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Comment on “Doubly hybrid density functional xDH-PBE0 from a parameter-free global hybrid model PBE0” [J. Chem. Phys. 136, 174103 (2012)]

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Double hybrid functionals (see Refs. 1 and 2 for reviews) have recently emerged as an interesting “third way” option between DFT (density functional theory) and high-level *ab initio* methods: their accuracy approaches the latter at only moderate cost increase over the former, especially when RI (resolution of the identity^{3,4}) is applied in the MP2 (2nd-order Møller-Plesset) phase.

There are two basic implementations of double hybrids in the literature. In the original Grimme approach⁵ (denoted gDH throughout the paper), a Kohn-Sham calculation is carried out with a fraction c_X of Hartree-Fock (HF) exchange and $(1 - c_X)$ of DFA (density functional approximation) exchange, plus DFA correlation damped by a factor $c_{C,DFA}$. Then, the MP2 correlation energy is evaluated in the basis of the Kohn-Sham orbitals obtained, scaled, and added to the energy total. In the more general DSD (dispersion-corrected, spin-component scaled double hybrid) form, the energy is given by

$$E = E_{NTVJ} + c_X E_{X,HF} + (1 - c_X) E_{X,DFA} + c_{C,DFA} E_{C,DFA} + c_{2ss} E_{2ss} + c_{2ab} E_{2ab} + c_{disp} E_{dispersion}, \quad (1)$$

where E_{NTVJ} stands for the sum of nuclear repulsion, kinetic energy, electron-nuclear attraction, and Coulomb energies; $E_{X,HF}$ is the Hartree-Fock-like exchange energy; $E_{X,DFA}$ and $E_{C,DFA}$ represent the density functional exchange and correlation energies, respectively; E_{2ss} the same-spin MP2-like correlation energy; E_{2ab} its opposite-spin counterpart; and $E_{dispersion}$ is an empirical dispersion model.⁶ The orbitals are evaluated self-consistently for the given values of c_X and $c_{C,DFA}$: typically, c_X falls in the 50%–70% range, and $c_{C,DFA}$ is considerably less than unity.

In the XYG3⁷ or xDH⁸ approach, on the other hand, the orbitals used for the evaluation of all terms in Eq. (1) are evaluated for a standard hybrid with full DFA correlation (i.e., $c_{C,DFA} = 100\%$), and with $c_{X,HF}$ as appropriate for a conventional hybrid DFA, i.e., typically in the 20%–25% range.

It has been argued that the xDH approach is more appropriate, based on the fact that the orbitals employed in Eq. (1) would be more realistic Kohn-Sham orbitals for the system.⁷ On the other hand, the very low RMSD values over extensive training sets obtained for functionals like B2GP-PLYP⁹ and DSD-PBEP86¹⁰ speak for themselves. Goerigk

and Grimme, in Section 5.3 of their GMTKN30 benchmark paper,¹¹ address the issue specifically for XYG3 vs. B2PLYP⁵ and B2GP-PLYP. They consider the average occupied-virtual gap in the orbital energies and find it to be relatively indifferent to the percentage of GGA correlation, but quite sensitive to the percentage of HF exchange, with smaller percentages yielding smaller band gaps (i.e., perturbation denominators), and hence higher effective percentages of MP2-like correlation.¹²

The purpose of the present work is to make a head-to-head comparison, for the same training set, of the performance of DSD functionals and what we will term xDSD functionals, which are the same forms as in Eq. (1) but with orbitals for all terms obtained as in xDH functionals, i.e., from a hybrid GGA calculation with a set percentage of HF exchange and undamped correlation.

Details and references for the (m)GGA exchange functionals attempted here are given in the supplementary material.¹³ Both the D2¹⁴ and D3BJ^{15,16} dispersion models were considered.

All calculations were carried out using the Gaussian 09 Rev. D.01 program system¹⁷ running on the Faculty of Chemistry computing farm at the Weizmann Institute of Science.

Six reference datasets were used, which constitute an updated version of the training set used in Refs. 10 and 18. They cover atomization energies, main group barrier heights, noncovalent interactions, and late transition metal catalysis. Further details and references are given in the supplementary material.¹³ The arithmetic average of all six RMSDs, AveRMSD, is used as the principal metric. Key results and optimized functional parameters can be found in Table S1 of the supplementary material,¹³ detailed results in an Excel workbook there.

For xDH-PBE0, AveRMSD is 3.04 kcal/mol; in contrast, the DSD-PBEPBE-D3BJ functional has just 1.51 kcal/mol (compared to 1.62 in Refs. 10 and 18). Comparison of the parameters reveals that, while the DFT and opposite-spin MP2 coefficients are not too different, xDH-PBE0 has a much larger fraction of HF exchange in the final result (83.4% vs. 68% for DSD-PBE-D3BJ). Of course, $c_{disp} = c_{2ss} = 0$ in xDH-PBE0; relaxing said constraints and reoptimizing, AveRMSD drops to 1.60 kcal/mol, not significantly different from DSD-PBEPBE-D3BJ. The optimal c_{2ss} is quite small: constraining it to zero increases AveRMSD by just 0.06 kcal/mol.

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The underlying orbitals in xDH-PBE0 and xDSD-PBE0-D3BJ are those of the PBE0 functional¹⁹ with $c_X = 1/4$. We then proceeded to consider additional data points (xDSD-PBE_x-D2 in Table S1¹³) where the orbitals were obtained with $c_X = \{0, 1/3, 3/8, 1/2, 0.68, 3/4, 1\}$. Predictably, for $c_X = 0$ or 1, the AveRMSD is elevated (albeit still lower than xDH-PBE0); less obvious perhaps is that the lowest AveRMSD values are obtained for $c_X = 1/2$, with $c_X = 0.68$ marginally higher.

In fact, xDSD-PBE₆₈-D3BJ performs somewhat *better* (AveRMSD = 1.37 kcal/mol) than DSD-PBEPBE-D3BJ (AveRMSD = 1.51 kcal/mol), which has the same c_X but damped DFT correlation in the orbitals. It is worth noting that the c_X parameters of the two functionals are basically identical: $c_X = 0.683$ for xDSD vs. 0.680 for DSD. This suggests that the relatively poor performance of xDH-PBE0 is not due to the choice of reference orbitals but to the absence of both same-spin MP2 and a dispersion correction (which are known^{20,21} to contain very similar information).

What about other functionals? Let us consider orbitals with $c_X = 1/2$ for the xDSD forms, and the simpler D2 dispersion correction, i.e., a simple multivariate-linear optimization.

xDSD-S₅₀VWN5-D2, where the underlying DFT functional is just a local density approximation, puts in a surprisingly good performance (AveRMSD = 1.39 kcal/mol). xDSD-B₅₀B95-D2, xDSD-B₅₀HLYP, and xDSD-TPSS₅₀ all perform somewhat worse. The winner is xDSD-PBE₅₀P86-D2 with just AveRMSD = 1.34 kcal/mol. Substituting the improved D3BJ dispersion correction and reoptimizing to obtain xDSD-PBE₆₉P86-D3BJ, AveRMSD can be lowered further to 1.22 kcal/mol, compared to 1.36 kcal/mol for DSD-PBEP86-D3BJ. Again, the parameters are now fairly similar between DSD and xDSD variants.

xDSD appears to have a slight edge over DSD for the (x)DSD-PBE and (x)DSD-PBEP86 combos, less so for (x)DSD-PBEhP95. Some caution against over-analysis is due here as the differences are arguably comparable to the remaining uncertainties in the reference data.

Eliminating same-spin correlation typically leads to a small increase in AveRMSD and an increase in the prefactor for the dispersion correction, consistent with the repeatedly noted^{20,21} similarity between dispersion and same-spin MP2 correlation energy. Eliminating both causes significant deterioration in AveRMSD; one or the other needs to be left in.

Finally, we considered how transferable the orbitals are. For instance, if we plug in PBE0 orbitals into xDSD-PBE₂₅P86 rather than using PBE₂₅P86 converged orbitals, this affects AveRMSD by a paltry 0.01 kcal/mol. This indicates that the results are fairly insensitive to the particular exchange and correlation forms employed for those “reference” orbitals.

Summing up, we have compared the performance of Grimme type gDH/DSD and Zhang-Xu-Goddard type xDH/xDSD forms for double hybrids. In the gDH and DSD

forms, KS orbitals with elevated HF exchange and damped DFT correlation are used, while in the xDH and xDSD forms, the KS orbitals are obtained from a conventional hybrid functional with undamped DFT correlation. Generally, the difference in performance between gDSD and xDSD functionals is very small, slightly favoring xDSD. Augmentation of the xDH form with either same-spin MP2 correlation or a dispersion correction markedly improves performance. Best xDSD results appear to be obtained for orbitals obtained with “exact exchange” fractions in the 50%–70% range. The orbitals for xDSD appear to be fairly transferable between different correlation functionals.

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¹³See supplementary material at <http://dx.doi.org/10.1063/1.4934819> for details of exchange and correlation functionals, details of training sets, Table S1, and an Excel spreadsheet containing detailed results for all the training sets and functionals.

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