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ABSTRACT

In two recent papers [A. D. Becke, J. Chem. Phys. **156**, 214101 (2022) and A. D. Becke, J. Chem. Phys. **157**, 234102 (2022)], we compared two Kohn–Sham density functionals based on *physical modeling* and *theory* with the best density-functional power-series fits in the literature. The best error statistics reported to date for a hybrid functional on the general main-group thermochemistry, kinetics, and noncovalent interactions (GMTKN55) chemical database of Goerigk *et al.* [Phys. Chem. Chem. Phys. **19**, 32184 (2017)] were obtained. In the present work, additional second-order perturbation-theory terms are considered. The result is a 12-parameter double-hybrid density functional with the lowest GMTKN55 WTMAD2 "weighted total mean absolute deviation" error (1.76 kcal/mol) yet seen for any hybrid or double-hybrid density-functional approximation. We call it "DH23."

The GMTKN55 ("general main-group thermochemistry, kinetics, and noncovalent interactions") database of Goerigk and coworkers[1] contains 1505 chemical reaction and barrier-height reference energies obtained from high-level wavefunction computations from over 50 sources. GMTKN55 and its predecessors, GMTKN24[2] and GMTKN30,[3] were compiled in order to assess the ever-growing number of density-functional theory (DFT) approximations in the literature. The database is composed of 55 subsets organized into five categories representing different chemical reaction types: basic properties, reactions between larger systems and isomerizations, barrier heights, and inter- and intra-molecular noncovalent interactions. Table S1 of the supplementary material describes the subsets in each category and Table S2 gives references to the original literature sources.

Although the intention of the authors of GMTKN55 was the *assessment* of density-functional approximations (DFAs), its complexity and diversity make GMTKN55 highly attractive as a database for *fitting* of DFAs as well. The first (we believe) such fit was by Santra, Sylvetsky, and Martin,[4] who trained double-hybrid (DH) functionals on the full GMTKN55 data. Very recently, Becke[5,6] has trained hybrid DFAs on a slightly reduced variant of GMTKN55. The focus of Becke's work was to test a suite of physically and theoretically motivated density-functional *models* against heavily fit functionals such as ωB97X-V[7] and ωB97M-V[8] from the work of Mardirossian and Head-Gordon. Until Becke's work, ωB97X-V and ωB97M-V, trained on the massive MGCDB84[9] "main-group chemistry database," were the best-performing hybrid functionals tested on GMTKN55.[1,10] Since Santra and Martin had GMTKN55 second-order perturbation theory (PT2) correlation energies in hand from their DH computations, they suggested to Becke that it might be interesting to combine their PT2 energies with his DFT models. This Communication describes the outcome of that suggestion. In the end, we obtain a double-hybrid density functional with the lowest GMTKN55 error statistics reported to date.

To begin, we briefly review the exchange and correlation models used by Becke in his GMTKN55 trials. Full details can be found in Refs. 5 and 6. Our parent functional,[6] which will be appended by power-series and PT2 terms later, is

$$E_{XC}^{0} = E_X^{exact} + a_{NDC}^{opp} U_{NDC}^{opp} + a_{NDC}^{par} U_{NDC}^{par} + a_{DC}^{opp} E_{DC}^{opp} + a_{DC}^{par} E_{DC}^{par} + a_X^{BR}(E_X^{BR} - E_X^{exact}) + E_{C_6}^{XDM} + s_{RC}(E_{C_8}^{XDM} + E_{C_{10}}^{XDM}). \quad (1)$$

The opposite-spin (opp) and parallel-spin (par) NDC terms are explicit models of *non*-dynamical potential energy of correlation[11] ("B05"). B05 is highly nonlocal, requiring the exact-exchange energy density at every grid point. The DC terms are total energies of dynamical correlation modeled as in Refs. 12 and 13. The term $a_X^{BR}(E_X^{BR} - E_X^{exact})$, involving the Becke-Roussel (BR) exchange model,[14] simulates non-dynamical correlation by virtue of the locality of BR exchange. The C_6, C_8, and C_{10} dispersion terms are from the XDM (exchange-hole dipole moment) model of Becke and Johnson.[15–18] The five "a" pre-factors and the s_{RC} pre-factor allow for fine tuning to GMTKN55 data by least squares fitting. The "repulsion correction" factor s_{RC} controls the interplay between the correlation terms and the dispersion terms to give correct Pauli repulsion when atomic densities overlap. All terms in the parent functional are fully described in the Appendixes of Ref. 5.

Each term in Eq. (1) is based on an underlying reference-point-by-reference-point model of its associated exchange/correlation hole. Each model is governed by exact short-range behavior and normalization constraints at every point. The BR, NDC, and XDM models rely on the Taylor expansion of the exact spherically averaged exchange hole to second order[19] as follows:

$$h_{X\sigma}^{exact}(\boldsymbol{r}, s) = -\rho_\sigma - Q_\sigma s^2 + \cdots, \tag{2}$$

where

$$Q_\sigma = \frac{1}{6}\left(\nabla^2\rho_\sigma - 2D_\sigma\right) \tag{3}$$

and

$$D_\sigma = \tau_\sigma - \frac{1}{4}\frac{(\nabla\rho_\sigma)^2}{\rho_\sigma}, \tag{4}$$

and τ_σ is the kinetic-energy density (without a 1/2 factor), which is given by:

$$\tau_\sigma = \sum_i (\nabla\psi_{i\sigma})^2. \tag{5}$$

In the above, $\boldsymbol{r}$ is the reference point, s is the interelectronic distance, and σ is the electron spin. Q_σ is called the exchange-charge curvature. The DC dynamical correlation holes satisfy well-known interelectronic cusp conditions, as discussed in Ref. 12. Thus, each term in Eq. (1) reflects "good local physics" (as asserted in the title) at every reference point.

In Ref. 6, exchange and correlation power series were added to Eq. (1) to investigate whether significant improvements could thereby be made. We invoked a dimensionless power-series variable,

$$q_\sigma = \frac{Q_\sigma - Q_\sigma^{UEG}}{|Q_\sigma^{UEG}|}, \tag{6}$$

where

$$Q_\sigma^{UEG} = -\frac{1}{5}(6\pi^2)^{2/3}\rho_\sigma^{5/3} \tag{7}$$

is the exchange-charge curvature of the uniform electron gas (UEG). This variable, too, reflects "good local physics." If q_σ is positive (negative), then the local exchange-energy density is enhanced (attenuated) with respect to the UEG. Conversely, for dynamical correlation, positive (negative) q_σ implies attenuation (enhancement) of the local correlation-energy density with respect to its UEG counterpart. q_σ is predominantly positive in valence regions and negative inside atomic cores.

As q_σ has infinite range, $-\infty < q_\sigma < +\infty$, remapping into a finite domain is desirable. We use the same mapping for exchange, opposite-spin correlation, and parallel-spin correlation, but with different constants γ_X, γ_{Copp}, and γ_{Cpar} for each:

$$w_{X\sigma} = \frac{\gamma_X q_\sigma}{\sqrt{1+\gamma_X^2 q_\sigma^2}},\ w_{C\alpha\beta} = \frac{\gamma_{Copp} q_{\alpha\beta}}{\sqrt{1+\gamma_{Copp}^2 q_{\alpha\beta}^2}},\ w_{C\sigma\sigma} = \frac{\gamma_{Cpar} q_\sigma}{\sqrt{1+\gamma_{Cpar}^2 q_\sigma^2}}, \tag{8}$$

with

$$q_{\alpha\beta} = \frac{Q_\alpha + Q_\beta - Q_\alpha^{UEG} - Q_\beta^{UEG}}{|Q_\alpha^{UEG} + Q_\beta^{UEG}|} \tag{9}$$

and $\gamma_X = 0.11$, $\gamma_{Copp} = 0.14$, and $\gamma_{Cpar} = 1.6$. The range of the w variable(s) is $-1 \le w \le +1$, and $w = 0$ corresponds to the UEG limit. We then add exchange, opposite-spin, and parallel-spin power series to the parent functional, Eq. (1), as follows:

$$\begin{aligned} E_{XC} = E_{XC}^0 + c_{X,0}(E_X^{UEG} - E_X^{exact}) + \sum_{i=1}^{m_X} c_{X,i} \sum_\sigma \int e_{X\sigma}^{UEG} w_{X\sigma}^i d^3\boldsymbol{r} \\ + \sum_{i=0}^{m_{Copp}} c_{Copp,i} \int e_{C\alpha\beta}^{UEG} w_{C\alpha\beta}^i d^3\boldsymbol{r} + \sum_{i=0}^{m_{Cpar}} c_{Cpar,i} \\ \times \sum_\sigma \int e_{C\sigma\sigma}^{UEG} f_\sigma^{SCC} w_{C\sigma\sigma}^i d^3\boldsymbol{r}, \end{aligned} \tag{10}$$

with respective expansion orders m_X, m_{Copp}, and m_{Cpar}. An additional *self-correlation* correction

$$f_\sigma^{SCC} = \frac{D_\sigma}{\tau_\sigma} \tag{11}$$

is inserted into parallel-spin correlation terms to guarantee zero correlation energy in all one-electron systems. We subtract E_X^{exact} from the $i = 0$ term in the exchange series to enforce the UEG limit. The UEG limit is not, however, enforced for correlation. Full details are available in Ref. 6, where this functional is called "B22plus."

The overall performance of a DFA on GMTKN55 will be assessed[1] by the weighted total mean absolute deviation (WTMAD2),

$$\text{WTMAD2} = \frac{1}{\sum_{i=1}^{55} N_i} \sum_{i=1}^{55} N_i \frac{56.84\text{kcal/mol}}{|\Delta E|_{\text{avg},i}} \text{MAD}_i. \tag{12}$$

The MAD (mean absolute deviation) of each subset i is weighted by the energy ratio $56.84/|\Delta E|_{\text{avg},i}$ and the number of data N_i in the set, as given in Table S1. The constant 56.84 kcal/mol is the average of $|\Delta E|_{\text{avg},i}$ over all the sets. 62 of the 1505 reactions in GMTKN55 involve elements heavier than Kr: namely, all 28 reactions in the HEAVY28 set, four reactions in the HEAVYSB11 set, and 30 reactions in the HAL59 set. These require core pseudopotentials (PPs) in their computation. We omitted them in Refs. 5 and 6 in favor of the 1443 reactions involving all-electron calculations only. Here, we do the same in our initial fits to touch base with our earlier work. We call this "all-electron" database GMTKN54 and its

analogous [Eq. (12)] error measure WTMAD2(54). As the HEAVY28 set is excluded in WTMAD2(54), the summations in Eq. (12) are over 54 sets instead of 55, but we retain the 56.84 kcal/mol constant and the N_i values of Table S1 for compatibility with the literature. We will test on the full GMTKN55 database when our initial fits are completed.

Pre-factors and expansion coefficients are determined by least squares fitting. We fit to the GMTKN54 (or GMTKN55) data, taking the weight of each data point from Eq. (12) except for the W4-11 atomization energies, which are weighted by 1 (see Ref. 5). Note that this is *not* the same as minimizing the WTMAD2 directly, as has been done by the Martin group in Ref. 4 and later papers. For "B22plus" in Ref. 6, we chose optimum expansion orders $m_X = 2$, $m_{Copp} = 3$, and $m_{Cpar} = 4$ for a total of 12 series expansion coefficients. With the six pre-factors in E_{XC}^0 included, B22plus has 18 linear parameters altogether. We used BHandHLYP orbitals computed with the Gaussian 16 program[20] and the Dunning aug-cc-pVTZ basis set[21] (def2-TZVP[22] for K and Ca and cc-pVTZ for the C_{60} isomers). All correlation and power-series terms were computed using an in-house "postG" code. Technical details are given in the supplementary material, Appendix S1. The resulting B22plus WTMAD2(54) was 2.76 kcal/mol, substantially better than the previous best hybrid functionals, "B22" of Ref. 5 at 3.31 kcal/mol and ωB97M-V at 3.37 kcal/mol. See Ref. 6 for additional information and statistics.

We now consider the further addition of second-order perturbation theory (PT2) terms in the *double*-hybrid DFA framework. Contemporary double hybrids originated with Grimme[23] and employ an MP2-like (Møller–Plesset perturbation theory) correlation component evaluated using Kohn–Sham DFT orbitals instead of Hartree–Fock (HF) orbitals. This is known as in Görling–Levy perturbation theory, GLPT2.[24] The benefits of using GLPT2 vs HF-MP2 as originally proposed in Ref. 25 are analyzed in Ref. 26. The authors of the GMTKN55 paper[1] clearly showed that double hybrids are superior to hybrid functionals, which use only occupied orbitals. The literature on double hybrids is vast. A recent review by Martin and Santra[27] provides an overview of the current status of the field. Earlier reviews may be found in Refs. 28–30, and a comprehensive study of DH functionals on the GMTKN55 database has been presented by Mehta *et al.*[31]

ωB97M(2) from Mardirossian and Head-Gordon[32] is considered by many to be the leading double hybrid today. It has 14 independent parameters and is a "meta"-GGA (generalized gradient approximation) power series functional obtained after prescreening *trillions* of candidates. The WTMAD2 of ωB97M(2) on GMTKN55 is 2.13 kcal/mol.[33] Santra, Semidalas, and Martin[34] have reported WTMAD2s as low as 1.85 kcal/mol by experimenting with an "XYG8" functional form that includes separate LDA (local density approximation) and GGA coefficients and a sequence of input orbitals with varying amounts of exact-exchange fraction, as inspired by Refs. 35 and 36. These are not constrained to the correct asymptotic C_6 limit, as is ωB97M(2). They recover about 50%–60% of the correct C_6.

In the present work, we add PT2 terms to Eqs. (1) and (10) in a manner that respects the correct asymptotic C_6 limit. Our functional therefore reflects not only good local physics but good long-range physics as well. Independent opposite-spin and parallel-spin PT2 correlation energies are appended to Eq. (10) as follows:

$$\begin{aligned} E_{XC} = {} & E_{XC}^0 + c_{X,0}\left(E_X^{UEG} - E_X^{exact}\right) + \sum_{i=1}^{m_X} c_{X,i} \sum_\sigma \int e_{X\sigma}^{UEG} w_{X\sigma}^i d^3\boldsymbol{r} \\ & + \sum_{i=0}^{m_{Copp}} c_{Copp,i} \int e_{C\alpha\beta}^{UEG} w_{C\alpha\beta}^i d^3\boldsymbol{r} + \sum_{i=0}^{m_{Cpar}} c_{Cpar,i} \\ & \times \sum_\sigma \int e_{C\sigma\sigma}^{UEG} f_\sigma^{SCC} w_{C\sigma\sigma}^i d^3\boldsymbol{r} \\ & + a_{PT2}^{opp}\left(E_{PT2}^{opp} - \frac{1}{2}E_{C_6}^{XDM}\right) + a_{PT2}^{par}\left(E_{PT2}^{par} - \frac{1}{2}E_{C_6}^{XDM}\right), \end{aligned} \tag{13}$$

where

$$E_{PT2}^{par} = E_{PT2}^{\alpha\alpha} + E_{PT2}^{\beta\beta}. \tag{14}$$

The logic in the added PT2 terms is simple. Lochan, Jung, and Head-Gordon[37] have stated that, at long range for two non-overlapping closed-shell systems, the opposite-spin and parallel-spin parts of the inter-system MP2 correlation energy are equal. Assuming that MP2 (PT2) and XDM give the correct asymptotic dispersion energy, we therefore have

$$E_{PT2}^{opp} = E_{PT2}^{par} = \frac{1}{2}E_{C_6}^{XDM} \tag{15}$$

at long range. The parent functional, Eq. (1), contains a full $E_{C_6}^{XDM}$ term. Hence, the PT2 terms in Eq. (13) must vanish asymptotically. By Eq. (15), they do.

PT2 energies are computed by the Q-Chem 6.0 program[38] using "resolution of the identity" (RI-MP2) speed-ups. As is common practice in DH applications, single-excitation terms, non-zero in principle in GLPT2, have been omitted. For the PT2 correlation energies, the same frozen-core settings were used as in Ref. 4. These calculations were run on the Weizmann Faculty of Chemistry's HPC facility "ChemFarm."

In our preliminary explorations, we discovered some welcome simplifications of Eq. (13). Power-series orders m_X, m_{Copp}, and m_{Cpar} beyond quadratic offered no improvements. Furthermore, the entire exchange series can be removed with negligible degradation of the WTMAD2(54). Most significantly, B05 non-dynamical correlation terms in the parent functional, Eq. (1), are *not important* in a DH context despite being critical to the success of B22plus.[6] PT2 correlation handily compensates B05, with WTMAD2(54) affected by less than ~0.05 kcal/mol if the latter is omitted. This is a major win, as the exact-exchange energy density required by B05 at every grid point is available in very few quantum chemistry programs. Hereafter, then, all results pertain to the simplified functional,

$$\begin{aligned} E_{XC} = {} & E_X^{exact} + a_{DC}^{opp} E_{DC}^{opp} + a_{DC}^{par} E_{DC}^{par} + a_X^{BR}\left(E_X^{BR} - E_X^{exact}\right) \\ & + E_{C_6}^{XDM} + s_{RC}\left(E_{C_8}^{XDM} + E_{C_{10}}^{XDM}\right) \\ & + \sum_{i=0}^{2} c_{Copp,i} \int e_{C\alpha\beta}^{UEG} w_{C\alpha\beta}^i d^3\boldsymbol{r} + \sum_{i=0}^{2} c_{Cpar,i} \\ & \times \sum_\sigma \int e_{C\sigma\sigma}^{UEG} f_\sigma^{SCC} w_{C\sigma\sigma}^i d^3\boldsymbol{r} \\ & + a_{PT2}^{opp}\left(E_{PT2}^{opp} - \frac{1}{2}E_{C_6}^{XDM}\right) + a_{PT2}^{par}\left(E_{PT2}^{par} - \frac{1}{2}E_{C_6}^{XDM}\right), \end{aligned} \tag{16}$$

with 12 linear coefficients altogether. This is two fewer than the number of parameters in ωB97M(2). We also note that after eliminating the exchange series from Eqs. (13), Eq. (16) *exactly* models the hydrogen atom at *every* reference point. Only BR-based functionals have this nice property.[14] We shall call the functional of Eq. (16) "DH23."

To connect with our previous work,[5,6] first tests have been carried out with BHandHLYP orbitals and the Dunning aug-cc-pVTZ basis set[21] (def2-TZVP[22] for K and Ca and cc-pVTZ for the C_{60} isomers). The resulting WTMAD2(54) is 2.18 kcal/mol, about 0.6 kcal/mol lower than for our B22plus hybrid. Next, we expand from the Dunning triple-zeta basis to the quadruple-zeta def2-QZVPP basis.[22] For subsets involving anions (AHB21, BH76 and BH76RC, G21EA, IL16, WATER27) or rare-gas interactions (RG18), diffuse functions are added using def2-QZVPPD.[39] We drop down, however, to def2-TZVPP for the very large UPU23 and C60ISO systems and the two largest isomers (1 and 4) in the ISOL24 subset. The BHandHLYP quadruple-zeta WTMAD2(54) is 1.76 kcal/mol, a substantial reduction from the Dunning triple-zeta 2.18 kcal/mol value.

BHandHLYP orbitals incorporate 50% Hartree–Fock (HF) exchange. It has been argued by Goerigk and Grimme,[3] and there is systematic computational evidence,[34] that orbitals with 20%–30% HF may offer better DH performance. We explore this by using "B1LYP" orbitals[40] with 25% HF exchange. We observe a slight decrease in the WTMAD2(54) from 1.76 (BHandHLYP) to 1.72 (B1LYP) kcal/mol, employing the same def2 basis sets described above. For completeness, B1LYP calculations have also been performed using diffuse basis functions everywhere (def2-QZVPPD, except def2-TZVPPD for UPU23, C60ISO, and the two largest ISOL24 isomers, 1 and 4). Universal diffuse functions have a minor effect on the WTMAD2(54), giving a value of 1.74 kcal/mol. Similar observations were made in Ref. 41.

The 1.72 kcal/mol WTMAD2(54) achieved here is more than 1 kcal/mol lower than the 2.76 kcal/mol of B22plus, our best hybrid functional of Ref. 6, and does not depend on the cumbersome B05 non-dynamical correlation energy. Readily available and economical (thanks to resolution of the identity RI-MP2 technology[42–44]) PT2 correlation is used instead. How important are the power-series terms in Eq. (16)? Omitting them loses six parameters, but raises our best B1LYP def2-QZVPP WTMAD2(54) from 1.72 to 2.11 kcal/mol, almost 0.4 kcal/mol higher. This is, nevertheless, rather good for DH with only six parameters. Table I summarizes our WTMAD2(54) results for BHandHLYP vs B1LYP input orbitals and the aug-cc-pVTZ vs def2-QZVPP basis sets.

TABLE I. WTMAD2(54) on GMTKN54, in kcal/mol.

Input orbitals/basis set	Equation (16)	Equation (16) without power series
BHandHLYP/aVTZ[a]	2.18	2.24
BHandHLYP/QZVPP[b]	1.76	2.05
B1LYP/QZVPP[b]	1.72	2.11
B1LYP/QZVPPD[c]	1.74 (12 parameters)	2.14 (6 parameters)

[a]aug-cc-pVTZ with exceptions noted in the text.
[b]def2-QZVPP with exceptions noted in the text.
[c]def2-QZVPPD with exceptions noted in the text.

TABLE II. Coefficients of Eq. (16) for B1LYP orbitals and the QZVPP[a] basis set, fit to the full GMTKN55 database.

a_{DC}^{opp}	0.010	$c_{Copp,0}$	0.449	a_{PT2}^{opp}	0.403
a_{DC}^{par}	1.536	$c_{Copp,1}$	−0.240	a_{PT2}^{par}	0.193
a_X^{BR}	0.164	$c_{Copp,2}$	0.553		
s_{RC}	−0.299	$c_{Cpar,0}$	−0.040		
		$c_{Cpar,1}$	−0.487		
		$c_{Cpar,2}$	0.772		

[a]def2-QZVPP with exceptions noted in the text.

Having established, on a foundation of all-electron calculations, that B1LYP orbitals and the def2-QZVPP basis set are good choices, we now perform a fit on the full GMTKN55 database, including the 62 reactions whose calculations require core pseudopotentials. To accommodate PPs, additional considerations and modifications beyond the descriptions in Refs. 5 and 6 were necessary for our XDM dispersion model. We defer discussion of these to the supplementary material, Appendix S2.

The GMTKN55 fit coefficients are given in Table II. The exact exchange fraction is a sizable 83.6%. The UEG limit for opposite-spin correlation is 0.86, not far from 1, and for parallel-spin correlation is roughly 0.92 (using that the UEG limit of E_{DC}^{par} is about half the correct value[12]). The negative value, −0.299, of the repulsion-correction scale factor s_{RC} implies that PT2 overestimates dispersion energy at intermediate range. This echoes previous findings of Martin *et al.*[27,45]

In Table III, we list WTMAD2s for each of the GMTKN55 chemical categories and for the complete database. For comparison, we include data for four additional leading DH functionals: ωB97M(2)[32] of Mardirossian and Head-Gordon, and XYG8[f1]@B_{20}LYP,[34] revDSD-PBEP86-D4,[33] and xDSD$_{75}$-PBEP86-D4[33] of Martin *et al.* The number of parameters in these functionals is 14 for ωB97M(2) and eight for the last three vs 12 for DH23. All computations employ the def2-QZVPP basis set with exceptions as noted earlier. DH23 has the smallest WTMAD2 on the full GMTKN55 database at 1.76 kcal/mol, followed by XYG8[f1]@B_{20}LYP at 1.85 kcal/mol. The categories "basic properties of small systems" and "reaction and isomerization energies of large systems" are clearly led by DH23, but XYG8[f1]@B_{20}LYP has a slight edge for barrier heights and (all) noncovalent interactions. See Table S3 of the supplementary material for MADs of all the considered functionals on all the GMTKN55 subsets. Noteworthy is the superior performance of DH23 on the "mindless benchmarking" MB16-43 set of artificial molecules, designed to test the robustness of DFAs. Table III is represented by a radar plot in Fig. 1.

Let us comment, finally, on the asymptotic C_6 limit. DH23 and ωB97M(2) recover the correct limit by design. XYG8[f1]@B_{20}LYP, revDSD-PBEP86-D4, and xDSD$_{75}$-PBEP86-D4 recover about 50%, 90%, and 80%, respectively. The importance of enforcing the correct C_6 limit is debatable in molecules near equilibrium structures. See the work of Wu and Truhlar[46] for an assessment on very large

TABLE III. WTMAD2 (kcal/mol) for GMTKN55 categories.[a]

DH23[b]	ωB97M(2)[c]	XYG8[d]	revDSD[e]	xDSD[f]
Basic properties and reaction energies of small systems:				
1.18	1.39	1.42	1.75	1.63
Reaction energies for large systems and isomerization reactions:				
2.06	2.61	2.32	3.59	3.07
Reaction barrier heights:				
1.81	1.66	1.65	2.02	1.95
Intermolecular noncovalent interactions:				
1.99	2.44	1.99	2.29	2.28
Intramolecular noncovalent interactions:				
2.19	3.00	2.17	2.08	2.11
All noncovalent interactions:				
2.09	2.72	2.07	2.18	2.20
All GMTKN55:				
1.76	2.13	1.85	2.25	2.12

[a]See Table S1 of the supplementary material.
[b]Present work, Eq. (16).
[c]Reference 32.
[d]XYG8[f1]@B20LYP, Ref. 34 (parameter values in line 5 of Table I).
[e]revDSD-PBEP86-D4, Ref. 33 (parameter values in line 6 of Table S2).
[f]xDSD75-PBEP86-D4, Ref. 33 (parameter values in line 1 of Table I).

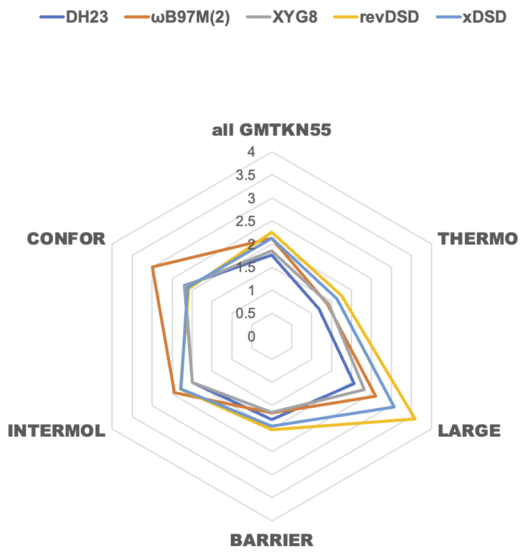

FIG. 1. Radar plot of WTMAD2s of GMTKN55 chemical categories in Table III. Functional designations as in the header of Table III. THERMO: Basic properties and reaction energies of small systems. LARGE: Reaction energies for large systems and isomerization reactions. BARRIER: Reaction barrier heights. INTERMOL: Intermolecular noncovalent interactions. CONFOR: Intramolecular noncovalent interactions.

systems containing 200–910 atoms. Nevertheless, good physics is our goal for DH23.

Of the many hundreds of hybrid and double-hybrid DFAs tested on the GMTKN55 database so far, DH23, at 1.76 kcal/mol, has the lowest WTMAD2. This is gratifying, given the simple manner in which it was derived. ωB97M(2) was derived from trillions of prescreening fits. The functionals XYG8[f1]@B_{20}LYP, revDSD-PBEP86-D4, and xDSD$_{75}$-PBEP86-D4 are the result of many trials with the zoo[1] of known local-density, GGA, and *meta*-GGA exchange and correlation functionals. DH23, on the other hand, is based on explicit exchange–correlation hole models satisfying exact short-range-behavior and normalization constraints at every point, and a power-series variable q_σ governing the enhancement/attenuation of exchange and correlation energy densities with respect to the UEG, again, at every point. With minimal experimentation, DH23 was quickly and straightforwardly derived from its hybrid-functional parents.[5,6]

The calibrations of this work are on main-group and organic thermochemistry, including noncovalent interactions. Preliminary tests on 3d transition-metal reactions, described in Appendix S3 of the supplementary material, are encouraging. A full assessment of the performance of DH23 in transition-metal chemistry will be undertaken in future work.

See the supplementary material for tables of the 55 subsets of the GMTKN55 database and their original literature references, and the GMTKN55 MADs for the five DH functionals compared in this work. Also technical details of the "postG" calculations, modifications of the XDM dispersion formulas to accommodate core pseudopotentials, and preliminary 3d transition-metal results, are presented in Appendixes S1–S3.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Axel D. Becke: Conceptualization (equal); Writing – original draft (lead); Writing – review & editing (lead). **Golokesh Santra**: Conceptualization (equal); Writing – review & editing (supporting). **Jan M. L. Martin**: Conceptualization (equal); Writing – original draft (supporting); Writing – review & editing (supporting).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

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