THE JOURNAL OF
PHYSICAL
CHEMISTRY A
LETTERS

2008, *112,* 3−8
Published on Web 12/15/2007

Double-Hybrid Functionals for Thermochemical Kinetics

Alex Tarnopolsky, Amir Karton, Rotem Sertchook, and Dana Vuzman
Department of Organic Chemistry, Weizmann Institute of Science, IL-76100 Reḥovot, Israel

Jan M. L. Martin*
Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113

Received: October 19, 2007; In Final Form: November 20, 2007

We propose two new double-hybrid functionals, denoted B2K-PLYP and mPW2K-PLYP, which yield thermochemical performance comparable to existing double-hybrid functionals but offer superior performance for barrier heights of various kinds. We show that the new functionals yield excellent performance for all of the following: (a) main-group thermochemistry; (b) main-group thermochemical kinetics; (c) late transition metal reactions. In addition, B2K-PLYP performs well for weak interactions.

I. Introduction

Recently, Grimme and co-workers have proposed a family of what they term “double hybrid exchange-correlation functionals”.[1,2] (The term was coined earlier[3] for multistep methods involving both DFT and ab initio steps. In terms of the “Jacob’s Ladder” outlined by Perdew,[4] double hybrids may be termed “fifth-rung functionals”.) For equilibrium thermochemistry, these functionals offer performance markedly superior to conventional DFT functionals and approach that of composite ab initio methods such as G1 and G2 theory,[45] at a small fraction of the latter’s computational cost.

Operationally, a “double hybrid” calculation consists of the following steps. First, the Kohn−Sham equations are solved self-consistently for a given hybrid DFT functional. Second, the MP2 (second-order perturbation theory) correlation energy is then calculated in the space of the converged Kohn−Sham orbitals (effectively making it second-order Görling−Levy perturbation theory).[5] Finally, the total energy is obtained as

$$E_{\mathrm{xc}} = (1 - c_1)E_{\mathrm{x,GGA}} + c_1 E_{\mathrm{x,HF}} + (1 - c_2)E_{\mathrm{c,GGA}} + c_2 E_2 \tag{1}$$

where $E_{\mathrm{x,GGA}}$ and $E_{\mathrm{c,GGA}}$ represent the exchange and correlation parts of the underlying DFT functional, $E_{\mathrm{x,HF}}$ an E_2 are the Hartree−Fock type exchange energy and MP2 correlation energy, respectively, in the basis of the converged Kohn−Sham orbitals, and c_1 and c_2 are empirical mixing coefficients. The specific $E_{\mathrm{c,GGA}}$ considered by Grimme was Lee−Yang−Parr (LYP),[6] combined with the Becke88 exchange functional[7] into B2-PLYP[1] (with $c_1 = 0.53$ and $c_2 = 0.27$), and with modified Perdew−Wang (mPW) exchange[8] into mPW2-PLYP[2] (with $c_1 = 0.55$ and $c_2 = 0.25$).

Energy calculations of this type can in fact be carried out, with some nonstandard input decks, using unmodified versions of certain popular quantum chemical codes such as Gaussian 03.[9] Very recently, Neese et al.[10] implemented analytical first derivatives for such methods in the freeware ORCA quantum chemistry program system.[11]

With conventional MP2 codes, the MP2 step represents a considerable additional expense, which would seem to obviate one of the main advantages of DFT over wavefunction ab initio methods. However, with the RI-MP2 approximation,[12] this issue can basically be eliminated at very little loss in accuracy.

A physical rationale for these functionals[13] may lie in the fact that although typical DFT correlation functionals will be superior to MP2 in the description of short-range correlation, MP2 is very well suited for the description of long-range correlation, and a “marriage of convenience” between the two correlation methods may thus have a fighting chance of handling both types of correlation.

Our group is heavily involved in organic (e.g., ref 14) and organometallic (see, e.g., refs 15−18) mechanistic chemistry. Much of our research involves multiple competing reaction pathways with intermediate energies and reaction barrier heights that are within a few kcal/mol of each other. As such, we are highly interested in a functional that can handle all of the following with 1−2 kcal/mol accuracy: (1) main-group thermochemistry; (2) main-group barrier heights; (3) reactions at late transition metal centers. As we found in a recent validation study,[19] none of the currently available offerings satisfy more than two out of these three criteria.

We will show below that double-hybrid functionals do offer such an option and will propose two new double-hybrid functionals, B2K-PLYP and mPW2K-PLYP, that offer particularly good performance for barrier heights without appreciably compromising on thermochemistry.

II. Computational Methods

All calculations reported here were carried out using a locally modified version of the Gaussian 03 electronic structure program[9] running on the Martin group Linux cluster at Weizmann.

---

* On sabbatical from: Department of Organic Chemistry, Weizmann Institute of Science, IL-76100 Reovot, Israel. Electronic address: gershom@weizmann.ac.il.

10.1021/jp710179r CCC: $40.75

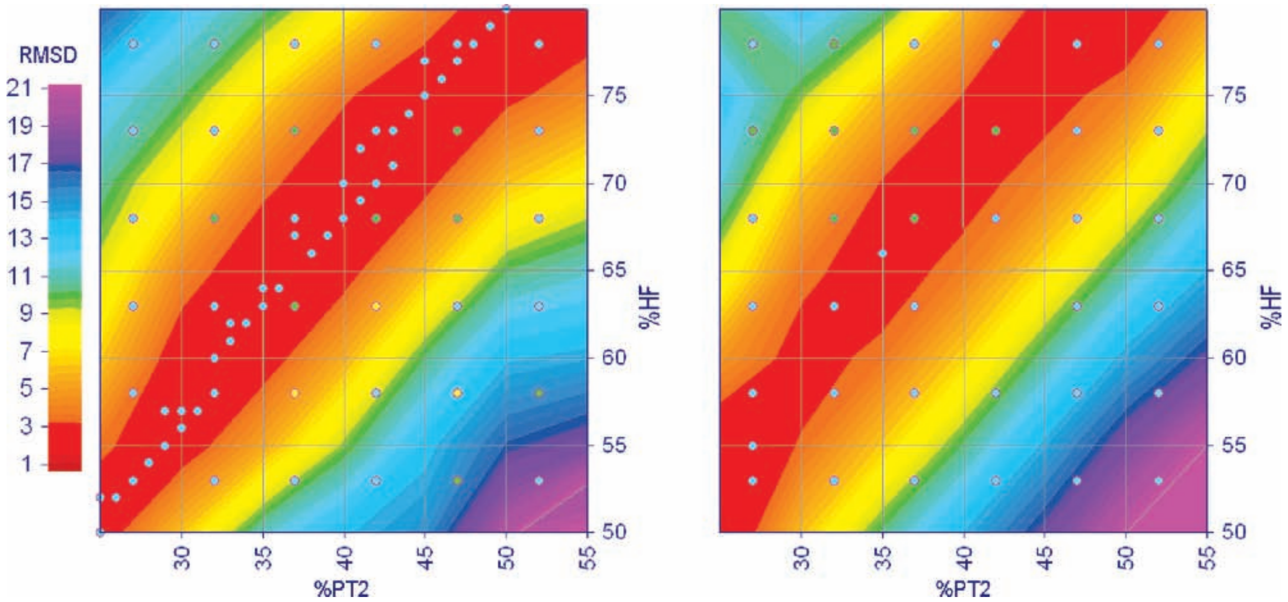

Figure 1. RMSD (kcal/mol) for the AE6 data set of double-hybrid B2-PLYP forms as a function of the percentages of MP2-type correlation (abscissa) and HF-type exchange (ordinate). Results with the aug-pc2 basis set are presented in the left-hand pane, with the aug-pc3 basis set in the right-hand pane.

A number of validation data sets were used. These include the following: (a) the BMK validation set[20] of 464 energetics, as well as various subsets thereof; (b) the "representative" AE6 (six atomization energies) and BH6 (six barrier heights) sets of Lynch and Truhlar;[21] (c) the training set for the W3[22] and W4[23] ab initio computational thermochemistry approaches,[22] which consist of 33 small molecules with experimentally very well-established atomization energies, and which span the gamut from essentially pure dynamical correlation to strong nondynamical correlation (W3); (d) the Truhlar group sets of 38 hydrogen-transfer barrier heights (HTBH38)[24] and 38 non-hydrogen-transfer barrier heights (NHTBH38);[24] (e) the weak interactions data set of Zhao and Truhlar.[25] In all cases, the reference geometries for these data sets were employed without further geometry optimization.

The basis sets used belong to the "polarization consistent" family of Jensen.[26−30] We primarily considered two basis sets: aug-pc2 (which is of triple-ζ spdf +diffuse quality, and quite close to the Kohn−Sham basis set limit for DFT calculations) and aug-pc3 (which is of quadruple- to quintuple-zeta spdfg +diffuse quality, and was required for basis set convergence in the double-hybrid calculations). As required for the proper treatment of second-row atoms in high oxidation states,[31] high-exponent *d* functions were added. To verify convergence, we also carried out some calculations using the even larger aug-pc4 basis set.

In the comparisons, we considered a number of other exchange-correlation functionals, such as B3LYP,[32] BMK,[20] PBE0,[33] B1B95,[34] B97-1[35] TPSSKCIS,[36−38] BB1K,[39] mPW1B95,[40] PW6B95,[41] and PWB6K,[41] as well as the very recent M06 (Minnesota-06) family of functionals.[42−44]

III. Results and Discussion

Initially, to get our bearings, we mapped the AE6 surface[21] with both the aug-pc2 and aug-pc3 basis sets. The result can be seen in the left-hand and right-hand panes of Figure 1, respectively.

Perhaps the most striking feature of both graphs is that neither has a clearly defined minimum, but that both exhibit a "canal" or "straits", at the bottom of which the rms deviation is fairly constant. For the aug-pc2 basis set, the straits run roughly along a line going through (52,25) and (74,45); for the aug-pc3 basis set, they run roughly through (54,45) and (78,45). One of the prices one pays for the introduction of MP2-like correlation energy is that one inherits the slow basis set convergence of dynamical correlation in wavefunction ab initio theory: as a result, the aug-pc2 atomization energies exhibit very significant basis set incompleteness, and optimizing a double-hybrid with such a small basis set will lead to an exaggerated MP2 admixture coefficient to compensate. As a result, a double hybrid optimized for such a basis set will be a basis set-specific one, rather than allow for establishing systematic convergence to the one-particle basis set limit.

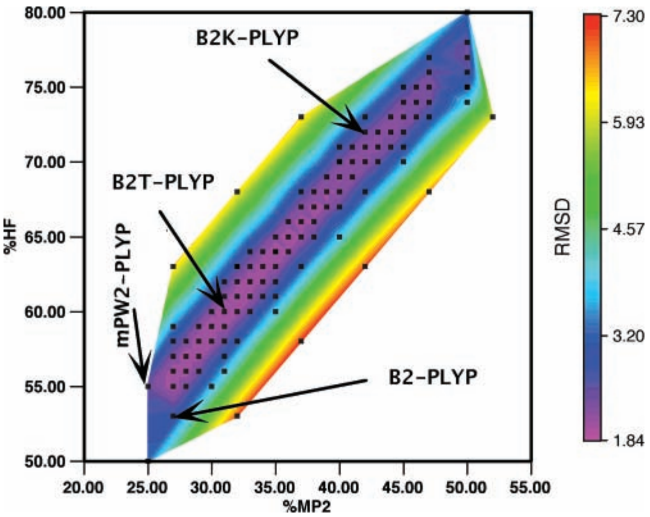

Figure 2. RMSD (kcal/mol) for the W3 atomization energies data set of double-hybrid B2-PLYP forms as a function of the percentages of MP2-type correlation (abscissa) and HF-type exchange (ordinate). The aug-pc3 basis set was used throughout.

We then proceeded to consider a larger set of reference data, namely the training set for the W3 ab initio computational thermochemistry method.[22] Here, only the aug-pc3 basis set was considered, and we limited ourselves to the region around the "straits". The latter run approximately on a line through the

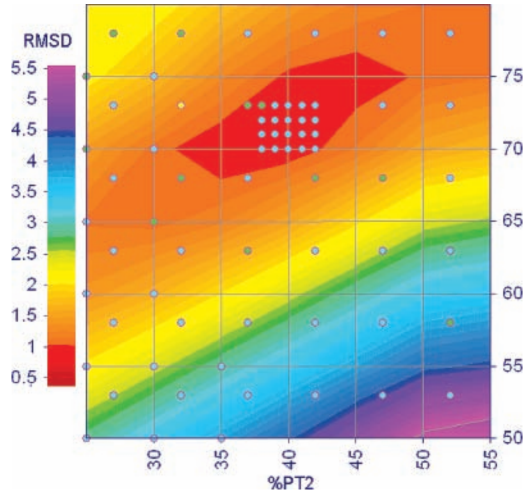

Figure 3. RMSD (kcal/mol) for the BH6 hydrogen-transfer barrier data set of double-hybrid B2-PLYP forms as a function of the percentages of MP2-type correlation (abscissa) and HF-type exchange (ordinate). The aug-pc2 basis set was used throughout; the aug-pc3 surface is nearly indistinguishable.

TABLE 1: RMS Errors of Various Functionals (in kcal/mol)[a]

		B2-PLYP	B2K-PLYP	B2T-PLYP	PBE2K-PLYP	O2K-PLYP	mPW2-PLYP	mPW2K-PLYP	B3LYP	PBE0	B97-1	BMK	M06L	M06	M06-2X	M06-HF
	BH6/apc-2	2.48	0.54	1.44	0.63	0.65	1.93	0.72	5.24	5.08	5.06	1.97	5.08	1.97	1.43	2.31
	W3/apc2+d	2.54(2.58)	4.05(3.58)	3.08(2.84)	3.00	4.67	3.11(2.79)	3.68(3.05)	3.59	3.91	3.87	3.58	5.22	3.56	3.98	---
	W3/apc3+d	2.55(2.59)	2.84(2.30)	2.15(1.95)	2.34	3.42	2.29(1.97)	2.44(1.98)	3.19	3.66	4.01	3.47	4.91	3.38	3.83	---
	W3/apc4	2.68(2.72)	2.58(2.05)	2.04(1.83)			2.20(1.90)	2.27(1.84)								
	W3/apc2+d/CBS10	3.63(3.65)	2.72(2.57)	2.59(2.57)			2.60(2.49)	2.99(2.93)								
	W3/apc3+d/CBS15	3.12(3.15)	2.36(1.97)	2.12(2.00)			2.25(2.05)	2.40(2.16)								
	W3/apc4/CBS20	2.98(3.01)	2.33(1.89)	2.05(1.91)			2.19(1.96)	2.24(1.94)								
non-H	HAT	4.16	3.10	2.71	3.12	3.29	4.93	3.00	9.12	7.53	6.48	2.28	8.08	4.42	2.27	
transfer	SN2	1.92	0.50	1.18	0.72	1.42	2.64	0.59	2.91	1.59	2.73	1.78	2.56	1.42	1.68	1.88
reactions	UAR	1.12	1.67	1.09	1.82	2.03	1.62	1.63	2.95	2.71	2.13	1.61	2.20	1.91	1.05	
	NHTBH38//BMK	2.71	1.97	1.79	2.03	2.31	2.40	1.92	5.66	4.57	4.19	1.91	4.97	2.82	1.76	
weak	HB6	0.17	0.55	0.26	1.07	0.68	0.30	0.83	0.96	0.36	0.48	0.84	0.26	0.37	0.25	0.53
interactions	CT7	0.86	0.77	0.76	1.08	0.60	0.30	1.04	0.91	1.33	1.38	0.58	1.79	0.79	0.44	0.62
	DI6	0.34	0.32	0.29	0.60	0.36	0.33	0.49	0.85	0.44	0.39	0.83	0.51	0.38	0.32	0.59
	WI9	0.26	0.22	0.19	0.35	0.21	0.18	0.37	0.80	0.45	0.38	0.98	0.29	0.29	0.26	0.34
	nonbonded int.//BMK	0.50	0.50	0.43	0.81	0.48	0.27	0.71	0.87	0.76	0.78	0.83	0.95	0.53	0.34	0.60
H-transfer	HTBH38/apc2	2.43	0.86	1.59	0.92	0.99	2.33	0.96	5.15	4.98	5.22	1.88	5.11	2.57	1.57	2.58
	Pd-reactions	0.98	1.17	0.85	2.13	2.05	0.88	1.08	2.22	0.79	1.92	7.25	1.54	5.84	8.42	6.84
	(w/o complexes)	0.91	1.18	0.57	2.35	2.16	0.73	1.18	1.78	0.66	1.89	8.34	1.34	6.66	8.87	6.21

[a] Double hybrid definitions: B2-PLYP = (53,27); B2T-PLYP = (60,31); B2K-PLYP = (72,42); mPW2-PLYP = (55,25); mPW2K-PLYP = (72,42). Values in parentheses for the W3 set are exclusive of ozone. For this molecule, post-CCSD(T) correlation effects account for over 3 kcal/mol of the total atomization energy.[23] For approximate mean absolute deviations, multiply by 0.6745: Huber, P. J. *Robust statistics*; Wiley-IEEE: New York, 2004; p 108.

(56,27) and (73,45) points. The global minimum appears to lie at (60,31), but deterioration of performance along the "straits" is quite slow. The (53,27) point, which is equivalent to B2-PLYP,[1] lies well uphill from the straits: holding either c_1 or c_2 constant, one-dimensional minima would be (55.5,27) and (53,25). It is reasonable to assume that at the one-particle basis set limit, the "straits" would move to lower MP2 correlation by about 1%. However, we found that comparing to nonrelativistic, clamped-nuclei total atomization energies instead of experimental values including these effects (absent from all DFT and double-hybrid values) on average takes the straits to *higher* MP2 correlation by about 1%.

Let us now turn to barrier heights. A plot of the rms error for the BH6 set of representative barrier heights is given in Figure 3. The plot there is given with the aug-pc2 basis set: the plot with aug-pc3 is essentially indistinguishable from it. This is consistent with quantum chemical common sense, which would dictate that reaction barrier heights would exhibit less basis set sensitivity than total atomization energies.

The other outstanding feature of this plot is the presence of a single minimum basin, which is fairly shallow in the vicinity of the (72,40) global minimum.

One could consider the (72,40) point as a "kinetics double hybrid", but inspection of Figure 2 reveals that performance for atomization energies is unacceptably compromised. Fixing the percentage of either variable and taking the W3-optimal value for the other leads to (70,40) or (72,42) as solutions: we term the latter to be B2K-PLYP, where the "K" obviously stands for "kinetics". The (60,31) optimum for thermochemistry alone we denote B2T-PLYP.

Substituting the mPW (modified Perdew−Wang) exchange functional for B88 exchange leads to very similar profiles. As mPW2PLYP[2] was optimized using a much larger basis set which approaches aug-pc3 in size, its minimum is not biased by an "overly rich" MP2 admixture, and mPW2PLYP can basically be considered optimal. We do propose mPW2K-PLYP at (72,42) as another "kinetics double hybrid".

Table 1 summarizes performance of the double-hybrid functionals for a variety of test data sets defined by the Truhlar group and ourselves.

For hydrogen-transfer barrier heights, the BMK functional yields an rms error of only 1.88 kcal/mol, compared to about 5

TABLE 2: Performance for Subsets of the BMK Validation Set (RMS Errors in kcal/mol)[a]

	gradients	reaction energies	all neutrals	cationic molecules	cations from pas	all cations	anionic molecules	all anions	transition states	everything
no. of systems		62	219	64	8	88	47	58	24	
B2K-PLYP		3.40	3.83	[4.74]	1.61	[5.03]	7.26	7.25	1.03	[4.50]
B2-PLYP		2.98	3.23	[4.82]	1.70	[4.48]	4.92	4.74	2.56	[3.65]
B2T-PLYP		2.97	3.30	[4.53]	1.62	[4.35]	7.02	6.60	1.76	[3.97]
mPW2-PLYP		2.91	3.37	[4.94]	1.85	[4.64]	5.44	5.17	2.44	[3.81]
mPW2K-PLYP		3.39	4.52	[4.95]	1.62	[5.29]	6.80	6.91	1.14	[4.79]
B3LYP	10.41	4.43	8.14	5.73	2.69	5.72	8.11	9.08	5.04	7.77
B97-1	10.01	4.17	4.77	6.12	4.15	5.48	6.90	6.29	5.20	5.32
PBE0	12.33	4.29	8.49	7.72	4.97	11.78	6.65	9.70	4.92	9.32
B1B95	12.18	3.06	4.34	6.44	1.69	5.79	7.16	6.58	3.54	5.06
TPSSh	10.44	5.5	7.31	8.4	6.60	9.51	8.08	8.40	6.80	6.22
TPSS25TPSS	11.68	4.59	12.65	11.2	6.26	10.09	12.99	11.91	4.79	11.55
TPSS1KCIS	11.68	4.44	6.18	7.79	3.65	7.78	7.02	7.63	5.14	6.65
TPSS25KCIS	13.17	3.6	9.07	7.26	3.34	7.03	10.48	9.78	3.39	8.53
mPW1B95	13.64	3.04	5.13	7.39	2.03	6.56	6.65	6.13	3.71	5.58
mPW25B95	11.39	3.13	7.09	8.66	2.76	7.65	5.61	5.28	4.79	6.76
PW6B95	12.28	2.82	11.86	5.85	1.95	17.4	6.60	17.2	3.79	[4.81][a]
mPW1K	19.16	4.81	15.84	11.46	7.37	10.17	15.47	13.94	1.80	14.02
BB1K	18.87	3.31	9.60	7.65	1.71	6.75	12.42	11.28	1.75	9.12
PWB6K	21.78	3.73	12.45	8.80	3.50	12.65	12.74	14.03	1.65	12.39
BMK	12.58	3.69	4.49	6.97	2.36	6.60	8.42	7.86	1.96	5.58
TPSS20B95	10.3	4.73	6.46	6.57	4.58	8.26	7.94	8.77	4.31	7.06
TPSS25B95	11.89	4.25	7.22	6.45	4.66	7.97	9.47	9.58	3.52	7.51
TPSS33B95	15.58	3.72	9.89	7.43	4.89	8.26	12.29	11.55	2.43	9.43
TPSS42B95	20.34	3.63	13.71	9.59	5.26	9.49	15.67	14.27	1.64	12.44
M06L	10.49	5.09	6.66	8.81	4.67	8.31	8.07	7.39	4.92	6.97
M06	12.86	4.15	4.60	6.64	3.19	6.35	6.32	5.96	2.81	5.16
M06-2X	15.69	2.12	[4.27][b]	5.95	2.95	5.31	[5.23][c]	[4.81][c]	1.67	[5.79][b,c]

[a] The aug-pc3+d basis set (combined with cc-pwCVQZ[48] for Na and Mg) was used for the double hybrids, aug-pc2+d or equivalent for the DFT functionals. For the double-hybrid functionals, error statistics for cations exclude the two excited-state cations N_2^+ ($a^2\Pi_u$) and H_2S^+ (A^2A_1), hence the square brackets. [b] Excluding atomic total energies. [b] Excluding SF_6 and CF_4 (convergence issues). [c] Excluding ClO_4^-.

kcal/mol each for B3LYP, PBE0, and B97-1. B2-PLYP and mPW2-PLYP only yield slightly worse rms errors than BMK: most strikingly, however, B2K-PLYP and mPW2K-PLYP bring the rms error for such barriers *below 1 kcal/mol*. Substituting various other exchange functionals still yields lower than 1 kcal/mol rms errors, suggesting this hybrid is not an artifact of the specific exchange correlation functional used.

What about non-hydrogen-transfer barrier heights? Over Truhlar's NHTBH38 set, we do see an improvement from B2-PLYP to B2K-PLYP and from mPW2-PLYP to mPW2K-PLYP, albeit not as pronounced as for the hydrogen-transfer reactions. Overall performance is comparable to that of BMK and M06-2X, and markedly superior to the other DFT functionals. Considering the various subsets of NHTBH38, we find a spectacular improvement for nucleophilic substitutions (an rms error of 0.5 kcal/kmol for B2K-PLYP), a less spectacular one for heavy-atom transfers, and a mild deterioration for unimolecular and recombination reactions.

For thermochemistry, we considered the W3 set with both the aug-pc2 and aug-pc3 basis sets, as well as extrapolated to the infinite basis set limit. We find then, in fact, that the performance of B2-PLYP deteriorates for basis sets larger than aug-pc2, whereas that of B2K-PLYP satisfyingly improves with the basis set. At the infinite basis set limit, B2T-PLYP, B2K-PLYP, and mPW2-PLYP all clearly outperform the conventional DFT functionals. Performing Petersson's CBS extrapolation[46] on the MP2 correlation energy greatly mitigates basis set incompleteness in the MP2 results but can be dispensed with for the larger basis sets.

We now turn to the prototype reactions at Pd. In our previous validation study,[19] PBE0 was found to yield the best agreement with benchmark ab initio data for this set, in a virtual tie with B1B95. (This study predates publication of the M06 family by about a year: in the present work, we found the third-rung functional M06-L to yield very good performance, but the hybrids M06, M06-2X, and M06-HF to fail as dramatically as BMK.) It is seen in Table 1 that all of the double-hybrid functionals perform excellently for this data set, B2-PLYP and B2T-PLYP somewhat better than B2K-PLYP and mPW2-PLYP somewhat better than mPW2K-PLYP.

Finally, we considered the weak interactions data set of Zhao and Truhlar.[25] Overall, the double hybrids all outperform the conventional functionals except M06, M06-2X, and (to a lesser extent) M06-HF. Particularly, mPW2-PLYP performs very well across the board, and it offers by far the best performance for charge-transfer complexes. Aside from those, B2K-PLYP is quite satisfying.

We will finally consider (Tables 2 and 3) a larger thermochemical data set, namely, the BMK data set of 464 systems, which inter alia includes essentially all of the widely used G3-99 set.[45] For the 209 neutral molecules in the BMK set, B2-PLYP and B2T-PLYP yield similar RMSDs of 3.18 and 3.22 kcal/mol, respectively, and B2K-PLYP is somewhat worse at 3.83 kcal/mol. All of these values improve on the conventional DFT functionals surveyed in refs[19,20] as well as on the M06 family.

Considering various subsets of the neutral molecules, we find that the double-hybrid functionals yield either the best performance, or one of the best performances, for the various subclasses. The performance of B2T-PLYP for hydrocarbons, rmsd = 1.44 kcal/mol, is almost too good to be true. The various kinetics functionals, except for BMK, have a particularly hard time with the nonhydrogen systems: B2K-PLYP, at 5.22 kcal/mol, still outperforms all conventional functionals except (marginally) PW6B95. Similar remarks apply to the inorganic hydrides.

Two of the cations in the BMK set are in excited states, for which the MP2 correction is intrinsically unusable. For the

TABLE 3: Performance for Additional Subsets of the BMK Set (RMS Deviations in kcal/mol)

	neutral molecules	non-hydrogen systems	hydrocarbons	substituted hydrocarbons	radicals	inorganic hydrides	H-bonded dimers
no. of systems	209	71	27	46	38	27	4
B2K-PLYP	3.83	5.22	2.40	3.15	2.41	3.37	0.15
B2-PLYP	3.23	3.95	1.70	3.09	2.85	2.61	0.23
B2T-PLYP	3.22	4.38	1.44	2.95	2.13	2.96	0.18
mPW2-PLYP	3.32	4.34	2.14	2.80	2.43	3.09	0.32
mPW2K-PLYP	4.23	5.61	5.11	3.76	2.63	2.90	0.32
B3LYP	7.86	11.76	5.71	4.82	3.10	5.33	0.43
B971	4.85	5.48	5.58	4.84	3.35	3.99	0.14
PBE0	6.44	7.12	9.49	5.68	3.46	5.05	0.19
B1B95	4.33	5.65	3.38	4.01	2.31	3.83	1.04
TPSS25TPSS	12.82	18.03	4.96	9.37	7.61	12.72	0.37
TPSS21KCIS	7.47	10.82	3.34	4.56	3.78	7.57	0.34
TPSS25KCIS	9.05	13.21	2.99	5.92	4.42	8.86	0.34
mPW1B95	5.15	5.75	7.29	5.05	2.82	3.31	0.43
mPW28B95	5.91	6.28	8.42	6.29	3.65	3.13	0.43
mPW25B95	7.17	7.72	9.60	7.81	4.72	3.71	0.44
PW6B95	3.98	5.20	3.52	3.34	2.35	3.57	0.31
mPW1K	16.20	22.24	7.42	14.58	8.37	14.68	0.36
BB1K	9.79	13.40	4.53	8.71	5.05	9.19	0.86
PWB6K	10.86	14.95	4.20	9.34	6.07	10.34	0.22
BMK	4.37	6.18	2.16	3.43	3.15	2.95	0.60
M06L	6.68	8.51	4.99	5.82	3.88	7.12	0.26
M06	4.56	6.17	3.04	3.53	2.37	4.79	0.28
M06-2X	[4.33][a]	[6.45][a]	2.40	3.11	2.28	2.77	0.15

[a] Excluding SF_6 and CF_4 (convergence issues).

remaining cations, the double hybrids outperform all conventional DFT functionals. For anions, B2-PLYP actually delivers the best performance, whereas the higher percentage of HF exchange in B2K-PLYP entails a considerable sacrifice in performance. Even so, B2K-PLYP still handily outperforms B3LYP, BMK, PBE0, and the whole TPSS family considered.

The activation barrier for $HOF + C_2H_4 \rightarrow HF + C_2H_4O$, a prototype for Rozen's epoxidation reaction, is 18.26 kcal/mol at the W1 level.[14] This barrier, which involves a transition state with quite "unorthodox" HO^+ and F^- moieties, is quite a difficult test for DFT functionals.[14] With the aug-pc3 basis set, B2-PLYP and mPW2-PLYP yield significantly underestimated barriers of 12.56 and 14.35 kcal/mol, respectively, and B2K-PLYP reaches a respectable 17.12 kcal/mol. It was already noted[14] that basis set convergence for this reaction is somewhat slow even at the DFT level: basis set extrapolation increases barriers by roughly 1 kcal/mol for all methods, bringing B2K-PLYP in essentially perfect agreement with the W1 reference value. We note that, although the M06 functional yields an excellent 16.78 kcal/mol, the other members of the family are seriously in error: M06L 0.25, M06-2X 25.95, M06-HF 34.87 kcal/mol.

We finally note that, although all electrons were correlated for the data reported, we found that freezing inner-shell electrons does not materially detract from the quality of the results.

IV. Conclusions

We have proposed two new double-hybrid functionals, B2K-PLYP and mPW2K-PLYP, and shown that they yield excellent performance for all of the following: main-group thermochemistry, main-group thermochemical kinetics, and late transition metal reactions. It can be carried out with an unmodified version of the Gaussian 03 electronic structure code.[47]

We do not mean to present B2K-PLYP as a panacea. Its very high percentage of Hartree−Fock exchange intrinsically makes it vulnerable to severe nondynamical correlation, as well as (for open-shell systems in unrestricted Kohn−Sham frameworks) to spin contamination. In addition, the slow basis set convergence of the MP2-type correlation component requires the use of much larger basis sets than typically would be employed for DFT calculations, although CBS extrapolation offers some succor there. Nevertheless, we feel B2K-PLYP could be quite useful in cases where higher accuracy than currently achievable with DFT methods is desired, but which are beyond the reach of benchmark ab initio calculations.

Acknowledgment. Research at Weizmann was funded by the Israel Science Foundation (grant 709/05), the Minerva Foundation (Munich, Germany), and the Helen and Martin Kimmel Center for Molecular Design. J.M.L.M. is the incumbent of the Baroness Thatcher Professorial Chair of Chemistry as well as a member ad personam of the Lise Meitner-Minerva Center for Computational Quantum Chemistry. He thanks Prof. George C. Schatz for sabbatical hospitality, Drs. Yan Zhao and Mark A. Iron for helpful information on the M06 family, and Prof. George A. Petersson for enlightening discussions on the CBS extrapolation.

Supporting Information Available: Complete reference for Gaussian 03, additional detail for the reference data sets, and a table of atomization energies (PDF format). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Grimme, S. *J. Chem. Phys.* **2006**, *124*, 034108.

(2) Schwabe, T.; Grimme, S. *Phys. Chem. Chem. Phys.* **2006**, *8*, 4398.

(3) Zhao, Y.; Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2004**, *108*, 4786; *Phys. Chem. Chem. Phys.* **2005**, *7*, 43.

(4) Perdew, J. P.; Schmidt, K. In *Density Functional Theory and its Application to Materials*; Van Doren, V., Van Alsenoy, C., Geerlings, P., Eds.; AIP Conference Proceedings No. 577; AIP: New York, 2001; p 1; http://dx.doi.org/10.1063/1.1390175. In Perdew's metaphor, ground level would be Hartree theory and Heaven the exact density functional, and successive rungs of the ladder correspond to additional pieces of information that enter the functional. Rung one employs just the density and corresponds to the local spin density approximation. Rung two introduces the density gradient and is occupied by the various GGAs (generalized gradient approximations) such as BLYP and PBE. Rung three introduces the kinetic energy density or the Laplacian and is occupied by the various meta-GGAs such as TPSS.[36] Hybrid GGAs and meta-GGAs, which involve the occupied

orbitals, constitute the fourth rung. Rung five additionally employs the virtual orbitals, and double-hybrid functionals constitute one special case thereof.

(5) Görling, A.; Levy, M. *Phys. Rev. B* **2007**, *47*, 13105.

(6) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(7) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(8) Adamo C.; Barone, V. *J. Chem. Phys.* **1998**, *108*, 664.

(9) Frisch, M. J.; et al. *Gaussian 03*, revision C.01; Gaussian, Inc.: Wallingford, CT, 2004.

(10) Neese, F.; Schwabe, T.; Grimme, S. *J. Chem. Phys.* **2007**, *126*, 124115.

(11) ORCA is an electronic structure program package written by F. Neese, with contributions from U. Becker, D. Ganiouchine, S. Kossmann, T. Petrenko, C. Riplinger, and F. Wennmohs. See also: http://www.thch.uni-bonn.de/tc/orca.

(12) For a brief review of the Resolution of the Identity (RI) approach, see: Kendall, R. A.; Früchtl, H. A. *Theor. Chem. Acc.* **1997**, *97*, 158.

(13) Neese, F. Outstanding Young German Scientist lecture (Lise Meitner-Minerva Center for Computational Quantum Chemistry, Hebrew University of Jerusalem, Israel, June 19, 2007).

(14) Sertchook, R.; Boese, A. D.; Martin, J. M. L. *J. Phys. Chem. A* **2006**, *110*, 8275.

(15) Sundermann, A.; Uzan, O.; Milstein, D.; Martin, J. M. L. *J. Am. Chem. Soc.* **2000**, *122*, 7095.

(16) Sundermann, A.; Uzan, O.; Martin, J. M. L. *Organometallics* **2001**, *20*, 1783.

(17) Rybtchinski, B.; Oevers, S.; Montag, M.; Vigalok, A.; Rozenberg, H.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **2001**, *123*, 9064.

(18) Iron, M. A.; Sundermann, A.; Martin, J. M. L. *J. Am. Chem. Soc.* **2003**, *125*, 11430.

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

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

(21) Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2003**, *107*, 8996; erratum **2004**, *108*, 1460.

(22) Boese, A. D.; Oren, M.; Atasoylu, O.; Martin, J. M. L.; Kállay, M.; Gauss, J. *J. Chem. Phys.* **2004**, *120*, 4129.

(23) Karton, A.; Rabinovich, E.; Martin, J. M. L.; Ruscic, B. *J. Chem. Phys.* **2006**, *125*, 144108.

(24) Zhao, Y.; González-García, N.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 2012; erratum **2006**, *110*, 4942.

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

(26) Jensen, F. *J. Chem. Phys.* **2001**, *115*, 9113; erratum **2002**, *116*, 3502.

(27) Jensen, F. *J. Chem. Phys.* **2002**, *116*, 7372.

(28) Jensen, F. *J. Chem. Phys.* **2002**, *117*, 9234.

(29) Jensen, F.; Helgaker, T. *J. Chem. Phys.* **2004**, *121*, 3463.

(30) Jensen, F. *J. Phys. Chem. A* **2007**, *111*, 11198.

(31) Martin, J. M. L. *J. Mol. Struct. (THEOCHEM)* **2006**, *771*, 19 and references therein.

(32) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(33) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865; erratum **1997**, *78*, 1396. Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158.

(34) Becke, A. D. *J. Chem. Phys.* **1996**, *104*, 1040.

(35) Becke, A. D. *J. Chem. Phys.* **1997**, *107*, 8554. Hamprecht, F.; Cohen, A. J.; Tozer, D. J.; Handy, N. C. *J. Chem. Phys.* **1998**, *109*, 6264.

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

(37) Krieger, J. B.; Chen, J.; Iafrate, G. J.; Savin, A. Construction of an accurate self-interaction-corrected correlation energy functional based on an electron gas with a gap. In *Electron Correlations and Materials Properties*; Gonis, A., Kioussis, N., Eds.; Plenum: New York, 1999; ISBN 0-30646282-6.

(38) Zhao, Y.; Lynch, B. J.; Truhlar, D. G. *Phys. Chem. Chem. Phys.* **2005**, *7*, 43−52.

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

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

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

(42) Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.* **2006**, *125*, 194101.

(43) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2006**, *110*, 13126 (2006).

(44) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2007**, Online First (2007) [Mark S. Gordon issue]. http://dx.doi.org/10.1007/s00214-007-0310-x.

(45) Raghavachari, K.; Curtiss, L. A. In *Quantum-Mechanical Prediction of Thermochemical Data*; Cioslowski, J., Ed.; Kluwer: Dordrecht, The Netherlands, 2001; pp 67−98.

(46) Nyden, M. R.; Petersson, G. A. *J. Chem. Phys.* **1981**, *75*, 1843. Petersson, G. A.; Al-Laham, M. A. *J. Chem. Phys.* **1991**, *94*, 6081. Petersson, G. A.; Tensfeldt, T.; Montgomery, J. A. *J. Chem. Phys.* **1991**, *94*, 6091. Montgomery, J. A.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1994**, *101*, 5900.

(47) The following nonstandard route will do the required steps for a B2K-PLYP calculation:

```
#P blyp/Gen IOp(3/76=0280007200,3/78=0580005800) extraoverlay scf=tight

[blank line]

8/10=90/1; 9/16=-3/6;

[blank line, followed by rest of input]
```

To carry out a CBS extrapolation on the MP2 energy, replace the last line by

```
8/10=90/1; 9/16=-3,75=2,81=Nmin/6,4;
```

where Prof. Petersson recommends setting the pair extrapolation parameter N_{min} to 5 for an spd basis set, 10 for an spdf basis set, and so forth. To freeze inner-shell electrons, replace “8/10=90” by “8/10=2”.

(48) Peterson, K. A.; Dunning, T. H. *J. Chem. Phys.* **2002**, *117*, 10548.