	29.88614			-4.82351		
9	-60.25778			-48.17574		
10	-13.22205			3.64802		
11	15.23694			34.02248		
X	56			28		

Table 2 Density Functionals

Method	Year	Ref(s).	exchange				correlation			
			$\nabla\rho$	X	τ ?	UEG ?	$\nabla\rho$	τ ?	SCorF ?	UEG ?
BLYP	1988	2, 3	B88	0	no	yes	LYP	no	yes	no
SPWL	1992	5, [146]	Slater	0	no	yes	PW91-L	no	no	yes
B3PW91	1993	2, 4, 7	B88	20	no	yes	PW91	no	no	yes
B3LYP	1994	2, 3, 8	B88	20	no	yes	LYP	no	yes	no
BB95	1996	2, 10	B88	0	no	yes	B95	yes	yes	yes
B1B95	1996	2, 10	B88	28	no	yes	B95	yes	yes	yes
G96LYP	1996	3, 9	G96	0	no	yes	LYP	no	yes	yes
PBE	1996	11	PBE	0	no	yes	PBE	no	no	yes
B1LYP	1997	2, 3, 14	B88	25	no	yes	LYP	no	yes	no
mPWPW91	1998	4, 15	mPW	0	no	yes	PW91	no	no	yes
mPW1PW91 [a]	1998	4, 15	mPW	25	no	yes	PW91	no	no	yes
B98	1998	16	B98	21.98	no	no	B98	no	no	no
B97-1	1998	19	B97-1	21	no	no	B97-1	no	no	no
PBE1PBE [b]	1999	22	PBE	25	no	yes	PBE	no	no	yes
MPW1K	2000	27	mPW	42.8	no	yes	PW91	no	no	yes
B97-2	2001	19	B97-2	21	no	no	B97-2	no	no	no
τ-HCTHh	2002	34	τ-HCTHh	15	yes	no	τ-HCTHh	no	no	no
TPSS	2003	41	TPSS	0	yes	yes	TPSS	yes	yes	yes

TPSSh	2003	42	TPSS	10	yes	yes	TPSS	yes	yes	yes
X3LYP	2004	3, [47]	X	21.8	no	yes	LYP	no	yes	no
BB1K	2004	2, 10, [68]	B88	42	no	yes	B95	yes	yes	yes
BMK	2004	[50]	BMK	42	yes	no	BMK	no	no	no
MPW1B95	2004	10, 15, [51]	mPW	31	no	yes	B95	yes	yes	yes
MPWB1K	2004	10, 15, [51]	mPW	44	no	yes	B95	yes	yes	yes
TPSS1KCIS	2005	21, 41, [60]	TPSS	13	yes	yes	KCIS	yes	yes	yes
PW6B95	2005	[58]	PW6B95	28	no	yes	PW6B95	yes	yes	yes
PWB6K	2005	[58]	PWB6K	46	no	yes	PWB6K	yes	yes	yes
B97-3	2005	[64]	B97-3	26.93	no	no	B97-3	no	no	no
M05	2005	[65]	M05	28	yes	yes	M05	yes	yes	yes
M05-2X	2005	Present	M05-2X	56	yes	yes	M05-2X	yes	yes	yes

[a] also called mPW0 and MPW25

[b] also called PBE0.

Table 3: Mean Errors[a] (kcal/mol for Ionization Potentials (IP) and Electron Affinities (EA) and kcal/mol per Bond for Atomization Energies (AE))

Method	MGAE109/05		IP13/3		EA13/3		TMUE
	MSEPB	MUEPB	MSE	MUE	MSE	MUE	
PW6B95	-0.02	**0.40**	2.24	3.24	0.72	**1.78**	**0.81**
M05-2X	-0.02	**0.48**	1.69	3.54	0.53	2.03	**0.93**
BMK	-0.04	**0.47**	2.74	4.21	0.28	**1.56**	**0.94**
B1B95	-0.23	**0.55**	-0.13	**2.18**	3.02	3.16	**0.96**
MPW1B95	0.31	0.62	0.36	**2.14**	2.72	2.91	**0.98**
M05	-0.01	**0.53**	-0.41	2.87	2.81	2.96	0.99
B98	-0.50	0.64	1.99	3.21	0.30	**1.84**	1.00
B97-3	-0.37	0.59	1.56	3.51	0.82	2.07	1.02
B97-2	-0.20	0.65	0.46	**2.21**	2.41	2.89	1.02
TPSS1KCIS	-0.05	0.67	0.91	2.63	1.84	2.81	1.07
B97-1	-0.39	0.75	0.99	2.84	1.09	2.02	1.07
B3PW91	-0.13	0.66	3.70	4.25	-0.12	2.09	1.14
τ-HCTHh	-0.21	0.75	3.62	4.03	-1.18	**1.83**	1.17
PBE1PBE	0.11	0.91	2.44	3.23	1.50	2.76	1.31
mPW1PW91	-0.73	0.88	3.17	3.72	1.09	2.62	1.32
TPSS	0.63	1.03	1.80	3.11	0.51	2.31	1.36
TPSSh	-0.12	0.98	1.96	3.17	1.40	2.81	1.37
MPWB1K	-0.84	0.98	0.51	**2.05**	3.99	4.11	1.38
B3LYP	-0.69	0.91	3.58	4.72	-1.51	2.29	1.41
BB1K	-1.32	1.34	0.13	**2.09**	4.28	4.36	1.70
PWB6K	-1.41	1.43	1.57	2.28	3.23	3.59	1.72
X3LYP	-1.26	1.42	2.58	4.73	-0.41	3.04	1.89
BLYP	-0.47	1.49	-0.41	4.87	-0.11	2.63	1.93
mPWPW91	1.72	2.01	2.93	4.15	-1.56	2.26	2.24
G96LYP	-1.39	1.96	-1.12	4.64	1.33	2.93	2.31
BB95	2.18	2.34	-0.55	3.34	0.21	**1.99**	2.40
MPW1K	-2.33	2.34	3.41	3.53	2.79	3.71	2.59
B1LYP	-2.66	2.69	-0.13	3.80	2.56	3.64	2.89
PBE	2.80	3.03	2.11	3.58	-1.20	2.22	3.01
SPWL	16.89	16.89	4.34	5.18	-5.77	5.80	14.70
Average [b]		1.68		3.43		2.77	1.95

[a] MUEPB denotes mean unsigned error (MUE) per bond. MSE denotes mean signed error. TMUE denotes total MUE and it is defined as: TMUE = [MUEPB×109 +MUE(IP)×13+ MUE(AE)×13]/135.
[b] In all tables, where the last row is "Average" it is the average of that column for all functionals in the table.

Table 4: Mean Errors for Thermochemical Kinetics [a, b]

Methods	*X*	HTBH38/04		ΔE19	AMUE [c]
		MSE	MUE	MUE	
M05-2X	56	-0.39	1.34	**0.64**	**0.99**
BMK	42	-0.82	**1.32**	**0.92**	**1.12**
BB1K	42	-0.57	**1.16**	1.38	**1.27**
MPW1K	42.8	-0.60	**1.32**	1.31	**1.32**
MPWB1K	44	-0.85	**1.29**	1.41	**1.35**
PWB6K	46	-0.50	**1.28**	1.57	1.42
M05	28	-1.20	1.93	0.95	1.44
B97-3	26.93	-2.11	2.27	1.15	1.71
B1B95	28	-2.80	2.80	**0.78**	1.79
MPW1B95	31	-3.02	3.02	**0.86**	1.94
PW6B95	28	-3.14	3.14	**0.85**	1.99
B97-2	21	-3.09	3.24	1.08	2.16
mPW1PW91	25	-3.54	3.55	1.13	2.34
B3PW91	20	-4.02	4.03	1.05	2.54
B98	21.98	-4.16	4.16	0.97	2.57
B1LYP	25	-2.84	3.18	2.29	2.73
PBE1PBE	25	-4.22	4.22	1.29	2.76
B97-1	21	-4.40	4.40	1.48	2.94
B3LYP	20	-4.13	4.23	1.95	3.09
τ–HCTHh	15	-5.29	5.29	0.97	3.13
TPSS1KCIS	13	-4.69	4.69	1.64	3.16
X3LYP	21.8	-3.98	4.09	3.03	3.56
G96LYP	0	-6.25	6.26	2.26	4.26
TPSSh	10	-5.97	5.97	2.65	4.31
BB95	0	-8.14	8.14	1.63	4.89
BLYP	0	-7.52	7.52	2.29	4.90
TPSS	0	-7.71	7.71	2.53	5.12
mPWPW91	0	-8.43	8.43	1.97	5.20
PBE	0	-9.32	9.32	2.71	6.01
SPWL	0	-17.72	17.72	6.39	12.05
Average			4.57	1.70	3.14

[a] The MG3S basis used for all calculations in this table.
[b] MUE denotes mean unsigned error (kcal/mol). MSE denotes mean signed error (kcal/mol).

[c] AMUE in this table is calculated by averaging the two MUE columns, and it is a measure of the quality of a method for kinetics.

Table 5: Mean Errors for Noncovalent Databases (kcal/mol)[a, b, c]

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		
M05-2X	0.40	0.20	**0.30**	0.46	0.30	**0.38**	0.27	0.32	**0.29**	0.09	0.03	**0.06**	0.49	0.71	**0.60**	**0.33**
PWB6K	0.44	0.34	**0.39**	0.25	0.16	**0.21**	0.24	0.32	**0.28**	0.15	0.07	**0.11**	0.79	1.00	**0.90**	**0.38**
M05	0.58	0.53	0.55	0.68	0.30	**0.49**	0.23	0.24	**0.23**	0.14	0.06	**0.10**	1.12	1.34	**1.23**	**0.52**
MPWB1K	0.41	0.70	0.56	0.24	0.45	**0.34**	0.50	0.65	0.57	0.08	0.16	0.12	1.32	1.57	1.45	**0.61**
PW6B95	0.53	0.78	0.65	0.69	0.47	0.58	0.40	0.49	0.45	0.11	0.09	**0.10**	1.21	1.44	**1.32**	**0.62**
MPW1B95	0.50	0.86	0.68	0.47	0.31	**0.39**	0.50	0.63	0.56	0.10	0.16	0.13	1.46	1.70	1.58	0.67
B97-1	0.45	0.45	**0.45**	1.17	0.89	1.03	0.28	0.30	**0.29**	0.10	0.11	**0.10**	1.57	1.78	1.68	0.71
PBE1PBE	0.40	0.28	**0.34**	1.04	0.75	0.90	0.35	0.38	**0.37**	0.12	0.18	0.15	1.84	2.09	1.96	0.74
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	0.78
MPW1K	0.33	0.61	0.47	0.44	0.66	0.55	0.52	0.67	0.60	0.20	0.29	0.25	2.25	2.53	2.39	0.85
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
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
BMK	0.68	0.96	0.82	0.41	0.62	0.52	0.78	0.97	0.88	0.76	0.85	0.81	2.36	2.57	2.47	1.10
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	**0.39**	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
B1LYP	0.72	1.05	0.88	0.49	0.45	0.47	0.93	1.09	1.01	0.30	0.39	0.35	3.06	3.27	3.16	1.17
B97-3	1.16	1.50	1.33	0.48	0.63	0.56	0.82	0.98	0.90	0.49	0.58	0.53	2.49	2.70	2.59	1.18
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
mPWPW91	0.57	0.96	0.77	2.25	1.89	2.07	0.56	0.59	0.57	0.24	0.32	0.28	2.69	2.96	2.83	1.30
B3PW91	1.03	1.43	1.23	0.64	0.69	0.66	0.97	1.14	1.06	0.53	0.62	0.58	3.23	3.49	3.36	1.38

τ-HCTHh	1.94	2.58	2.26	1.60	1.42	1.51	0.75	1.01	0.88	0.44	0.33	0.38	2.11	2.37	2.24	1.45
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
BB95	1.83	2.21	2.02	1.48	1.27	1.38	1.18	1.35	1.27	0.57	0.66	0.62	2.96	3.18	3.07	1.67
SPWL	3.13	2.67	2.90	5.61	5.23	5.42	2.16	1.95	2.05	0.20	0.10	0.15	0.35	0.43	**0.39**	2.18
G96LYP	2.95	3.30	3.13	1.20	1.28	1.24	2.57	2.74	2.65	1.37	1.47	1.42	5.19	5.41	5.30	2.75
Average	0.88	1.11	1.00	1.14	1.02	1.08	0.73	0.84	0.79	0.31	0.34	0.33	2.21	2.43	2.32	1.10

[a] 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: π–π stacking

[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

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

Table 6: Composite energetic results (kcal/mol)

Method	Thermochem.	Kinetics	Noncovalent Interaction	Average [a]	Scaled average [b]
	TMUE	AMUE	MMMUE		
M05-2X	**0.93**	**0.99**	**0.33**	**0.75**	**0.36**
M05	0.99	1.44	**0.52**	**0.98**	**0.48**
PW6B95	**0.81**	1.99	**0.62**	**1.14**	**0.54**
PWB6K	1.72	1.42	**0.38**	1.18	**0.56**
MPWB1K	1.38	**1.35**	**0.61**	**1.11**	**0.56**
MPW1B95	**0.98**	1.94	0.67	1.20	0.58
BMK	**0.94**	**1.12**	1.10	**1.05**	0.61
B98	1.00	2.57	0.78	1.45	0.68
B97-1	1.07	2.94	0.71	1.57	0.71
B97-3	1.02	1.71	1.18	1.30	0.71
B1B95	**0.96**	1.79	1.25	1.33	0.73
PBE1PBE	1.31	2.76	0.74	1.60	0.74
mPW1PW91	1.32	2.34	0.95	1.54	0.76
BB1K	1.70	**1.27**	1.13	1.37	0.77
B97-2	1.02	2.16	1.23	1.47	0.77
TPSS1KCIS	1.07	3.16	0.99	1.74	0.82
MPW1K	2.59	**1.32**	0.85	1.58	0.84
B3PW91	1.14	2.54	1.38	1.69	0.88
B3LYP	1.41	3.09	1.13	1.87	0.91
τ-HCTHh	1.17	3.13	1.45	1.92	0.97
X3LYP	1.89	3.56	0.92	2.12	0.98
TPSSh	1.37	4.31	1.05	2.24	1.01
B1LYP	2.89	2.73	1.17	2.26	1.14
TPSS	1.36	5.12	1.22	2.57	1.14
mPWPW91	2.24	5.20	1.30	2.92	1.33
BLYP	1.93	4.90	1.63	2.82	1.35
BB95	2.40	4.89	1.67	2.99	1.43
PBE	3.01	6.01	1.14	3.39	1.50
G96LYP	2.31	4.26	2.75	3.11	1.68
SPWL	14.70	12.05	2.18	9.64	4.45
Average	1.95	3.14	1.10	2.06	1.00

[a] (TMUE+AMUE+MMMUE)/3 in kcal/mol.

[b] ((TMUE/1.95)+(AMUE/3.14)+(MMMUE/1.10))/3; note that the scaled average is unitless.

Table 7: Alkyl Bond Dissociation Energies (D_e, kcal/mol) [a, b]

Method	R–CH_3		R–OCH_3		MSE	MUE
	R=Me	R=*i*-Pr	R=Me	R=*i*-Pr		
Exp.	97.39	95.00	89.79	91.51		
M05-2X	97.37	94.01	90.65	90.93	-0.18	**0.61**
G3-RAD [c, d]	96.91	94.95	90.53	92.87	0.39	**0.66**
BMK [d]	97.99	93.42	88.81	87.99	-1.37	**1.67**
MPW1B95 [d]	98.90	92.78	88.79	86.68	-1.64	**2.39**
MPWB1K [d]	98.54	93.01	88.10	86.56	-1.87	**2.44**
PWB6K	97.96	92.64	87.48	86.21	-2.35	2.64
B1B95 [d]	97.58	91.05	87.83	86.01	-2.80	2.90
BB1K	97.58	91.75	87.02	85.17	-3.04	3.14
PW6B95	97.26	91.10	87.28	85.18	-3.22	3.22
B97-1	97.45	90.83	87.05	84.29	-3.52	3.55
BB95	98.35	90.15	87.79	83.69	-3.43	3.91
PBE	96.79	89.65	87.24	84.08	-3.98	3.98
B97-2	97.68	90.18	86.77	83.10	-3.99	4.14
τ-HCTHh	96.51	89.51	86.93	83.78	-4.24	4.24
B97-3	96.76	89.78	85.86	82.78	-4.63	4.63
B98	95.73	89.10	86.06	83.31	-4.87	4.87
X3LYP	95.73	89.10	86.06	83.31	-4.87	4.87
PBE1PBE	95.23	89.29	85.63	83.59	-4.98	4.98
M05	94.47	86.99	86.32	82.77	-5.79	5.79
mPWPW91	94.58	87.22	85.26	81.87	-6.19	6.19
mPW1PW91 [d]	93.28	87.16	84.37	82.86	-6.51	6.51
B3PW91	93.18	86.52	83.79	81.07	-7.28	7.28
MPW1K [d]	92.80	87.42	82.77	81.25	-7.36	7.36
TPSS1KCIS	92.11	85.56	83.07	80.44	-8.13	8.13
B3LYP [d]	91.58	85.01	82.58	80.06	-8.62	8.62
TPSSh	90.47	84.12	82.08	79.62	-9.35	9.35
TPSS	90.48	83.74	82.36	79.54	-9.39	9.39
B1LYP	89.73	83.44	80.46	78.25	-10.45	10.45
BLYP [d]	90.31	82.64	81.09	77.50	-10.53	10.53
G96LYP	89.01	80.68	79.64	75.40	-12.24	12.24
SPWL	115.56	108.51	108.10	105.49	15.99	15.99
Average [e]						5.70

[a] The B3LYP/6-31G(d) geometries are used in all calculations in this table.
[b] All DFT calculations in this table use 6-311+G(3df,2p) basis set.
[c] G3-RAD is the "Gaussian-3 for radicals" method of Ref. [104].
[d] Data for these methods are taken from a paper by Izgorodina et al.[72]
[e] Average excludes G3-RAD, which is a wave function method (not a density functional method)

Table 8: MUE (kcal/mol) for the TMAE4/05 and MLBE4/05 databases with the DZQ basis set

Method	TMAE4/05		MLBE4/05		MMUE [a]
	MSE	MUE	MSE	MUE	
BLYP	-0.86	**1.97**	9.23	9.23	**5.60**
M05	-5.98	**7.34**	-2.20	**4.97**	**6.15**
G96LYP	-5.71	**5.71**	6.99	8.10	**6.90**
TPSS	-6.18	8.38	7.00	7.00	**7.69**
B97-2	-10.07	10.95	-0.61	**5.52**	**8.24**
mPWPW91	-4.03	**7.28**	9.89	9.89	8.58
PBE	0.38	**5.87**	12.12	12.12	9.00
BB95	3.32	7.98	12.13	12.13	10.05
TPSSh	-15.97	15.97	1.42	**4.62**	10.30
τ-HCTHh	-5.91	13.07	3.56	7.68	10.38
TPSS1KCIS	-18.26	18.26	0.79	**4.39**	11.32
B97-1	-17.70	18.64	0.67	8.36	13.50
B3LYP	-21.47	21.47	-1.28	6.44	13.95
B98	-19.67	19.92	-0.73	8.00	13.96
X3LYP	-21.10	21.10	-1.75	6.86	13.98
B3PW91	-25.34	25.34	-2.54	**5.46**	15.40
PBE1PBE	-25.04	25.04	-3.34	6.31	15.68
PW6B95	-24.32	24.32	-4.00	7.36	15.84
B1B95	-25.13	25.13	-4.40	7.16	16.15
MPW1B95	-25.06	25.06	-4.64	7.61	16.33
B97-3	-22.80	22.80	-4.98	10.52	16.66
mPW1PW91	-26.46	26.46	-4.72	7.04	16.75
MPWB1K	-29.30	29.30	-11.35	11.52	20.41
BB1K	-29.56	29.56	-11.04	11.66	20.61
B1LYP	-27.14	27.14	-16.72	16.92	22.03
M05-2X	-21.92	29.42	-12.18	15.24	22.33
MPW1K	-31.83	31.83	-13.10	13.10	22.46
PWB6K	-33.90	33.90	-13.63	13.63	23.77
SPWL	23.03	23.03	30.30	30.30	26.66
BMK	-35.98	36.81	13.35	17.74	27.27
Average		19.97		9.90	14.93

[a] MMUE = (MUE(TMAE4/05) + MUE(MLBE4/05))/2

Table 9: Dipole Moments Predicted by Density Functionals [a,b]

Method	N6 [c]	LiCl	H_2CO	CuH	H_2O	BF	MS%E [d]	MU%E [e]	MSE	MUE
accurate	11.56 [f]	7.23 [g]	2.39 [g]	2.97 [h]	1.85 [g]	0.79 [g]				
PWB6K	15.00	7.19	2.59	3.23	2.01	0.80	9.2	**9.4**	0.67	**0.69**
M05-2X	14.85	7.16	2.68	3.25	2.04	0.81	10.2	10.6	0.66	**0.69**
MPWB1K	15.07	7.19	2.58	3.20	2.01	0.81	9.3	**9.5**	0.68	**0.69**
BB1K	15.12	7.20	2.56	3.15	2.00	0.83	9.4	**9.5**	0.68	**0.69**
BMK	15.27	7.26	2.63	2.91	2.04	0.87	10.2	10.9	0.70	**0.72**
MPW1K	15.20	7.21	2.60	3.25	2.01	0.86	11.1	11.2	0.72	0.73
MPW1B95	15.55	7.13	2.49	2.92	1.98	0.85	8.2	**9.3**	0.69	0.74
B1B95	15.66	7.14	2.47	2.89	1.98	0.87	8.5	9.9	0.70	0.76
PW6B95	15.68	7.11	2.48	2.87	1.98	0.84	7.8	9.6	0.69	0.77
B97-3	15.76	7.17	2.50	2.90	1.98	0.92	10.2	11.3	0.74	0.79
PBE1PBE	15.85	7.11	2.47	2.88	1.97	0.92	9.8	11.4	0.74	0.81
mPW1PW91	15.87	7.13	2.49	2.89	1.98	0.91	9.7	11.2	0.74	0.81
M05	15.97	7.08	2.52	2.91	2.00	0.80	8.0	**9.5**	0.75	0.82
B97-2	16.04	7.14	2.46	2.91	1.96	0.91	9.9	11.1	0.77	0.82
B98	16.07	7.11	2.48	2.84	1.97	0.91	9.7	11.8	0.76	0.85

B97-1	16.06	7.10	2.46	2.80	1.96	0.92	9.5	12.0	0.75	0.85
B1LYP	15.94	7.08	2.51	2.77	1.98	0.88	8.7	11.7	0.73	0.85
B3PW91	16.11	7.12	2.46	2.79	1.97	0.93	9.8	12.3	0.76	0.86
X3LYP	16.10	7.06	2.49	2.70	1.98	0.89	8.6	12.4	0.74	0.89
B3LYP	16.18	7.07	2.48	2.68	1.98	0.90	8.6	12.7	0.75	0.90
TPSS1KCIS	16.38	7.08	2.42	2.76	1.95	0.94	9.5	12.6	0.79	0.91
τ-HCTHh	16.41	7.11	2.44	2.72	1.96	0.92	9.4	12.7	0.80	0.92
TPSSh	16.54	7.09	2.41	2.81	1.94	0.97	10.7	13.2	0.83	0.93
TPSS	17.06	7.03	2.34	2.60	1.92	1.01	10.2	16.0	0.86	1.07
mPWPW91	17.10	6.98	2.31	2.36	1.93	0.98	8.1	17.4	0.81	1.13
BB95	17.04	6.98	2.28	2.28	1.92	0.96	6.9	17.4	0.78	1.13
PBE	17.08	6.96	2.29	2.34	1.93	1.00	8.2	17.9	0.80	1.13
G96LYP	17.18	7.01	2.34	2.29	1.94	0.99	8.3	17.8	0.83	1.15
BLYP	17.17	6.94	2.33	2.25	1.93	0.96	7.3	17.6	0.80	1.16
SPWL	17.42	6.95	2.37	2.16	2.00	0.99	8.6	19.4	0.85	1.22
Average								12.6		0.88

[a] All values are in Debyes.
[b] All DFT calculations are single-point calculations using the TZQ basis set.
[c] $NH_2(CH{=}CH)_6NO_2$ is denoted as N6.
[d] Mean percentage signed error

[e] Mean percentage unsigned error
[f] MP2/6-311+G(2df,2p) result. All calculations use MP2/6-31G geometry for this molecule.
[g] CCSD(T)/aug-cc-pVTZ result. All calculations use CCSD(T)/aug-cc-pVTZ geometry for these molecules.
[h] The reference dipole moment for CuH is an average of the values by the MCPF calculation and a CCSD(T)/ANO calculation performed in the present study, where ANO is the triple zeta atomic natural orbital basis set of Widmark et al. The geometry is taken from a previous study by Langhoff and Bauschlicher, and all calculations use this geometry (r_{Cu-H} = 1.509 Å).

Table 10: Results for Stacking and Hydrogen Bonding Interactions in Nucleobase Pairs (kcal/mol)

Methods	Stacking								Hydrogen Bonding				AMUE [b]
	A···T S	G···C S	C···C AP [a]	C···C D [a]	C···C S [a]	U···U S	MSE	MUE	A···T WC	G···C WC	MSE	MUE	
Best estimate [c]	11.60	16.90	9.90	9.43	-2.45	10.30			15.40	28.80			
M05-2X	10.28	16.25	10.52	10.02	-5.08	8.76	-0.82	1.22	14.56	28.58	-0.53	0.53	**0.87**
PWB6K	9.50	14.86	10.88	9.66	-5.93	7.94	-1.46	1.86	14.22	28.39	-0.79	0.79	**1.33**
MPWB1K	8.19	13.68	9.63	8.63	-7.02	6.51	-2.68	2.68	13.42	27.45	-1.67	1.67	**2.17**
PW6B95	7.68	13.10	9.48	8.46	-6.56	6.45	-2.84	2.84	13.26	26.68	-2.13	2.13	**2.49**
MPW1B95	7.47	12.83	8.98	8.08	-7.10	6.01	-3.24	3.24	13.18	26.80	-2.11	2.11	**2.67**
M05	5.77	11.95	7.86	7.66	-6.40	5.79	-3.84	3.84	13.68	27.07	-1.72	1.72	2.78
PBE1PBE	3.54	10.44	5.30	5.81	-8.40	3.97	-5.84	5.84	14.42	28.43	-0.67	0.67	3.25
B97-1	3.54	10.26	5.64	6.31	-8.01	4.05	-5.65	5.65	14.08	27.44	-1.34	1.34	3.50
BMK	5.42	11.54	6.37	6.17	-9.14	4.42	-5.15	5.15	12.49	26.30	-2.71	2.71	3.93
τ-HCTHh	2.39	9.38	4.54	5.14	-8.87	3.05	-6.68	6.68	13.79	27.42	-1.49	1.49	4.08
TPSSh	1.42	8.47	3.75	4.46	-9.64	2.29	-7.49	7.49	13.37	26.80	-2.02	2.02	4.75
SPWL	12.59	18.90	11.62	10.70	-2.33	10.64	1.07	1.07	22.30	39.44	8.77	8.77	4.92
B3LYP	-0.10	7.39	2.87	3.64	-10.70	1.47	-8.52	8.52	12.73	26.17	-2.65	2.65	5.59
B97-3	0.71	7.60	3.45	4.24	-10.21	1.90	-8.00	8.00	11.78	24.78	-3.82	3.82	5.91
Average								4.58				2.32	3.45

[a] 6-31+G(d,p) is used for all calculations in this table.

[b] AP denotes antiparallel, D denotes displaced, and S denotes sandwich. The structures for all base pairs in this table can be found in Ref. [60] and Supporting Information.

[c] See Ref. [60] and references therein for the sources of these best estimate.

[d] AMUE=0.5 MUE (Stacking) + 0.5 MUE(Hydrogen Bonding)

Table 11: Predicted Energy for H and H_2^+ [a]

Methods	Energy (hartree)			Mean Errors (kcal/mol)	
	H	H_2^+ (1.4 bohr)	H_2^+ (2.0 bohr)	MSE	MUE
HF	-0.499946	-0.569830	-0.602521	0 [b]	0 [b]
PWB6K	-0.500452	-0.570071	-0.605866	-0.86	**0.86**
BB1K	-0.498539	-0.568421	-0.604787	0.11	**1.06**
BMK	-0.498903	-0.567576	-0.604547	0.27	**1.11**
X3LYP	-0.499785	-0.569126	-0.607086	-0.77	**1.14**
MPWB1K	-0.497995	-0.567491	-0.603772	0.64	**1.16**
M05-2X	-0.499743	-0.571127	-0.607252	-1.22	1.30
B1B95	-0.498260	-0.568153	-0.605486	0.08	1.32
B1LYP	-0.498204	-0.568099	-0.605644	0.07	1.38
PBE	-0.499854	-0.569849	-0.609222	-1.39	1.42
MPW1B95	-0.497603	-0.567017	-0.604200	0.73	1.43
M05	-0.497839	-0.570464	-0.607749	-0.79	1.67
G96LYP	-0.499052	-0.570323	-0.609532	-1.38	1.76
BB95	-0.497781	-0.567708	-0.607079	-0.06	1.85
BLYP	-0.497781	-0.567708	-0.607079	-0.06	1.85
PW6B95	-0.501499	-0.571477	-0.608338	-1.89	1.89
TPSS1KCIS	-0.500036	-0.572567	-0.609298	-2.01	2.01
PBE1PBE	-0.501227	-0.571595	-0.609083	-2.01	2.01
TPSSh	-0.500043	-0.572672	-0.609564	-2.09	2.09
TPSS	-0.500069	-0.573028	-0.610440	-2.35	2.35
B3LYP	-0.502346	-0.572079	-0.610047	-2.55	2.55
B98	-0.502865	-0.574646	-0.612113	-3.62	3.62
mPWPW91	-0.503098	-0.574019	-0.612966	-3.72	3.72
B97-1	-0.502785	-0.574955	-0.612360	-3.72	3.72
mPW1PW91	-0.503839	-0.574884	-0.612020	-3.86	3.86
MPW1K	-0.504420	-0.575563	-0.611473	-4.01	4.01
B3PW91	-0.504154	-0.575088	-0.612744	-4.12	4.12
B97-3	-0.503829	-0.575986	-0.613022	-4.30	4.30
B97-2	-0.504206	-0.578058	-0.615081	-5.24	5.24
τ-HCTHh	-0.507268	-0.580641	-0.618280	-7.09	7.09
SPWL	-0.478593	-0.540711	-0.583762	14.48	14.48
Average					2.88

[a] The cc-pVTZ basis set are employed in all calculations in this table.

[b] For a one-electron system, Hartree-Fock is the same as full configuration interaction for a given basis set, and the error in the density functional calculations are computed relative to these results.

Table 12: Bond Length, Dipole Moment, and Binding Energy of HCN–BF_3 [a]

Methods	R_{BN} (Å)	μ (D)	ΔE (kcal/mol)	M%UE [b]
Best estimate	2.473 [c]	4.14 [d]	-5.7 [e]	
M05	2.492	4.30	-5.0	5.6
PW6B95	2.427	4.39	-5.0	6.5
MP2	2.361	4.51	-6.3	8.0
B97-1	2.500	4.29	-4.6	8.1
PWB6K	2.292	4.77	-5.9	8.7
MPW1B95	2.348	4.60	-4.9	10.2
M05-2X	2.352	4.73	-6.5	11.3
PBE1PBE	2.348	4.64	-4.8	11.1
MPWB1K	2.253	4.89	-5.3	11.3
PBE	2.407	4.45	-4.3	11.4
τ-HCTHh	2.426	4.46	-4.2	11.9
B3LYP	2.535	4.23	-3.8	12.7
MPW1K	2.323	4.74	-4.7	12.7
BB1K	2.346	4.63	-4.5	12.9
BMK	2.351	4.72	-4.5	13.3
B1B95	2.432	4.39	-3.8	13.6
B97-3	2.615	4.09	-3.6	14.6
B3PW91	2.465	4.37	-3.2	16.6
TPSSh	2.230	4.98	-4.3	18.1
TPSS	2.239	4.93	-4.1	18.8
BB95	2.538	4.12	-2.7	18.6
SPWL	1.731	6.97	-12.1	70.4
Average [f]	2.364	4.65	-4.9	14.8

[a] All DFT and MP2 results are for the aug-cc-pVTZ basis set.
[b] Mean percentage unsigned error.
[c] Experimental result[119]
[d] Experimental result[120]
[e] MCG3//MCQCISD/3 result[118]
[f] Average excludes MP2, which is a wave function method, not a density functional method.

Table 13: Dissociation Energies (kcal/mol) and B_1 values for eight bond breaking processes. [a]

Process	D_e			B_1
	Experiment [a]	BLYP	B1LYP//B1LYP [b]	
$CH_4 \rightarrow CH_3 + H$	112.7	109.9	109.5	0.4
$LiCl \rightarrow Li + Cl$	113.9	108.2	107.4	0.8
$AgCu \rightarrow Ag + Cu$	40.9	41.7	36.2	5.5
$Cu_2 \rightarrow 2Cu$	47.2	46.4	39.7	6.7
$VS \rightarrow V + S$	17.4	111.1	93.7	17.4
$CN \rightarrow C + N$	17.9	190.9	173.0	17.9
$O_3 \rightarrow 3O$	21.9	170.1	126.3	21.9 [c]
$ZrV \rightarrow Zr + V$	39.8	72.7	32.9	39.8

[a] The TZQ basis set is used. The TZQ basis always uses spherical harmonic *d* and *f* functions (5D 7F sets)

[b] The experimental values for CH_3–H, CN are calculated by using the experimental atomization energies from Database/3.[71] The experiment value for O_3 is taken from Database4/05.[74] The experimental values for Cu_2, AgCu are taken from a previous paper,[57] and the experimental values for VS and ZrV are taken from a recent paper.[66] All dissociation energies in this table are zero-point-exclusive and spin-orbit-inclusive.

[c] We put $n = 2$ in eq 33 in this case because two bonds are broken (not counting the long "bond").

Table 14: Signed errors and mean unsigned errors (kcal/mol) in bond energies [a]

Methods	X [b]	$B_1 < 10$					$B_1 > 10$					MMUE [c]
		Cu_2	AgCu	CH_3–H	LiCl	MUE	ZrV	VS	O_3	CN	MUE	
M05	28	0.0	1.2	-1.7	-2.6	1.4	-12.2	-2.7	-7.2	-1.1	5.8	3.6
B3LYP	20	-5.6	-2.9	-1.7	-4.9	3.8	-19.1	-8.6	-5.8	-1.5	8.8	6.3
B1B95	28	-5.5	-2.6	-0.5	-5.1	3.4	-23.7	-10.1	-5.9	-3.5	10.8	7.1
BLYP	0	-0.8	0.8	-2.8	-5.7	2.5	10.8	4.2	24.0	10.3	12.3	7.4
PBE1PBE	25	-6.3	-3.2	-3.3	-5.4	4.6	-25.1	-11.1	-6.1	-2.0	11.1	7.8
mPWPW91	0	-0.5	1.5	-3.1	-4.7	2.4	9.0	4.9	32.4	12.9	14.8	8.6
mPW1PW91	25	-7.8	-4.5	-3.7	-5.7	5.4	-28.3	-12.7	-11.3	-4.8	14.3	9.8
B1LYP	25	-7.5	-4.9	-3.2	-6.5	5.5	-25.6	-11.4	-19.7	-7.6	16.1	10.8
PBE	0	1.4	3.2	-2.6	-4.3	2.9	13.4	7.0	38.6	16.6	18.9	10.9
M05-2X	56	0.8	3.6	-0.7	1.7	1.7	-42.7	-17.8	-20.6	-7.0	22.0	11.9
BB95	0	2.2	3.7	-0.2	-2.4	2.1	20.3	9.1	41.7	16.1	21.8	12.0
BB1K	42	-8.6	-5.1	-0.6	-5.2	4.9	-41.2	-17.3	-27.3	-12.4	24.6	14.7
Average						3.4						9.2

[a] All DFT calculations in this table use the TZQ basis set with consistently optimized geometries.
[b] Percentage of Hartree-Fock exchange in each functional.
[c] MMUE = 0.5[MUE($B_1 < 10$) + MUE($B_1 > 10$)]

Figure Caption

Figure 1. The τ enhancement factors for the M05 and M05-2X functionals.

Figure 2. M05 enhancement factor F_{XC} of eq 22 as a function of the reduced gradient s of eq 23 with $\alpha_\tau = 0.2$ for various spin-unpolarized ($\rho_\alpha = \rho_\beta$) densities ranging from the high-density ($r_s = 0$) to the exchange-only limit ($r_s \rightarrow \infty$)

Figure 3. M05 enhancement factor F_{XC} of eq 22 as a function of the reduced gradient s of eq 23 with $\alpha_\tau = 1$ for various spin-unpolarized ($\rho_\alpha = \rho_\beta$) densities ranging from the high-density ($r_s = 0$) to the exchange-only limit ($r_s \rightarrow \infty$)

Figure 4. M05-2X enhancement factor F_{XC} of eq 22 as a function of the reduced gradient s of eq 23 with $\alpha_\tau = 0.2$ for various spin-unpolarized ($\rho_\alpha = \rho_\beta$) densities ranging from the high-density ($r_s = 0$) to the exchange-only limit ($r_s \rightarrow \infty$)

Figure 5. M05-2X enhancement factor F_{XC} of eq 22 as a function of the reduced gradient s of eq 23 with $\alpha_\tau = 1$ for various spin-unpolarized ($\rho_\alpha = \rho_\beta$) densities ranging from the high-density ($r_s = 0$) to the exchange-only limit ($r_s \rightarrow \infty$)

Figure 6. Effect of level of theory on the relative bond dissociation energies (in kcal/mol) for R-CH_3 species (R = methyl, ethyl, isopropyl, *tert*-butyl)

Figure 7. Effect of level of theory on the relative bond dissociation energies (in kcal/mol) for R-OCH_3 species (R = methyl, ethyl, isopropyl, *tert*-butyl)

Figure 1.

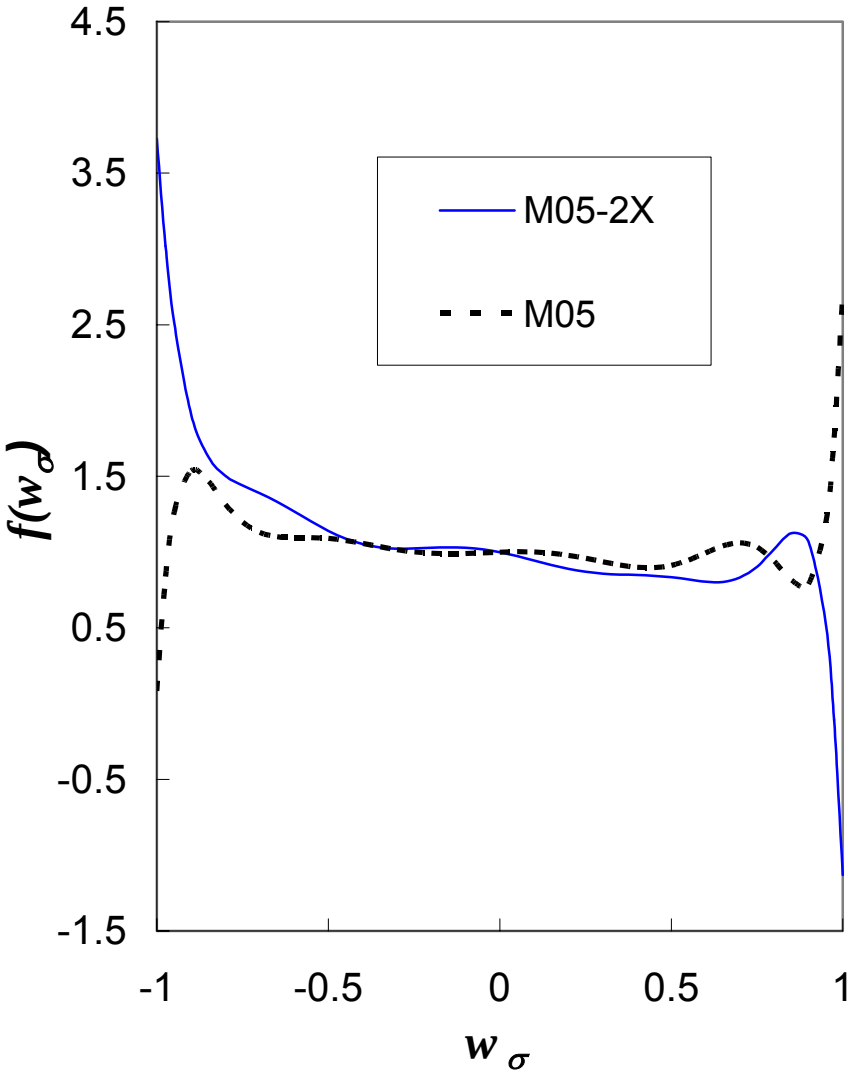


Figure 2.

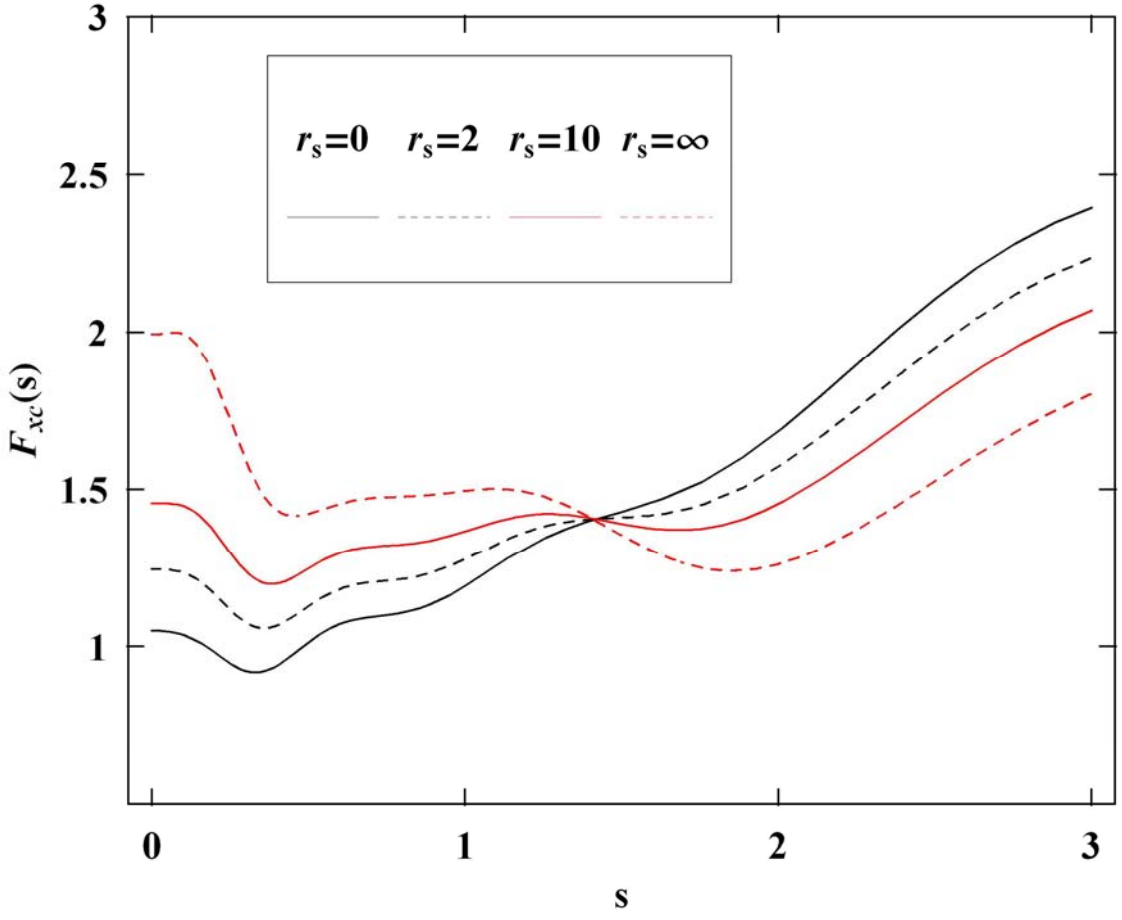


Figure 3.

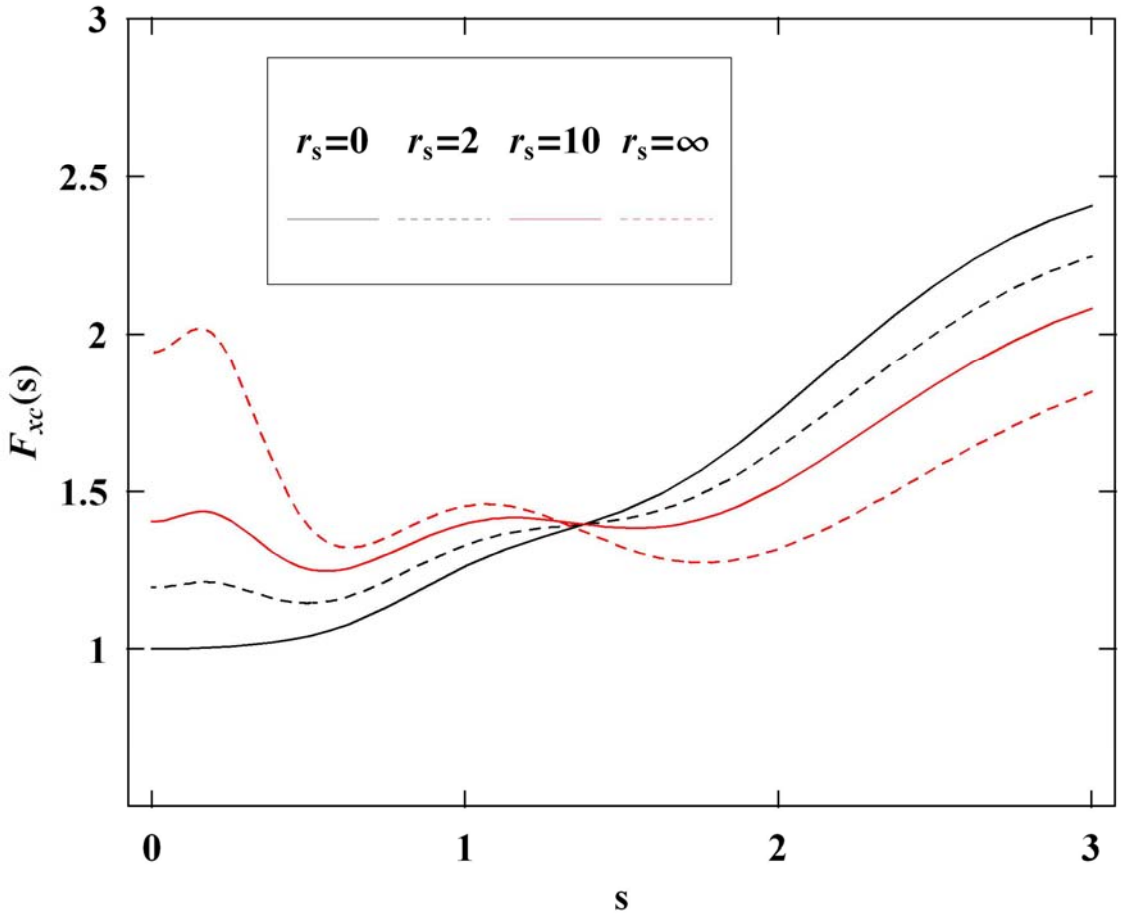
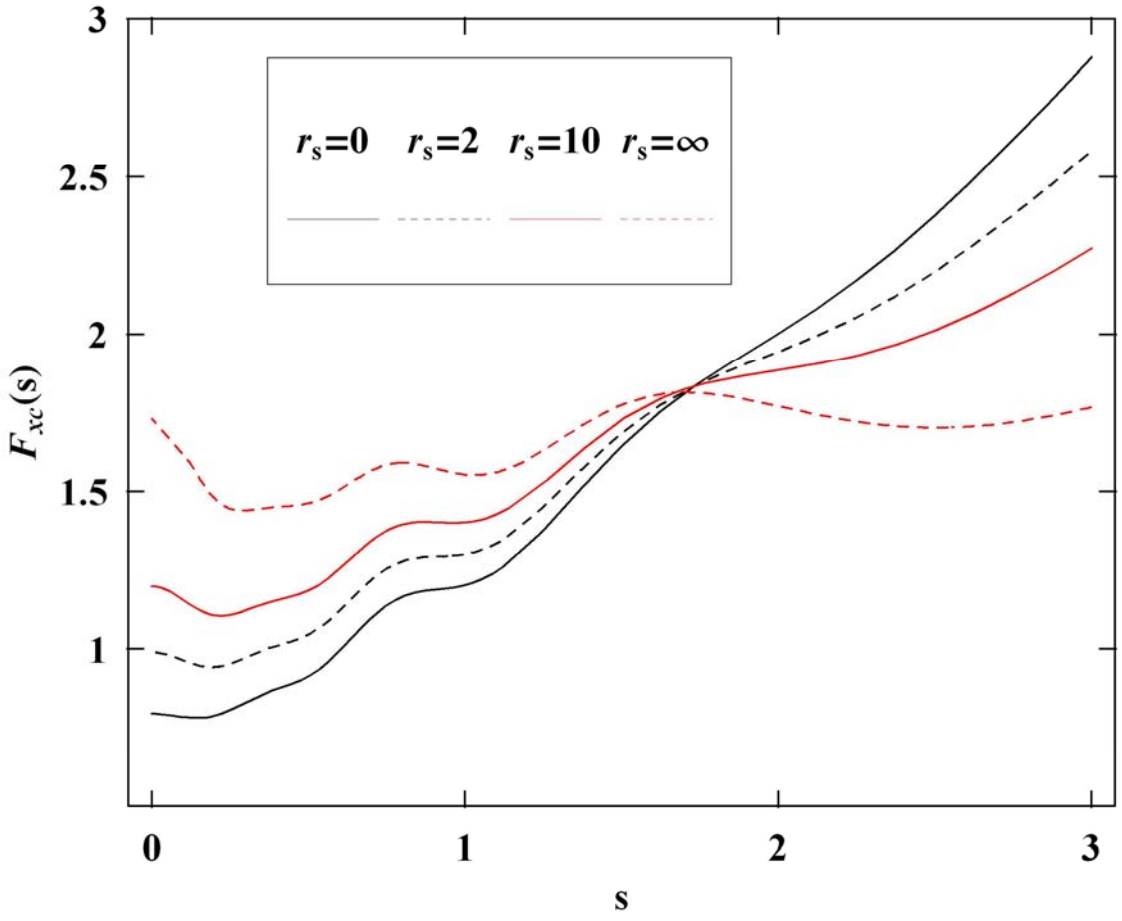


Figure 4.



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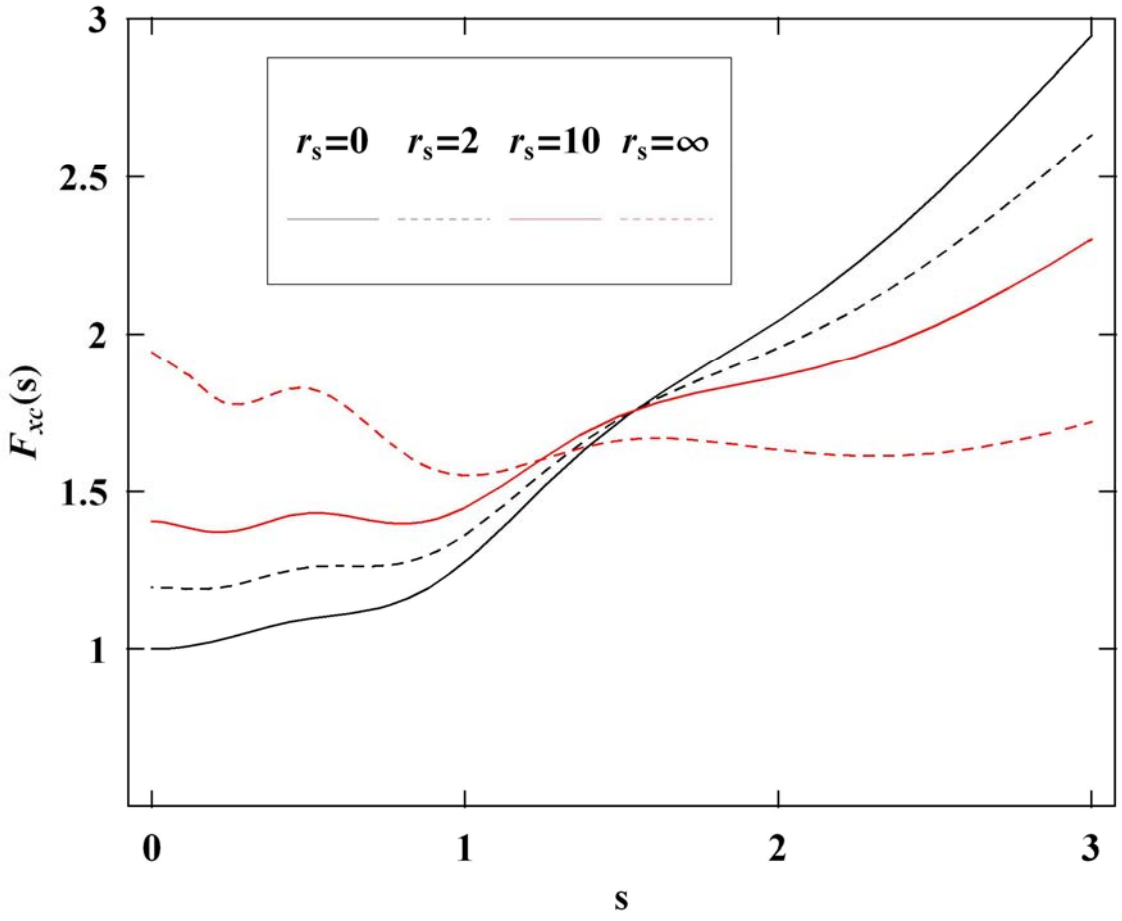
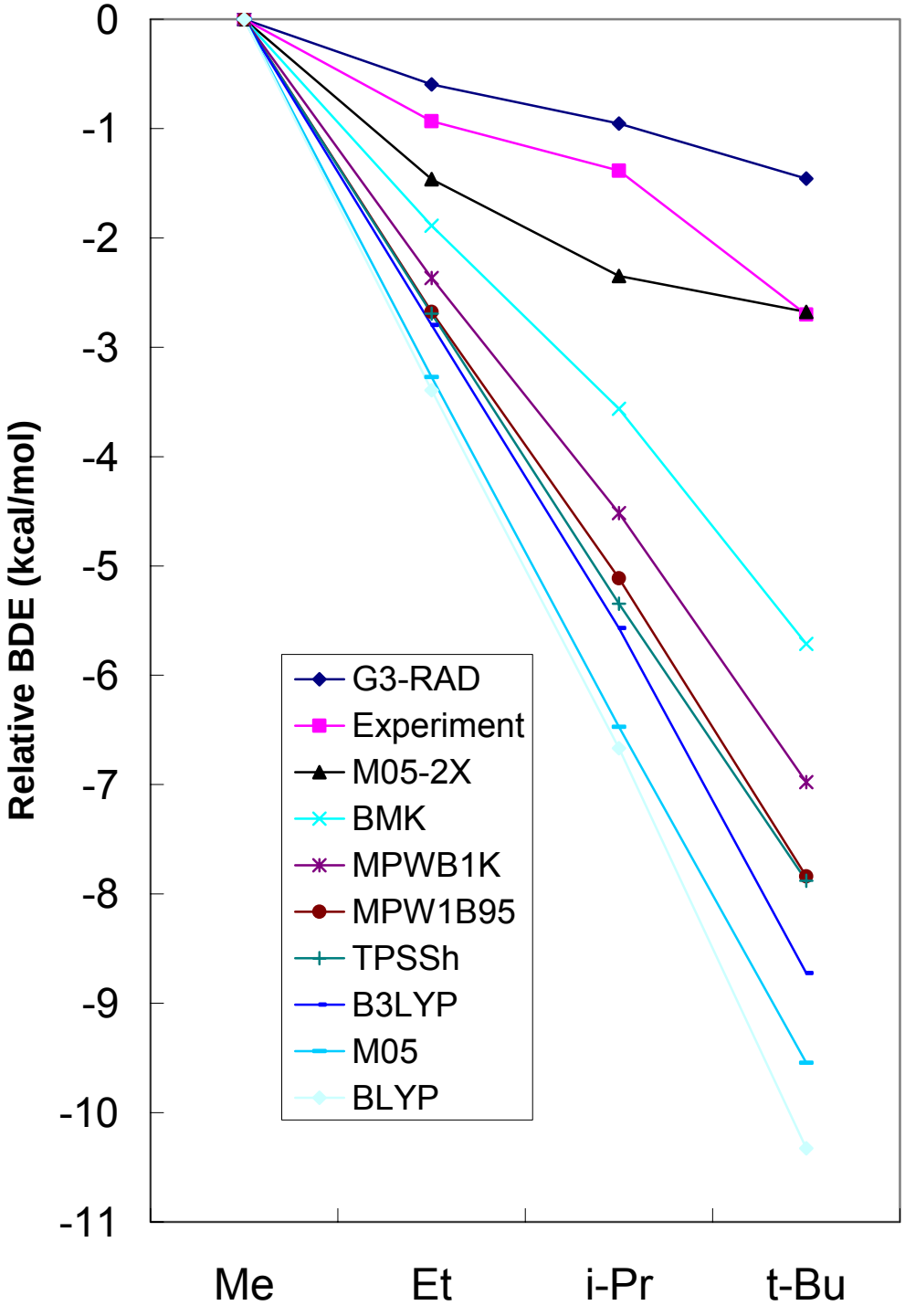


Figure 6.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Et
i-Pr
t-Bu
G3-RAD
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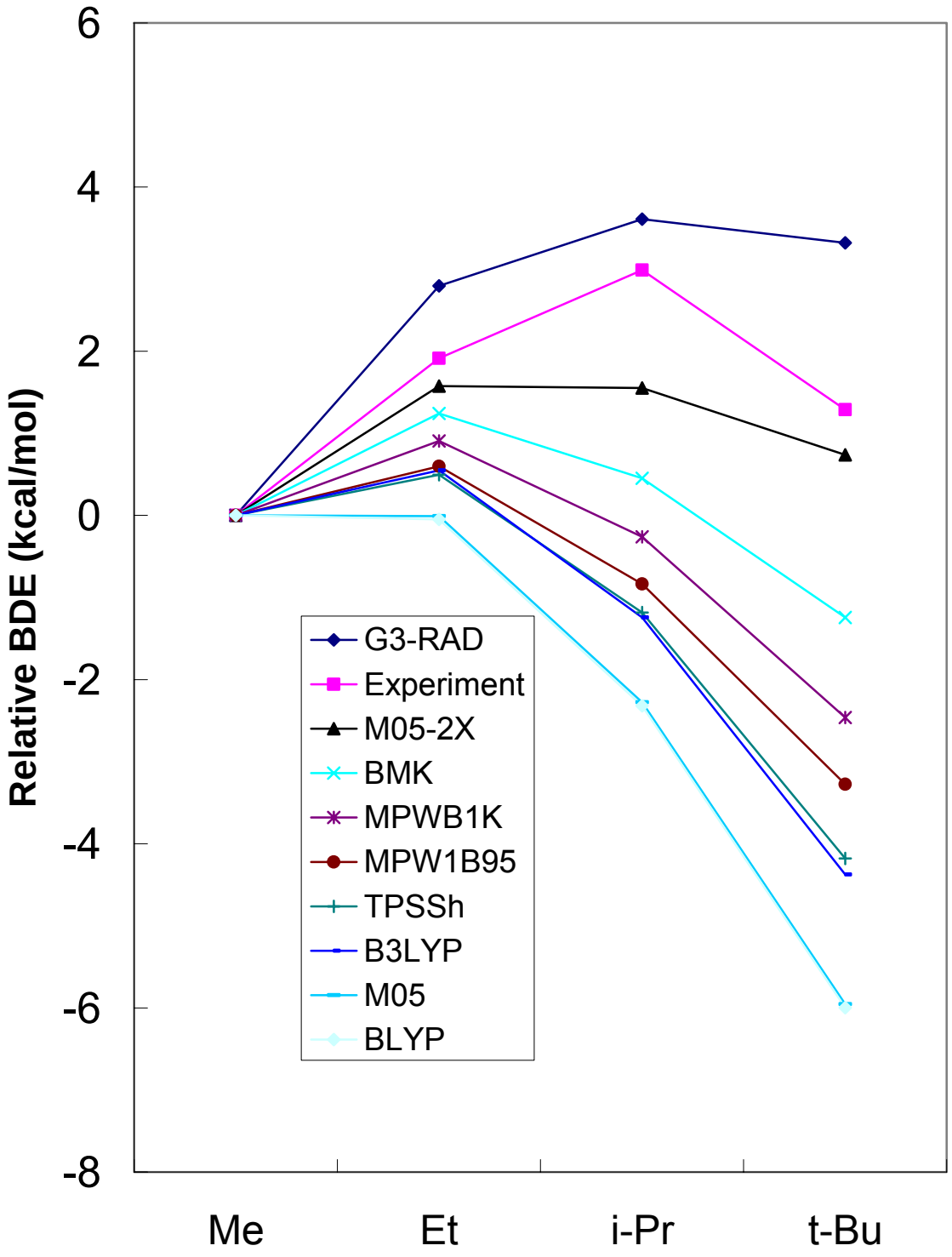
BMK
MPWB1K
MPW1B95
TPSSh
B3LYP
M05
BLYP

Figure 7.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-6
-8
Relative BDE (kcal/mol)
Me
Et
i-Pr
t-Bu
G3-RAD
Experiment
M05-2X
BMK
MPWB1K
MPW1B95
TPSSh
B3LYP
M05
BLYP