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 Rehovot, 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 earlier1 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 Görßing–Levy perturbation theory).5 Finally, the total energy is obtained as

$$E_{xc} = (1 - c_1)E_{x,GGA} + c_1E_{x,\text{HF}} + (1 - c_2)E_{c,GGA} + c_2E_2$$  

(1)

where $E_{x,GGA}$ and $E_{c,GGA}$ represent the exchange and correlation parts of the underlying DFT functional, $E_{x,\text{HF}}$ 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 $E_{x,GGA}$ considered by Grimme was Lee–Yang–Parr (LYP),6 combined with the Becke88 exchange functional7 into B2-PLYP1 (with $c_1 = 0.53$ and $c_2 = 0.27$), and with modified Perdew–Wang (mPW) exchange8 into mPW2-PLYP2 (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 03.3 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 functionals13 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 program8 running on the Martin group Linux cluster at Weizmann.
A number of validation data sets were used. These include the following: (a) the BMK validation set\(^2\) 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;\(^2\) (c) the training set for the W3\(^2\) and W4\(^2\) ab initio computational thermochemistry approaches,\(^2\) 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)\(^2\) and 38 non-hydrogen-transfer barrier heights (NHTBH38);\(^2\) (e) the weak interactions data set of Zhao and Truhlar.\(^2\) 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.\(^2\)-\(^3\) We primarily considered two basis sets: aug-pc2 (which is of triple-\(\zeta\) 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 spdf\(_g\) + 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,\(^3\) 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,\(^2\) BMK,\(^2\) PBE0,\(^3\) B1B95,\(^4\) B97-1\(^5\) TPSSKC\(^6\)-\(^8\) BB1K,\(^9\) mPW1B95,\(^10\) PW6B95,\(^11\) and PW6B6K,\(^11\) as well as the very recent M06 (Minnesota-06) family of functionals.\(^12\)-\(^4\)

**III. Results and Discussion**

Initially, to get our bearings, we mapped the AE6 surface\(^2\) 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.

We then proceeded to consider a larger set of reference data, namely the training set for the W3 ab initio computational thermochemistry method.\(^2\) 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 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.

**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.
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, 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 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 kcal/mol for the other functionals.
TABLE 2: Performance for Subsets of the BMK Validation Set (RMS Errors in kcal/mol)\(^a\)

<table>
<thead>
<tr>
<th>no. of systems</th>
<th>gradients</th>
<th>reaction energies</th>
<th>all neutrals</th>
<th>cationic molecules</th>
<th>cations from pas</th>
<th>all cations</th>
<th>anionic molecules</th>
<th>all anions</th>
<th>transition states</th>
<th>everything</th>
</tr>
</thead>
<tbody>
<tr>
<td>62</td>
<td>219</td>
<td>64</td>
<td>8</td>
<td>88</td>
<td>47</td>
<td>58</td>
<td>24</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B2K-PLYP</td>
<td>3.40</td>
<td>3.83</td>
<td>1.61</td>
<td>5.03</td>
<td>7.26</td>
<td>7.25</td>
<td>1.03</td>
<td>[4.50]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B2-PLYP</td>
<td>2.98</td>
<td>3.23</td>
<td>1.70</td>
<td>4.48</td>
<td>4.92</td>
<td>4.74</td>
<td>2.56</td>
<td>[3.65]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B2T-PLYP</td>
<td>2.97</td>
<td>3.30</td>
<td>1.62</td>
<td>4.35</td>
<td>7.02</td>
<td>6.60</td>
<td>1.76</td>
<td>[3.97]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>mPW2-PLYP</td>
<td>2.91</td>
<td>3.37</td>
<td>1.85</td>
<td>4.64</td>
<td>5.47</td>
<td>5.17</td>
<td>2.44</td>
<td>[3.81]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>mPW2K-PLYP</td>
<td>3.39</td>
<td>4.52</td>
<td>1.62</td>
<td>5.29</td>
<td>6.80</td>
<td>6.91</td>
<td>1.14</td>
<td>[4.79]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B3LYP</td>
<td>10.41</td>
<td>4.43</td>
<td>2.69</td>
<td>5.72</td>
<td>8.11</td>
<td>9.08</td>
<td>5.04</td>
<td>7.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B97-1</td>
<td>10.01</td>
<td>4.17</td>
<td>1.45</td>
<td>5.48</td>
<td>6.90</td>
<td>6.29</td>
<td>5.20</td>
<td>5.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBE0</td>
<td>12.33</td>
<td>4.29</td>
<td>4.97</td>
<td>11.78</td>
<td>6.65</td>
<td>7.90</td>
<td>4.92</td>
<td>9.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B1B95</td>
<td>12.18</td>
<td>3.06</td>
<td>1.69</td>
<td>5.79</td>
<td>7.16</td>
<td>6.88</td>
<td>3.54</td>
<td>5.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPSSH</td>
<td>10.44</td>
<td>5.5</td>
<td>6.60</td>
<td>9.51</td>
<td>8.08</td>
<td>8.40</td>
<td>6.80</td>
<td>6.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPSS1K CIS</td>
<td>11.68</td>
<td>4.44</td>
<td>3.65</td>
<td>7.78</td>
<td>7.02</td>
<td>7.63</td>
<td>5.14</td>
<td>6.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPSS25K CIS</td>
<td>13.17</td>
<td>3.6</td>
<td>3.34</td>
<td>7.03</td>
<td>10.48</td>
<td>9.78</td>
<td>3.39</td>
<td>8.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>mPW1B95</td>
<td>13.64</td>
<td>3.04</td>
<td>2.03</td>
<td>6.56</td>
<td>6.65</td>
<td>6.13</td>
<td>3.71</td>
<td>5.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td>mPW25B95</td>
<td>11.39</td>
<td>3.13</td>
<td>2.76</td>
<td>7.65</td>
<td>5.61</td>
<td>5.28</td>
<td>4.79</td>
<td>6.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PW6B95</td>
<td>12.28</td>
<td>2.82</td>
<td>1.95</td>
<td>17.4</td>
<td>6.60</td>
<td>17.2</td>
<td>3.79</td>
<td>[4.81](^b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>mPW1K</td>
<td>19.16</td>
<td>4.81</td>
<td>7.37</td>
<td>10.17</td>
<td>15.47</td>
<td>13.94</td>
<td>1.80</td>
<td>14.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BB1K</td>
<td>18.87</td>
<td>3.31</td>
<td>1.71</td>
<td>6.75</td>
<td>12.42</td>
<td>11.28</td>
<td>1.75</td>
<td>9.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PW6Bk</td>
<td>21.78</td>
<td>3.73</td>
<td>3.50</td>
<td>12.65</td>
<td>12.74</td>
<td>14.03</td>
<td>1.65</td>
<td>12.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BMK</td>
<td>12.58</td>
<td>3.69</td>
<td>2.36</td>
<td>6.60</td>
<td>8.42</td>
<td>7.86</td>
<td>1.96</td>
<td>5.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPSS20B95</td>
<td>10.33</td>
<td>4.73</td>
<td>4.58</td>
<td>8.26</td>
<td>7.96</td>
<td>8.77</td>
<td>4.31</td>
<td>7.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPSS33B95</td>
<td>15.58</td>
<td>3.72</td>
<td>4.89</td>
<td>8.26</td>
<td>12.29</td>
<td>11.55</td>
<td>2.43</td>
<td>9.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPSS42B95</td>
<td>20.34</td>
<td>3.63</td>
<td>5.26</td>
<td>9.49</td>
<td>15.67</td>
<td>14.27</td>
<td>1.64</td>
<td>12.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M06L</td>
<td>10.49</td>
<td>5.09</td>
<td>4.67</td>
<td>8.31</td>
<td>8.07</td>
<td>7.39</td>
<td>4.92</td>
<td>6.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M06</td>
<td>12.86</td>
<td>4.15</td>
<td>3.19</td>
<td>6.35</td>
<td>6.32</td>
<td>5.96</td>
<td>2.81</td>
<td>5.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M06-2X</td>
<td>15.69</td>
<td>2.12</td>
<td>2.95</td>
<td>5.31</td>
<td>5.23</td>
<td>4.81(^c)</td>
<td>1.67</td>
<td>[5.79](^c)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) The aug-pc3+d basis set (combined with cc-pwCVQZ\(^d\) 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\(_2^+\) (\(\alpha\)T\(_2\)) and H\(_2^+\) (A\(^2\)A\(_2\)), hence the square brackets. \(^b\) Including atomic total energies. \(^c\) Including SF\(_6\) and CF\(_4\) (convergence issues). \(^d\) Excluding CIO\(_3^\).
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 the whole TPSS family considered.

The activation barrier for HOF + C₂H₄ → HF + C₂H₄O, a prototype for Rozen’s epoxidation reaction, is 18.26 kcal/mol at the W1 level.¹⁴ This barrier, which involves a transition state bent 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. Peterson 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

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. Peterson 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

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 GGA’s (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. Hybrid GGAs and meta-GGAs, which occupy the involved
orbitals, constitute the fourth rung. Rung five additionally employs the virtual orbitals, and double-hybrid functionals constitute one special case thereof.

(9) Frisch, M. J.; et al. Gaussian 03, revision C.01; Gaussian, Inc.: Wallingford, CT, 2004.
(11) ORCA is an electronic structure program package written by F. Neese, with contributions from U. Becker, D. Gianciouich, S. Kossmann, T. Petrenko, C. Riplinger, and F. Wennmohs. See also: http://www.thc.uni-bonn.de/orca.
(47) The following nonstandard route will do the required steps for a B2K-PLYP calculation: #P blyp/Gen 10p(3/76);0200007200,3/78;0680005800 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=1min/6,4;
where Prof. Petersson recommends setting the pair extrapolation parameter S_min to 5 for an spd basis set, 10 for an spd basis set, and so forth. To freeze inner-shell electrons, replace "8/10=90/1" by "8/10=2/0".