Towards chemical accuracy for the thermodynamics of large molecules: new hybrid density functionals including non-local correlation effects†

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Two hybrid density functionals that include a second-order perturbation correction for non-local correlation effects are tested for the full G3/05 test set. Very large AO basis sets including core-polarization/correlation functions have been employed that yield for the first time results quite close to the basis set limit for this set. The B2-PLYP functional and the new mPW2-PLYP approach with a modified exchange part give by far the lowest MAD over the whole G3/05 set ever reported for a DFT method (2.5 and 2.1 kcal mol^{-1}, respectively). The big improvement compared to common density functionals is further demonstrated by the reduction of the maximum and minimum errors (outliers) and by much smaller errors for complicated molecular systems.

Since the ascent of density functional theory (DFT) initiated by the Hohenberg–Kohn theorem it has become the most widely used quantum chemical method[1,2] in chemistry and physics. Although no systematic way of improving DFT is known, important progress has been achieved over the years in finding helpful functional descriptions. Perdew *et al.* has introduced a metaphoric picture for this development known as "Jacob's ladder"[3] where DFT methods are sorted by their rung of the ladder based upon the information of electron density that they use: (1) local density approximation (LDA); (2) generalized gradient approximation (GGA) depending on the density gradient; (3) meta-GGA additionally depending on the density Laplacian or the kinetic energy density; (4) hyper-GGA which takes non-local information of occupied orbitals into account by adding Hartree–Fock (HF) exchange; and (5) simultaneous usage of information from occupied and virtual orbitals.

There is a great need for and interest in functionals of the fifth rung because they include non-local, dynamical electron correlation (NLEC) contributions that are *e.g.* responsible for the important van der Waals (dispersive) interactions. NLEC effects are, however, also important for the thermodynamics of large but electronically quite simple organic molecules as shown recently for the isomerizations of alkanes.[4] Several such DFT methods exists that are *e.g.* based on the random phase approximation, many-body perturbation theory, or coupled-cluster type DFT (see, for example, ref. 5–12). All these non-empirical schemes are currently at a development stage and furthermore computationally demanding and hence only applicable to small molecular systems.

Recently, a new semi-empirical hybrid functional with corrections from perturbation theory termed B2-PLYP[13] has been proposed. The idea has its roots in the Görling–Levy perturbation theory (GL-PT) which uses the Kohn–Sham orbitals to calculate the exchange and correlation energy of the non-interacting system.[5,6] In the new method, first a standard hybrid functional of the form

$$E_{\mathrm{XC}}^{\mathrm{hybrid-GGA}} = a_1 E_{\mathrm{X}}^{\mathrm{GGA}} + (1 - a_1) E_{\mathrm{X}}^{\mathrm{HF}} + a_2 E_{\mathrm{C}}^{\mathrm{GGA}}. \qquad (1)$$

is defined where $E_{\mathrm{X}}^{\mathrm{GGA}}$ and $E_{\mathrm{C}}^{\mathrm{GGA}}$ are common semi-local exchange (X) and correlation (C) functionals and $E_{\mathrm{X}}^{\mathrm{HF}}$ is the HF exchange energy. With this hybrid-GGA a normal, self-consistent KS calculation is carried out. The resulting KS orbitals and eigenvalues are then subsequently used as input for a standard second-order Møller–Plesset type perturbation theory (PT) correction of the (spin–orbital) form

$$E_{\mathrm{C}}^{\mathrm{KS-PT2}} = \frac{1}{4} \sum_{iajb} \frac{|\langle ij||ab\rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}. \qquad (2)$$

Here, i and j label occupied and a and b virtual KS orbitals with one-particle energies ε. This non-local correlation replaces part of the local GGA correlation energy similar to the replacement in the exchange part, *i.e.*, the final exchange–correlation energy is given by

$$E_{\mathrm{XC}} = E_{\mathrm{XC}}^{\mathrm{Hybrid-GGA}} + (1 - a_2) E_{\mathrm{C}}^{\mathrm{KS-PT2}}. \qquad (3)$$

This functional contains only two global scaling factors (a_1 and a_2) that have been determined empirically for B2-PLYP as 47% B88 exchange and 73% LYP correlation. Note, that compared to most other hybrid functionals, the amount of HF exchange is quite large in B2-PLYP(53% *vs.* 20–40%). In contrast to the original GL-PT, single excitations are neglected and the PT correction is not evaluated self-consistently together with the GGA parts. Our approach has resemblance with the empirical multi-coefficient methods of Truhlar[14]

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where the standard MP2 correlation energy (evaluated with HF orbitals) is added to a scaled DFT/HF energy.

Although in the first publication of B2-PLYP a wide set of different molecules (including transition metals) had already been successfully considered, a systematic study of large molecules that are the primary target of DFT is missing. Thus, in this work we apply the B2-PLYP functional to the full G3/05 test set[15] for further validation of its performance. This expands the initial study on the G2 set[13] by 123 new heats of formation (HOF) to a total of 271 values, by 105 ionization potentials (IP), 63 electron affinities (EA), 10 proton affinities (PA) and 6 binding energies of hydrogen-bridged complexes (a few complexes that are dominated by dispersive interactions have already been studied with B2-PLYP in ref. 13). This test set contains many large molecules and heavy atoms up to Kr which are difficult to handle by other computational techniques. It will be shown here that perturbatively corrected functionals of the 2-PLYP type can reach on average unprecedented chemical accuracy (1–2 kcal mol^{-1}) for this difficult set. Furthermore, a new functional derived from B2-PLYP is presented that makes use of mPW exchange[16] instead of B88[17] and is therefore termed mPW2-PLYP. The reason to use mPW is its improved behavior in low-density (large gradient) regions which seem to be important in larger molecules with many relevant intramolecular interactions. For comparison, results obtained with B-LYP,[17,18] TPSS,[19] and B3-LYP[20,21] standard methods are also discussed. Also for the first time in a full G3/05 study we apply very large AO basis sets including core-polarization functions that provide DFT results quite close to the basis set limit.

All thermodynamic data have been computed in the same standard manner from total molecular and atomic energies without further empirical corrections as performed previously.[13,22] The other results (IP, EA, PA and H-binding) refer to electronic energies at 0 K with ZPVE corrections. The computations were performed with the TURBOMOLE program package.[23] The geometries were determined at the B3-LYP/TZV2P level of theory where TZV2P[24] labels a doubly polarized valence triple-ζ basis set with polarization functions taken from the cc-pVTZ basis[25] but discarding the highest angular momentum function. Harmonic vibrational frequencies were also computed at this level of theory and were scaled by a factor of 0.97 as recently recommended.[26] Note, that errors for the derived zero-point vibrational energies (ZPVE) directly show up as errors in the HOF. Because the ZPVE reach values on the order of 10^2 kcal mol^{-1} for many molecules in the G3/05 set, this may in part limit the ultimate accuracy of such a 'brute-force' approach to a mean absolute deviation (MAD) with respect to experiment of about 0.5–1 kcal mol^{-1}.

Subsequent 2-PLYP single point energy calculations were carried out with a larger CQZV3P basis set. This is composed of a quadruple-ξ basis (QZV[27]) augmented with polarization functions from the cc-pVQZ basis.[25] We discarded the highest angular momentum basis function (f (g) for (non)-hydrogen atoms) because this saves a lot of computation time but effects the computed atomization energies less than added core-polarization/correlation functions. These additional steep basis functions (labeled wCT) were taken from the cc-pwCVTZ sets.[28] For anions and hydrogen bridged complexes diffuse functions were used that were taken from the aug-cc-pVTZ basis set. The wCT functions are not available for Li, Be, Na, and Mg and for third row elements. While wCT functions have been neglected for molecules containing alkaline or alkaline-earth metals, for the heavy atoms Ga–Kr the exponents have been estimated by splitting the wCT functions 2s2p2d1f of their second row homologous to a set of 3s3p3d2f. The larger exponent was scaled by 1.5 and the smaller ones by 1.5 and 0.75, respectively. We note in passing that the use of wCT functions has improved the results significantly for all tested density functionals and we thus strongly recommend them for accurate benchmark work when the inherent performance of the functionals for atomization energies should be evaluated. All electron perturbation corrections were obtained with the resolution-of-identity (RI) approximation for the two-electron integrals.[29,30] The necessary auxiliary basis sets were taken from ref. 31 where they have been fitted for the cc-pVQZ basis set. The estimated RI error for the HOF values is about 0.02 kcal mol^{-1} per atom.

For mPW2-PLYP the modified Perdew–Wang exchange functional[16] was implemented. Note that the empirical parameters b and d in the original publication have been set to 0.00426 instead of 0.0046 and to 3.72 instead of 3.73, respectively, in the case of the parameter d. These values were taken from the GAUSSIAN03 source code[32] and were found to be necessary to reproduce the exchange energies published by Adamo and Barone.[16] By minimizing the MAD for a subset of molecules from the G2/97 neutral test set, the parameters a_1 and a_2 have been determined. The optimum fractions of the GGA parts in mPW2-PLYP are 45% mPW exchange and 75% LYP correlation, respectively, which is very similar to the values in B2-PLYP. Otherwise, mPW2-PLYP energies and HOF are computed in the same way as for B2-PLYP.

In Table 1, statistical measures for the performance of B-LYP, TPSS, B3-LYP, B2-PLYP and mPW2-PLYP for the complete G3/05 test set are presented. The results for all

Table 1 Performance of the investigated functionals for the G3/05 test set (in kcal mol^{-1}). Given are the mean deviation (MD), the mean absolute deviation (MAD) as well as the minimum and maximum deviations. All values in the upper part of the table are based on CQZV3P//B3-LYP/TZV2P calculations

Functional	MD[a]	MAD	Min	Max
B-LYP	−0.1	7.3	−36.9	57.7
TPSS	3.9	5.8(4.7)[b]	−20.0	28.7
B3-LYP	−2.0	4.4(5.0)[b]	−26.1	15.4
B2-PLYP	−0.4	2.5	−14.6	13.3
mPW2-PLYP	−0.3	2.1	−13.7	12.2
X3LYP[b]		4.6		
B97-1[b]		4.3		
B97-2[b]		4.2		
O3LYP[b]		4.0		
MPW1B95[b]		4.0		
B98[b]		3.8		
VSXC[b]		3.8		
B1B95[b]		3.8		

[a] Exp.-calc. [b] Taken from ref. 15.

molecules and all DF considered are presented in detail in the ESI.†

From this table, it is seen, that the introduction of a perturbative correction yields an overall much better description of the thermodynamic properties of the molecules. The mean absolute deviations (MAD) from experiment are 7.3 (B-LYP), 5.8 (TPSS), 4.4 (B3-LYP), 2.5 (B2-PLYP) and 2.1 (mPW2-PLYP) kcal mol^{-1}. We have also listed some literature data for comparison that, however, have been obtained with smaller basis sets and also slightly different ZPVE corrections. As can be seen from the comparative entries in the second and third rows, this may influence the MAD by 0.5–1 kcal mol^{-1}. As expected, our results are better for functionals that systematically under-bind (B3LYP) or worse for those that over-bind (TPSS) due to basis set effects. In any case, both new 2-PLYP functionals represent a significant step towards chemical accuracy by underbidding all other methods by about 1.5 kcal mol^{-1} in the MAD, at least. This is further corroborated by the smaller absolute minimum and maximum deviations that give a total error range of about 30 kcal mol^{-1} for the 2-PLYP functionals but >40 kcal mol^{-1} for the others. The use of the mPW exchange part yields small but still substantially better results. Although our best result is still worse compared to the best wavefunction methods G3 and G3X (MAD of 1.1 and 1.0 kcal mol^{-1}, respectively[15]), one should keep in mind, that the G3 methods contain more empirical parameters (four in the high-level correlation correction) than the 2-PLYP functionals.

The improvements by the new ansatz and by mPW in particular are even more obvious by considering the error distributions for the HOF part of the test set which are shown in Fig. 1. For the five functionals, the decrease in the range of deviations supports a reduced MAD and a growing maximum at a deviation around 0 kcal mol^{-1}. TPSS is an exception because it reduces the error range compared to B-LYP but has a shifted maximum towards positive deviations (over-binding). On the other hand B3-LYP shows a clear tendency to under-bind especially for the larger molecules which is apparent from the shoulder in the negative region of the error distribution. This tendency is reduced by B2-PLYP and nearly absent in the mPW2-PLYP distribution that is very sharp and symmetric. This is an indication that the modification of the exchange part has improved the description as expected.

Furthermore, it should be emphasized that the new functionals also perform very well for energetic properties other than HOF although they were not parameterized against these

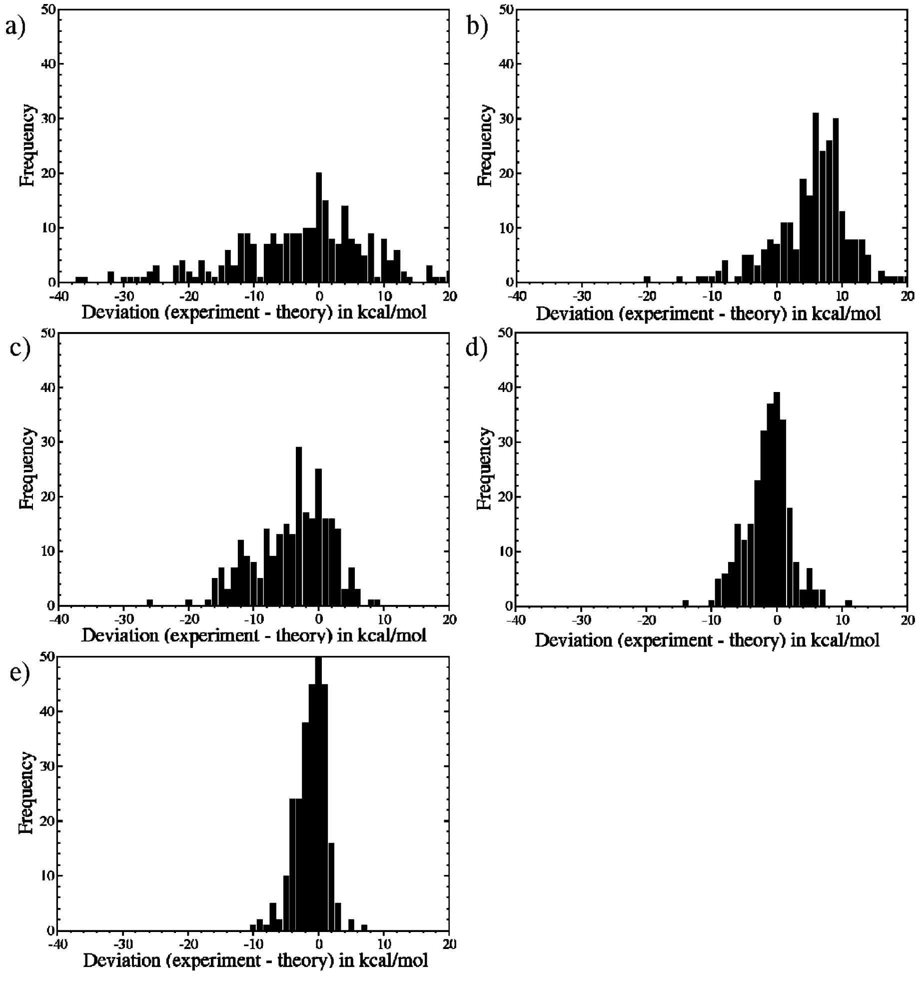

Fig. 1 Comparison of error distributions (binding in a 1 kcal mol^{-1} range) for heats of formation in the G3/05 set: (a) B-LYP, (b) TPSS, (c) B3-LYP, (d) B2-PLYP, and (e) mPW2-PLYP.

Table 2 Performance for G3/05 subsets: heats of formation (HOF), ionisation potentials (IP), electron affinities (EA), proton affinities (PA), and H-bonded complexes

	MAD/kcal mol^{-1}		
Set (# entries)	B3-LYP	B2-PLYP	mPW2-PLYP
HOF (271)	5.3	2.7	2.0
IP (105)	4.1	2.7	2.6
EA (63)	2.4	1.7	1.8
PA (10)	0.8	0.7	0.7
H-bonded (6)	0.7	0.5	0.6

data as is the case for B3-LYP, for example. Table 2 lists the MADs for the subsets in the G3/05 set and it can be seen that there is a general improvement in comparison to B3-LYP, the best of the conventional functionals. This indicates that the perturbation correction really introduces new physical (non-local correlation) effects into the functional. This analyses also reveals that the better performance of mPW2-PLYP compared to B2-PLYP mainly results from the HOF part of the set. Finally we want to comment on some of the remaining larger errors with the new functionals. For B2-PLYP (which seems to behave in this case similar to B3-LYP) these show up in particular for the larger (substiuted) hydrocarbons but this is by and large corrected with mPW2-PLYP. As noted already above, this can be assigned to the improved long-range (low-density) behavior of mPW compared to B88 exchange. More pathological cases (errors for HOF between 5 and 10 kcal mol^{-1}) that are also a problem for other functionals or *e.g.* Gn methods are the O_3, SiF_4, $Si(CH_3)$, PF_5, SF_6 and P_4 molecules. In the IP and EA sets, the largest errors occur for the diatomic molecules CN and C_2 and their ions which in part have incorrect ground states.

In summary we have made a big step towards chemical accuracy in the computation of thermodynamic properties of large molecules by introducing a perturbation correction that is based on Kohn–Sham orbitals and eigenvalues. To the best of our knowledge mPW2-PLYP gives by far the lowest MAD over the whole G3/05 set ever reported for a DFT method, with B2-PLYP being the second best. Note, that the spectacular improvements for this set that contains many large and difficult (*e.g.* perhalogenated) molecules could only be obtained with a big basis set including core polarization/correlation functions. This indicates that the new functionals really provide a better physical description of electronic structure. On the other hand, the price to pay for the better performance compared to conventional density functionals is a poorer convergence of the results with respect to the one-particle basis. Based on previous experiences with B2-PLYP for reaction barriers and geometries, we also expect mPW2-PLYP to perform equally well for these problems. However, it is also clear that our perturbative procedure is not the final answer to everything. For example, it breaks down for systems with a vanishing HOMO-LUMO gap, *e.g.* in dissociating covalent species or for bulk metals. It remains to be seen if our practicable step to the fifth rung of "Jacob's ladder" can be further improved semi-empirically and how far one can go with similar *ab initio* type approaches.

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