

Semiempirical hybrid density functional with perturbative second-order correlation

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A new hybrid density functional for general chemistry applications is proposed. It is based on a mixing of standard generalized gradient approximations (GGAs) for exchange by Becke (B) and for correlation by Lee, Yang, and Parr (LYP) with Hartree-Fock (HF) exchange and a perturbative second-order correlation part (PT2) that is obtained from the Kohn-Sham (GGA) orbitals and eigenvalues. This virtual orbital-dependent functional contains only two global parameters that describe the mixture of HF and GGA exchange (a_x) and of the PT2 and GGA correlation (c), respectively. The parameters are obtained in a least-squares-fit procedure to the G2/97 set of heat of formations. Opposed to conventional hybrid functionals, the optimum a_x is found to be quite large (53% with $c=27%$) which at least in part explains the success for many problematic molecular systems compared to conventional approaches. The performance of the new functional termed B2-PLYP is assessed by the G2/97 standard benchmark set, a second test suite of atoms, molecules, and reactions that are considered as electronically very difficult (including transition-metal compounds, weakly bonded complexes, and reaction barriers) and comparisons with other hybrid functionals of GGA and meta-GGA types. According to many realistic tests, B2-PLYP can be regarded as the *best* general purpose density functional for molecules (e.g., a mean absolute deviation for the two test sets of only 1.8 and 3.2 kcal/mol compared to about 3 and 5 kcal/mol, respectively, for the best other density functionals). Very importantly, also the maximum and minimum errors (outliers) are strongly reduced (by about 10–20 kcal/mol). Furthermore, very good results are obtained for transition state barriers but unlike previous attempts at such a good description, this definitely comes not at the expense of equilibrium properties. Preliminary calculations of the equilibrium bond lengths and harmonic vibrational frequencies for diatomic molecules and transition-metal complexes also show very promising results. The uniformity with which B2-PLYP improves for a wide range of chemical systems emphasizes the need of (virtual) orbital-dependent terms that describe nonlocal electron correlation in accurate exchange-correlation functionals. From a practical point of view, the new functional seems to be very robust and it is thus suggested as an efficient quantum chemical method of general purpose. © 2006 American Institute of Physics. [DOI: 10.1063/1.2148954]

I. INTRODUCTION

Kohn-Sham density-functional theory (KS-DFT) is now the most widely used method for electronic structure calculations in condensed matter physics and quantum chemistry.^{1,2} This success mainly results from significant “robustness,” i.e., providing reasonably accurate predictions for many properties of various molecules and solids.³ Considering basic energetic data for molecules (thermochemistry), the first step in that direction was the introduction of the generalized gradient approximations (GGAs) as corrections to the local-density approximation (LDA) that yields in general not much better results than Hartree-Fock (HF). According to Perdew *et al.*, the various steps forward in the development of more accurate density functionals (DFs) can be assigned to various rungs of “Jacob’s ladder” (see Ref. 4 and references therein). In that picture, the next two steps after GGA (second rung) correspond to the inclusion of exact ex-

change [as, e.g., in BH-LYP (Ref. 5) or B3-LYP (Refs. 6 and 7) functionals] and Laplacians or kinetic-energy density [as, e.g., in TPSS (Ref. 8)]. Empirically it is clear from many tests on standard benchmark sets of molecules (G1–G3 sets^{9–12}) that functionals including a small fraction (10%–25%) of exact exchange (hybrid functionals) perform significantly better than pure GGAs while the importance of kinetic-energy densities (meta-GGA functionals) is somewhat controversial.^{13–15} The fifth rung of the ladder in which in addition unoccupied Kohn-Sham orbitals are utilized leads to methods which converge in a sense to traditional wavefunction methods and Kohn-Sham versions of coupled-cluster type¹⁶ or second-order perturbation theory^{17–19} (PT2) have been proposed. The performance of these approaches is at the moment difficult to judge as they have not been applied to any of the standard test suites. There are indications, however, that *ab initio* KS-PT2 when done self-consistently using the optimized effective potential (OEP) method shows serious errors even for small benchmark systems.¹⁹ The topic

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of this work is an empirical version of KS-PT2 in the framework of a conventional hybrid functional that is (I) highly accurate in general chemistry applications and (II) avoids computational problems associated with *ab initio* KS-PT2 (OEP) approaches.

From a more physically motivated point of view where the corrections to the Hartree energy of electron-electron interaction are separated into exchange energy (EX) and static (near-degeneracy, left-right) and dynamic electron correlations (ECs), respectively, the situation seems quite clear.

- (1) Common exchange-only GGAs such as B88,²⁰ PBE,²¹ or OPTX (Ref. 22) introduce a localized exchange hole around each electron that mimics effects of static electron correlation.^{23,24} These effects are absent in HF and are at least in part necessary for an accurate description of molecules. The difference between HF and exchange-only KS-DFT energies is a rough measure of static (left-right) EC.²³ This aspect of EC is most problematic for simple (single-reference) wave-function theories (WFTs).
- (2) Exact (nonlocal) exchange is necessary to describe situations in which the exchange-correlation hole has a long-range component.²⁵ A fraction of exact exchange also helps to correct the self-interaction error of common GGAs and is thus important for the description of spin/charge-separation processes²⁶ or the accuracy of special types of transition states.¹⁵
- (3) The long-range ECs that are responsible for dispersive (van der Waals) interactions require consideration of virtual KS orbitals (fifth rung) and are thus essentially nonexistent in all current GGAs and meta-GGAs (including hybrids, see, e.g., Refs. 27–29 that describe also other DFT approaches to this problem). It can be expected that also on a medium-range scale such nonlocal correlations play an important role (for example, see Ref. 30) and thus more accurate DF must include virtual orbital-dependent terms. This is the basic motivation of the present work.

The problem can also be viewed from the point of WFT. If one is interested in large molecular systems, only low (e.g. second) order perturbation theory seems applicable, at least in the foreseeable future. If done *ab initio*, however, the resulting second-order Møller-Plesset perturbation theory³¹ (MP2) is not competitive to the best semiempirical KS-DFs and has only specialized application areas (electronically simple main-group compounds and van der Waals complexes). Although this behavior can be much improved [spin-component-scaled (SCS)-MP2 (Ref. 32)] there remain unsolved problems, e.g., spin-contaminated open-shell species or transition-metal complexes. It is hoped that a (semiempirical) combination of KS-DFT and PT2 will improve the description of EC in many aspects. This so-called “best of both worlds” strategy¹⁶ has already been explored successfully in the DFT multireference configuration-interaction (MRCI) method³³ (for related investigations on the use of KS orbitals in WFT, see, e.g., Refs. 34 and 35).

The paper is organized as follows. After an outline of the present approach in Sec. II, the technical details of the cal-

culations (Sec. III A) as well as a description of the necessary fit and validation sets of molecules (Sec. III B) are given. In Sec. IV the results for heats of formation of small molecules, reaction energies for a set of problematic systems, and equilibrium bond distances and vibrational frequencies are presented. Comparisons of the new with three standard hybrid functionals as well as with literature data are also used to assess the performance of the approach. As other DF the most popular B3-LYP (Refs. 6 and 7) hybrid GGA and two meta-GGA hybrids of almost nonempirical type [TPSSH (Ref. 36)] and a highly parametrized form [BMK (Ref. 15)], respectively, have been chosen.

II. THEORY

The present approach is based formally on the exact Kohn-Sham perturbation theory introduced by Görling and Levy^{17,18} (GLPT). This and related orbital-dependent approaches have recently been reviewed in this journal, and therefore for details the reader is referred to the corresponding articles.^{4,16,19,37} Briefly, in the GLPT the KS determinant is the zero-order wave function that yields the exact ground-state electron density. In the first order, the exact exchange KS method (which is the analog of HF in WFT) is derived for which reasonable computational approximations exist.³⁸ Higher-order terms yield electron correlation contributions, and in second order, expressions similar to that of MP2 in WFT are derived. On the contrary, however, in GLPT the KS orbitals depend (through the multiplicative exchange-correlation potential) in a complicated way on the perturbation-theory treatment, a problem which can be solved by OEP methods.

Our much simpler ansatz for a combination of KS-DFT and PT is based on the following expression for the exchange-correlation energy E_{xc} and is given by

$$E_{xc} = (1 - a_x)E_x^{GGA} + a_x E_x^{HF} + bE_c^{GGA} + cE_c^{PT2}, \quad (1)$$

where (in spin-orbital form)

$$E_c^{PT2} = \frac{1}{4} \sum_{ia} \sum_{jb} \frac{[(ia|jb) - (ib|ja)]^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}. \quad (2)$$

is the usual second-order Møller-Plesset-type expression for the correlation energy but here evaluated with the Kohn-Sham orbitals with corresponding eigenvalues ϵ . The indices ia and jb represent single occupied-virtual replacements and the terms in brackets denote regular two-electron integrals over the KS orbitals. In Eq. (1), a_x is the HF-exchange mixing parameter and b and c scale the contributions of GGA and perturbative correlation contributions, respectively. The term GGA denotes local exchange and correlation functionals consisting as usual of the LDA term with additional gradient corrections. Note that this functional reduces to the well-known pure B-LYP (Refs. 20 and 39) GGA for $a_x=0$, $b=1$, and $c=0$, while standard MP2 is recovered with $a_x=1$, $b=0$, and $c=1$ (see below). Although it is in principle possible to derive the KS potential from this expression and to solve the resulting equations self-consistently with the OEP approach, we propose a much simpler computational strategy. The KS equations are solved only with the GGA poten-

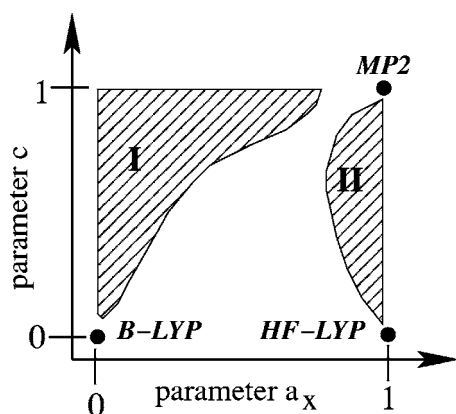


FIG. 1. Schematic description of possible methods arising from different combinations of HF exchange end PT2 mixing parameters. The dashed areas I and II can be excluded by physical reasoning (see text).

tial in Eq. (1) and the resulting orbitals are then inserted into Eq. (2) from which the second-order energy is obtained. Thus, in essence the method requires a usual self-consistent hybrid KS-DFT treatment followed by a standard MP2-type procedure which is computationally (within reasonable integral approximations) not much more laborious than standard DFT itself. Opposed to nonempirical versions of KS-PT2,¹⁹ the single excitations contribution is neglected, i.e., we implicitly assume for all Fock matrix elements $f_{ia}=0$.

In principle, for the GGA parts in Eq. (1) any of the well-known functionals available can be used. We tested B88,²⁰ OPTX,²² and PBE (Ref. 21) for exchange and LYP (Ref. 39) and PBE (Ref. 21) for correlation in various combinations. All in all, the combination of B88 and LYP yields the best results although replacing B88 by OPTX gave very similar results. The inferior results that have been obtained in preliminary computations with PBE and TPSS (Ref. 8) seem to indicate that in these functionals exchange-static and dynamical electron correlation effects are not well separated. Because the choice of the GGA parts is also influenced by the choice of the molecules in the data set and furthermore it seems not desirable to flush the market with many new functionals, only the results employing the combination of B88 and LYP will be presented. The other reason for considering these GGAs is that they are also part of the popular B3-LYP hybrid which allows some assessment of the effect of the PT2 term. The new functional [with suitably defined parameters a_x , b , and c (see below)] is termed in the following B2-PLYP.

Although this ansatz is clearly of semiempirical character, it is quite different from the pure empirical approach that is used frequently to determine new functionals, e.g., up to 16 parameters are fitted to a huge data set (several hundred points^{15,40}). We are not attempting any extensive fitting and there are only three parameters at our disposal. Theoretically, we can expect $b+c \approx 1$ and a quite small fraction of GGA exchange (large a_x) because the PT2 term also accounts for static EC effects. Figure 1 shows schematically the limiting cases when we assume $b=1-c$ and arrange the resulting methods in a diagram with a_x and c as independent variables.

The regions denoted as I and II in Fig. 1 represent physically absurd parameter combinations, i.e., in area I double

counting of static EC effects by the GGA exchange and PT2 parts, respectively, is to be expected. In area II the correlation treatment is also unbalanced with respect to dynamical and static effects. The scheme also suggests the B2-PLYP functional as an interpolation approach between pure GGA-DFT and MP2, respectively.

One of the intriguing questions concerning this approach is how the perturbational part (but with KS orbitals) behaves in cases that are known to be problematic for standard MP2. Parts of the test sets are selected to provide a conclusive answer to this critical question. Furthermore, one may also think of double-counting effects of EC between the GGA and PT2 parts (even outside areas I and II in Fig. 1) that would lead to quite inconsistent results for, e.g., saturated versus metallic systems.

III. TECHNICAL DETAILS

A. Calculations

All calculations were performed with the TURBOMOLE suite of programs.⁴¹ If not stated otherwise, the geometries were completely optimized at the B3-LYP (Refs. 6 and 7) level (taken mainly from Ref. 13) using a doubly polarized valence triple- ζ basis set^{42,43} (TZV2P). The polarization functions are taken from the cc-pVTZ basis⁴⁴ but with discarded highest angular momentum function. The geometries of the transition-metal systems were also taken from previous work⁴⁵ and have been obtained at the BP86 (Refs. 20, 46, and 47)/TZVP level. Subsequent single-point calculations were performed with quadruple- ζ basis sets^{43,48} ([$4s3p2d$] for H, [$7s4p3d2f$] for Be-F, [$9s6p3d2f$] for Al-Cl, [$11s6p5d3f1g$] for Cr-Zn, and [$11s7p4d2f1g$] for Br). The polarization functions for main-group elements were taken from the Dunning⁴⁴ cc-pVQZ basis set. For Au we use a [$6s4p3d$] atomic-orbital (AO) basis⁴³ and a relativistic effective core-potential (ECP) with 60 core electrons.⁴⁹ These AO basis sets (termed in the following QZV3P) are expected to provide DFT/HF and PT2 results that are within chemical accuracy of the basis set limit for atomization energies (errors <0.1 kcal/mol/first-row atom). For weakly bonded complexes the basis set superposition error (BSSE), which is not further corrected for, is also sufficiently small, e.g., for benzene dimers <0.1 kcal/mol and for more strongly bound systems on the order of 5%–10% of ΔE . The calculations for the second test set (Table IV) were performed with reduced basis set size for hydrogen (i.e., [$4s2p1d$]) and in some cases with TZV AO basis sets (see corresponding table footnote).

In the PT2 treatments the resolution-of-the-identity (RI) approximation^{50,51} for the two-electron integrals has been employed which yields errors for absolute PT2 correlation energies and relative energies less than 0.05% and 0.02 kcal/mol, respectively. The auxiliary basis sets were taken from Ref. 52 where they have been optimized for the Dunning cc-pVQZ AO basis sets.⁴⁴ All electrons were correlated in the PT2 treatments which is consistent with the GGA description of EC that is not separable in core and valence parts. The singlet state calculations were performed spin restricted while all open-shell systems were treated unrestricted.

Harmonic vibrational frequencies were calculated at the B3LYP/TZV2P level and scaled by a factor of 0.97 similar to what has recently been recommended⁵³ to calculate the zero-point vibrational energy (ZPVE) and thermal corrections to the enthalpy. The molecular heats of formation are obtained by adding the experimental heats of formation of the atoms to the calculated atomization energies. Our calculations are based on the values given in Ref. 10 and include atomic spin-orbit corrections. The enthalpies at 298 K are obtained by adding the difference $H(298\text{ K}) - H(0\text{ K})$ for the atoms from experiment¹⁰ and for the molecule as obtained from the scaled harmonic vibrational frequencies. The (ZPVE exclusive) reaction energies taken as reference in Table IV were obtained by correcting experimental enthalpies reversely as described above or refer to accurate theoretical data (see corresponding table footnote).

Because the new functional is constructed in an additive manner from the GGA and PT2 parts, it can be expected that the basis set dependence of the results is in between that of standard DFT and MP2, respectively. Preliminary calculations on a few systems from the second test set (see below) indicate that this holds for both computed reaction energies as well as for the BSSE of weakly bonded systems.

The new functional can also be used in single-point calculations with the Gaussian series of quantum chemical programs. For GAUSSIAN03, the route card must contain (all electrons correlated and omitting the basis set specification and other options)

```
# blyp iop (3/76=0470005300,3/78=0730007300)
extraoverlay scf=tight
<empty line>
8/10=90/1; 9/16=-3/6;
<empty line>
----title----
while for GAUSSIAN98 this analogously reads
# blyp iop (5/45=04700530,5/47=07300730)
extraoverlay scf=tight
<empty line>
8/10=4/1; 9/15=-3/6;
<empty line>
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B. Test sets

The initial basis for the evaluation of the methods is the G2/97 data set consisting of the heat of formations of 148 neutral molecules.¹⁰ Although this test set is frequently used and covers a wide range of different chemical structures and bonding situations it does not contain larger systems that are more relevant in chemistry. Furthermore, larger unsaturated and transition-metal compounds are not included. Because any empirical method that has been “trained” on a specific set of systems must be evaluated on a different set we propose to use a second set of systems and reactions for valida-

tion of the method (see Table IV). This selection not only includes ions but also many systems with complicated structure, i.e., large unsaturated, polyhalogenated, hypervalent, and strained organic systems. Many of these represent worst-case scenarios for both conventional DFT and perturbation theory and thus it represents more an attempt to falsify the new functional. This set is grown from experience over the last years and more or less is a merged version of those previously employed in assessments of improved versions of perturbation theory.^{13,32,54} In detail (Table IV), entries 1–31 are reactions involving main-group elements that are extended in entries 32–56 to charged species (proton affinities, ionization potentials, and electron affinities of some atoms including the late 3*d* metals). Molecules with transition metals and especially the difficult 3*d* metals in low oxidation states follow in entries 57–66. Reaction barriers [transition states (TSS)] both as closed-shell transformations and (bi)radical processes are also considered (entries 67–80). The latter were chosen from the Lynch and Truhlar database⁵⁵ with an emphasis on significant spin contamination or large errors for conventional density functionals. The systems 81–89 represent notoriously difficult van der Waals or hydrogen-bonded complexes. Some of the problems associated with these systems are discussed together with the results in Sec. IV B.

IV. RESULTS AND DISCUSSION

A. G2/97 set

The root-mean-square error surface for the G2/97 set with respect to the three parameters a_x , b , and c is found to be relatively steep and especially a_x tends to be quite large (between 0.5 and 0.6). Because also the relation $b+c=1$ strongly holds it was finally decided to reduce the number of parameters to two by setting $b=1-c$. In this way we found a minimum for $a_x=0.53$ and $c=0.27$ with a mean absolute deviation (MAD) of 1.8 kcal/mol. These parameters define the new B2-PLYP method (“2” indicates the number of parameters and the order of perturbation theory and PLYP denotes perturbative correlation with the LYP functional). Note that out of all the functionals tested here, B2-PLYP includes the largest fraction of HF exchange (10% in TPSSh, 20% in B3-LYP, and 42% in BMK). Changes for any of the two parameters of ± 0.01 (and adjusting the other accordingly) lead to changes of the MAD < 0.1 kcal/mol. Furthermore, even with a reasonable (physically motivated) guess for a_x and c (e.g., 0.5 and 0.25, respectively), quite small MAD values of about 2 kcal/mol can be obtained. Some exploration of the error surface with respect to the two parameters further indicates that a_x and c are strongly related and the number of parameters may be even reduced to one. There is, however, also an indirect influence of a_x on c as the HF-exchange admixture increases the orbital gap used in Eq. (2) and therefore decreases E_c^{PT2} .

Before discussing the results for the ΔH_f^0 values, the B2-PLYP total energies of some smaller molecules are given in Table I in comparison with the MP2 and B3-LYP data. As can be seen, the B2-PLYP energies are in between the corresponding MP2 and B3-LYP values. Although it is not of

TABLE I. Perturbative second-order correlation energies (E_c) and total energies $E(\text{in } -E_h)$ for small molecules at B2-PLYP, B3-LYP, and MP2 levels. The cc-pVQZ AO basis and B3-LYP/TZV2P optimized geometries are used.

Molecule	cE_c^{PT2}	E_c^{MP2}	$E(\text{B2-PLYP})$	$E(\text{B3-LYP})$	$E(\text{MP2})$
H ₂	0.0105	0.0331	1.1709	1.1805	1.1665
H ₂ O	0.0986	0.2830	76.4309	76.4696	76.3476
Ethene	0.1323	0.3559	78.5666	78.6292	78.4252
N ₂	0.1484	0.3974	109.5302	109.5769	109.3894
SO ₂	0.2974	0.7154	548.5807	548.7312	548.0224

much importance, for H₂ and H₂O (where experimental values are known) the B2-PLYP total energies are more accurate. Comparison of the MP2 and scaled B2-PLYP second-order energies (first two columns) shows that for the smaller systems the ratio of the two correlation energies is roughly on the order of the scaling factor c but that it increases to about 0.4 for SO₂. Thus, the PT2 part in the new functional is not just a scaled MP2 correlation energy but the KS orbitals and, even more important, the reduced KS occupied/virtual orbital energy gaps in Eq. (2) have a significant influence.

The results for the individual molecules in the G2/97 set are given in Table II and the error distributions for B2-PLYP and B3-LYP are displayed in Fig. 2; comparisons of statistical data for the same set of molecules from the literature can be found in Table III. Compared to other methods, B2-PLYP with MAD=1.8 kcal/mol is highly accurate as can be seen by MADs between 3 and 4 kcal/mol for common hybrid DFs and 7.3 kcal/mol for B-LYP. For B3-LYP and TPSSh we found MAD values of 3.6 and 4.6 kcal/mol, respectively, which compare well with literature data (3.1 and 4.5 kcal/mol (Refs. 12 and 56; the differences are attributed mainly due to different basis sets used). Even more important, also the maximum and minimum errors are strongly reduced (to a min-max range of 16 kcal/mol compared to 25, 29, and 39 kcal/mol for BMK, B3-LYP, and TPSSh, respectively). This indicates that the PT2 contribution really introduces new correlation effects into the DF and not merely represents a new fit. This is also demonstrated in Fig. 2 where the quite narrow Gaussian-type error distribution is shown for B2-PLYP that differs strikingly from the broad and nonsymmetric form of B3LYP. Compared to the best standard functionals available [X3LYP (Ref. 57) containing six empirical mixing parameters and B97-3 (Ref. 40) with 16 parameters] that yield MAD values of 2.8 and 2.3 kcal/mol and large min-max ranges >25 kcal/mol (see Table III), the new functional is clearly the winner, albeit including much less empiricism. Note that simple hybrid functionals that include only a large fraction of HF exchange (but no PT2 term) are much less accurate (e.g., BH-LYP with $\alpha_x=0.5$, $c=0$ gives a MAD of 20.7 kcal/mol and a min-max range of 67 kcal/mol). The here also tested BMK functional¹⁵ (42% HF exchange) is an exception as it is on the average for the G2/97 set slightly better than B3-LYP.

Considering the largest errors of B2-PLYP it is evident that they occur for the systems that are also problematic for the other DFs (BeH, SiF₄, SiCl₄, and SO₂) but that the errors are much smaller. There is also a rough correlation between the errors of B3-LYP and B2-PLYP indicating some funda-

mental problems of the B88 and LYP GGA parts. Only in two cases (N₂O and NO₂) is the new functional significantly worse than its competitors. A detailed analysis reveals that B2-PLYP gives the best result in 65 out of 148 cases (the corresponding numbers for the other three DF are 26–30) while it is worst only for seven molecules (there are 30, 85, and 26 worst-case counts for BMK, TPSSh, and B3LYP, respectively). Particularly impressive are the results for most of the halogenated compounds, especially entries 57–62 where all other functionals fail. The good performance for the radicals CN, ClO, CCH, and C₂H₃ is also interesting because they are problematic for standard MP2 due to spin contamination of the HF reference. These problems completely disappear in the PT2 part presumably due to the use of the (very weakly spin-contaminated) GGA orbitals in Eq. (2).

All in all, if the G2/97 set is taken as benchmark B2-PLYP is clearly the most accurate density-functional approach on the market. It is also comparable to G2 theory [similar MAD and min-max errors (see Table III)] but is not as accurate as G3, but one should keep in mind that these WFT-based approaches also employ empirical corrections and that G3 contains even more parameters (four) than B2-PLYP. In order to put these conclusions on a solid basis, chemically more realistic tests are considered in the next section.

B. Second test set

The results for the 89 reactions in the second data set as well as statistical data about the performance of the four functionals are given in Table IV. Pursuing this table, one finds that as for the G2/97 set, B2-PLYP greatly reduces the errors. According to the MAD and maximum absolute error (max), B2-PLYP can be considered as quite accurate with MAD=3.2 kcal/mol and a max value of 18.5 kcal/mol [entry 1 always excluded (see below)]. For this difficult data set, BMK performs less satisfactory than for the G2/97 selection (on which it has been more or less parametrized) and is here only about as good as TPSSh. The performance of B3-LYP is slightly poorer with MAD and max values of 5.6 and 30.2 kcal/mol, respectively. In summary one can say that B2-PLYP very clearly is the best of the four functionals. In 37 cases the error is smallest and only in four cases it is largest (e.g., entries 57 and 66). For comparison, e.g., BMK is 25 times the best functional but also in 30 cases worst (the corresponding numbers for B3-LYP and TPSSh are 13/27 and 14/28). In cases of large B2-PLYP errors (i.e.,

TABLE II. Deviations of calculated heats of formation ΔH_f^0 (298 K) (in kcal/mol) from experiment (experimental values are taken from Ref. 10) for the G2/97 neutral data set.

Entry	Molecule	ΔH_f^0 Expt.	Deviation ^a			
			B3-LYP	TPSSh	BMK	B2-PLYP
1	H ₂	0.0	0.9	3.3	-1.8	-0.8
2	LiH	33.3	0.4	1.0	-1.5	-1.0
3	BeH	81.7	8.7	10.9	7.2	6.8
4	CH	142.5	1.5	2.8	-0.3	-0.1
5	CH ₂ (³ B ₁)	93.7	2.1	8.5	-0.1	0.6
6	CH ₂ (¹ A ₁)	102.8	-0.2	-0.1	-1.8	-1.8
7	CH ₃	35.0	2.5	6.7	-0.2	0.6
8	CH ₄	-17.9	0.9	5.3	0.2	-0.6
9	NH	85.2	4.1	5.3	2.0	1.4
10	NH ₂	45.1	5.6	4.5	3.0	2.4
11	NH ₃	-11.0	2.5	0.3	1.6	0.3
12	OH	9.4	2.1	-0.6	0.8	0.8
13	H ₂ O	-57.8	-1.5	-5.5	-1.6	-1.4
14	HF	-65.1	-1.3	-3.0	-2.0	-0.7
15	SiH ₂ (¹ A ₁)	65.2	0.8	3.8	0.4	-0.8
16	SiH ₂ (³ B ₁)	86.2	1.2	9.6	-1.1	-0.2
17	SiH ₃	47.9	1.7	10.8	-0.2	0.0
18	SiH ₄	8.2	0.2	10.8	-0.4	-1.3
19	PH ₂	33.1	4.9	7.2	2.5	1.6
20	PH ₃	1.3	1.8	5.9	0.8	-1.4
21	H ₂ S	-4.9	-0.1	2.5	-0.6	-0.8
22	HCl	-22.1	-0.3	1.2	0.9	0.1
23	Li ₂	51.6	-3.6	-1.7	-7.6	-3.4
24	LiF	-80.1	-0.7	-3.6	0.1	0.9
25	C ₂ H ₂	54.2	-2.4	-2.5	-2.2	0.1
26	H ₂ C=CH ₂	12.5	-0.3	3.7	-0.1	-0.6
27	H ₃ C-CH ₃	-20.1	-0.6	7.1	1.4	-1.2
28	CN	104.9	-2.7	-4.8	-3.3	-0.5
29	HCN	31.5	0.0	-3.5	2.6	2.3
30	CO	-26.4	-3.9	-8.8	3.3	-0.2
31	HCO	10.0	1.8	0.0	4.1	2.6
32	H ₂ C=O	-26.0	0.0	-1.0	2.8	0.7
33	CH ₃ -OH	-48.0	-0.8	0.3	1.3	-1.0
34	N ₂	0.0	-0.5	-7.1	0.7	1.6
35	H ₂ N-NH ₂	22.8	4.5	1.1	5.1	1.0
36	NO	21.6	1.9	-2.6	1.8	2.2
37	O ₂	0.0	3.7	0.5	1.9	3.6
38	HO-OH	-32.5	-1.2	-5.6	-2.2	-1.8
39	F ₂	0.0	-0.2	1.9	-4.8	-1.0
40	CO ₂	-94.0	-1.2	-6.9	6.7	3.4
41	Na ₂	34.0	-0.2	1.4	-6.6	-0.5
42	Si ₂	139.9	-6.3	-2.6	-5.6	-4.6
43	P ₂	34.3	-3.4	-5.7	-4.1	-1.9
44	S ₂	30.7	1.6	4.6	2.8	1.9
45	Cl ₂	0.0	-1.1	2.6	5.4	-0.4
46	NaCl	-43.6	-4.8	-1.4	1.7	-2.1
47	SiO	-24.6	-6.7	-11.5	-3.9	-2.0
48	CS	66.9	-5.6	-5.4	-3.7	-1.6
49	SO	1.2	0.9	-0.2	1.7	1.9
50	ClO	24.2	1.8	2.6	1.1	0.0
51	ClF	-13.2	0.3	2.2	0.7	0.5
52	H ₃ Si-SiH ₃	19.1	-3.1	16.2	-1.6	-3.9
53	CH ₃ Cl	-19.6	-0.9	5.3	4.0	-0.1
54	H ₃ C-SH	-5.5	-1.7	4.9	1.4	-1.6
55	HOCl	-17.8	-0.7	-1.2	1.3	-0.2
56	SO ₂	-71.0	-11.7	-13.6	-5.3	-4.8
57	BF ₃	-271.4	-4.0	-8.6	6.0	1.5
58	BCl ₃	-96.3	-6.9	0.1	13.0	1.1

TABLE II. (Continued.)

Entry	Molecule	ΔH_f^0 Expt.	Deviation ^a			
			B3-LYP	TPSSH	BMK	B2-PLYP
59	AlF ₃	-289.0	-10.6	-12.8	-5.5	-2.0
60	AlCl ₃	-139.7	-10.2	-0.1	9.3	-0.8
61	CF ₄	-223.0	-5.8	-5.1	5.0	-0.2
62	CCl ₄	-22.9	-13.9	-2.3	7.0	-3.3
63	COS	-33.1	-0.5	-1.3	7.0	4.2
64	CS ₂	27.9	-1.8	2.2	3.4	3.6
65	COF ₂	-149.1	-6.4	-8.8	2.2	-2.4
66	SiF ₄	-386.0	-20.4	-22.6	-9.0	-9.4
67	SiCl ₄	-158.4	-19.7	-5.2	10.7	-6.7
68	N ₂ O	19.6	4.2	-0.1	1.1	6.8
69	CINO	12.4	2.7	2.6	1.8	3.2
70	NF ₃	-31.6	4.1	6.4	2.1	2.2
71	PF ₃	-229.1	-7.2	-9.0	-0.5	-3.5
72	O ₃	34.1	-5.9	-6.6	-12.0	0.6
73	F ₂ O	5.9	1.9	4.1	-3.7	0.0
74	ClF ₃	-38.0	2.5	9.1	-4.4	2.2
75	C ₂ F ₄	-157.4	1.2	2.2	11.0	5.2
76	C ₂ Cl ₄	-3.0	-12.5	0.2	8.8	-0.2
77	CF ₃ CN	-118.4	-5.2	-7.8	6.5	2.7
78	C ₃ H ₄ (propyne)	44.2	-2.7	0.8	-0.1	0.4
79	C ₃ H ₄ (allene)	45.5	0.9	4.7	2.1	1.1
80	C ₃ H ₄ (cyclopropene)	66.2	-4.5	3.4	-0.6	-2.1
81	C ₃ H ₆ (propylene)	4.8	-2.2	5.1	0.8	-1.4
82	C ₃ H ₆ (cyclopropane)	12.7	-3.9	7.3	2.3	-2.1
83	C ₃ H ₆ (propane)	-25.0	-3.3	7.7	1.6	-2.5
84	C ₄ H ₆ (butadiene)	26.3	-3.4	3.6	0.0	-1.4
85	C ₄ H ₆ (2-butyne)	34.8	-4.0	3.2	1.1	-0.3
86	C ₄ H ₆ (methylenecyclopropane)	47.9	-2.0	9.0	4.6	0.7
87	C ₄ H ₆ (bicyclobutane)	51.9	-9.4	6.3	-0.1	-4.4
88	C ₄ H ₆ (cyclobutene)	37.4	-8.0	3.8	4.6	-4.0
89	C ₄ H ₈ (cyclobutane)	6.8	-7.5	7.3	6.5	-3.7
90	C ₄ H ₈ (isobutene)	-4.0	-5.3	5.3	0.8	-2.8
91	C ₄ H ₁₀ (butane)	-30.0	-6.1	8.1	2.1	-3.9
92	C ₄ H ₁₀ (isobutane)	-32.1	-7.4	6.9	1.2	-4.6
93	C ₅ H ₈ (spiropentane)	44.3	-8.4	9.7	4.1	-3.0
94	C ₆ H ₆ (benzene)	19.7	-7.9	2.2	3.5	0.5
95	H ₂ CF ₂	-107.7	-0.6	2.5	3.4	0.8
96	CHF ₃	-166.6	-3.1	-1.1	4.2	0.4
97	H ₂ CCl ₂	-22.8	-4.3	3.6	5.8	-0.9
98	CHCl ₃	-24.7	-8.7	1.0	6.7	-2.0
99	CH ₃ -NH ₂	-5.5	1.4	3.6	3.1	-0.3
100	CH ₃ -CN	18.0	-0.4	-0.5	4.5	2.2
101	CH ₃ -NO ₂	-17.8	1.6	1.3	2.4	3.2
102	CH ₃ -O-N=O	-15.9	-0.2	0.0	1.2	0.5
103	CH ₃ -SiH ₃	-7.0	-3.6	9.6	0.0	-3.8
104	HCOOH	-90.5	-2.0	-6.3	4.3	0.4
105	HCOOCH ₃	-85.0	-2.3	-1.4	7.0	0.7
106	CH ³ CONH ₂	-57.0	-1.1	-1.8	7.2	0.3
107	CH ₂ -NH-CH ₂	30.2	-1.3	6.0	5.4	-0.8
108	NC-CN	73.3	-0.7	-7.8	4.0	5.4
109	(CH ₃) ₂ NH	-4.4	-0.4	5.9	4.0	-1.3
110	CH ₃ -CH ₂ -NH ₂	-11.3	-0.2	5.1	4.4	-0.6
111	H ₂ C=C=O	-11.3	1.4	0.3	6.2	3.3
112	H ₂ C-O-CH ₂ (oxirane)	-12.6	-3.0	4.0	3.6	-1.2
113	CH ₃ CHO	-39.7	-1.5	0.4	3.8	-0.1
114	O=CH-CH=O	-50.7	-2.7	-6.3	5.9	1.0
115	CH ₃ -CH ₂ OH	-56.2	-3.4	0.7	1.4	-2.4
116	CH ₃ -O-CH ₃	-44.0	-1.7	4.3	3.1	-1.5

TABLE II. (Continued.)

Entry	Molecule	ΔH_f^0 Expt.	Deviation ^a			
			B3-LYP	TPSSh	BMK	B2-PLYP
117	CH ₂ -S-CH ₂ (thiirane)	19.6	-4.4	6.7	5.5	-1.2
118	CH ₃ -SO-CH ₃	-36.2	-9.6	-0.4	-1.7	-5.9
119	CH ₃ -CH ₂ -SH	-11.1	-4.2	5.8	1.9	-2.6
120	CH ₃ -S-CH ₃	-8.9	-3.9	6.7	2.8	-2.5
121	H ₂ C=CHF	-33.2	0.5	3.7	3.1	1.2
122	CH ₃ -CH ₂ -Cl	-26.8	-3.6	5.8	4.2	-1.5
123	H ₂ C=CH-Cl	5.5	-2.4	3.5	3.2	-0.1
124	H ₂ C=CH-Cl	43.2	-3.3	-3.5	1.8	0.5
125	CH ₃ -CO ₂ -CH ₃	-51.9	-4.2	0.7	4.3	-1.5
126	CH ₃ COOH	-103.4	-4.6	-6.0	4.8	-1.1
127	CH ₃ COF	-105.7	-3.5	-2.3	4.5	-0.3
128	CH ₃ COCl	-58.0	-4.2	-0.2	6.4	-0.2
129	CH ₃ CH ₂ CH ₂ -Cl	-31.5	-6.2	6.6	4.8	-2.5
130	(CH ₃) ₂ CH-OH	-65.2	-6.7	0.5	1.6	-3.8
131	C ₂ H ₅ -O-CH ₃	-51.7	-3.8	5.3	4.0	-2.2
132	(CH ₃) ₃ N	-5.7	-2.9	7.7	4.8	-2.1
133	C ₄ H ₄ O (furan)	-8.3	-6.9	-0.5	6.3	-0.4
134	C ₄ H ₄ S (thiophene)	27.5	-10.3	1.0	2.1	-1.5
135	C ₄ H ₄ NH (pyrrole)	25.9	-4.3	2.4	8.6	1.2
136	C ₅ H ₅ N (pyridine)	33.6	-4.4	2.1	7.7	2.5
137	SH	34.2	1.9	2.8	0.7	0.8
138	CCH	135.1	-4.0	-3.3	-5.5	-2.2
139	C ₂ H ₃ (² A')	71.6	2.5	6.5	0.9	1.2
140	CH ₃ CO	-2.4	0.9	2.2	5.5	2.0
141	H ₂ COH	-4.1	1.7	2.2	2.0	0.6
142	CH ₃ O	4.1	3.1	5.0	3.6	0.1
143	CH ₃ CH ₂ O	-3.7	-0.2	5.2	3.2	-2.0
144	CH ₃ S	29.8	1.7	6.8	4.0	1.1
145	C ₂ H ₅	28.9	1.5	8.9	1.0	0.0
146	(CH ₃) ₂ CH	21.5	-1.1	9.6	1.3	-1.8
147	(CH ₃) ₃ C	12.3	-3.4	10.4	1.4	-2.8
148	NO ₂	7.9	4.8	1.5	0.9	6.0
Mean deviation			-2.2	1.6	2.0	-0.4
Mean absolute deviation			3.6	4.6	3.4	1.8
Maximum deviation			8.6	16.2	13.0	6.8
Minimum deviation			-20.4	-22.6	-12.0	-9.4

^aDeviation=expt.-calc. Absolute deviations larger than 5 kcal/mol are indicated in bold.

>10 kcal/mol), either the reaction energies are huge (entries 1 and 2) or the systems are very problematic in general so that the other functionals also provide large errors (self-interaction problem for He₂⁺ and stretched H₂⁺, closed-shell description of an almost perfect biradical, entry 27). Serious problems are noted only for the formation of S₈ from S₂ (the error of 18.5 kcal/mol is reduced to about 15 kcal/mol with an AO basis employing core-polarization/correlation functions) and some of the transition-metal complexes (especially entry 66) where the ligands seem in general to be slightly overbound. The MADs for the transition-metal subset are about 7 kcal/mol for both B3-LYP and B2-PLYP, 5 kcal/mol for BMK, and 3.2 kcal/mol for TPSSh. It is clear that the large HF and PT2 contributions are responsible for the behavior of the new functional in these cases but the relatively good results of BMK indicate that more flexible (special) functionals may work also with large α_x . However, it is also noted that the B2-PLYP errors are quite large only

for dissociations of CO ligands [or disrupting the bridging CO ligands in Co₂(CO)₈, entry 66] and the other deviations seem even more systematic than with the other functionals (especially B3-LYP).

Except for some other medium-sized errors for strained hydrocarbons (entries 4 and 7) and for the IP of the Be and Ni atoms, where the other functionals are even worse, B2-PLYP performs remarkably well. In particular, spectacular improvements are observed for entries 2, 5, 10, and 16 and all reaction barriers where even BMK is outperformed (which was designed for that purpose). The very good performance for the barriers is noteworthy because many previous attempts at such a good description often resulted in bad performance for equilibrium properties (see Ref. 15 for details). Furthermore, B2-PLYP is the only functional that yields the right sign for the isomerization energies of allene and pyridone and it is also the winner for anions and weakly bonded systems. However, dispersion-dominated complexes

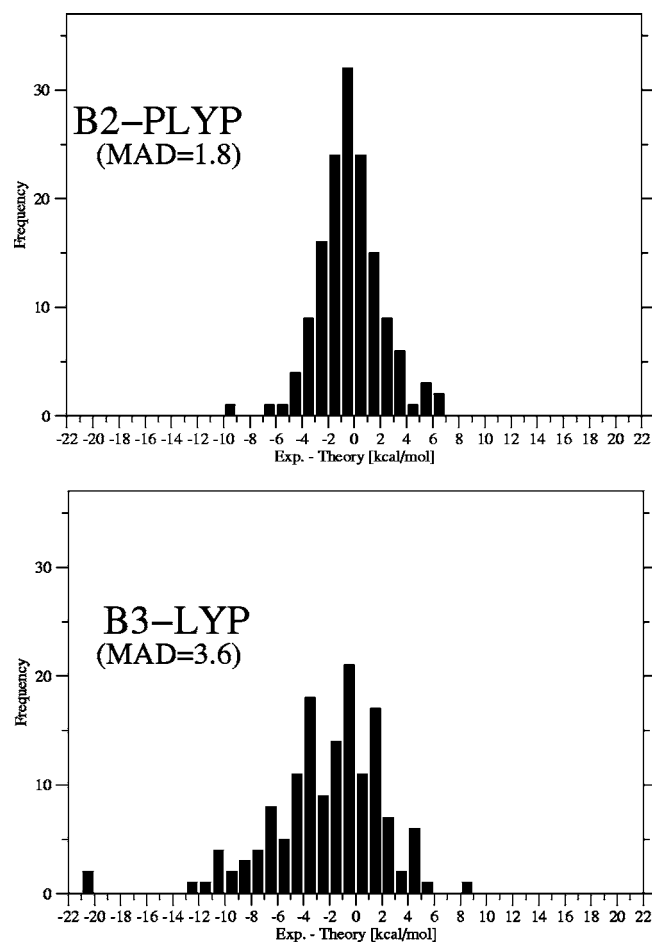


FIG. 2. Histograms of deviations for the G2/97 data set of molecules. Each vertical bar represents deviations for $\Delta H_f^0(298)$ in a 1 kcal/mol range.

s, e.g., the benzene dimer (entry 83), are only very weakly bound at the B2-PLYP level because the GGA parts are purely repulsive (similar to the other functionals) and the (attractive) PT2 contribution is too small. Compared to, e.g., B3-LYP, however, the improvement is substantial and B2-PLYP seems to work quite well for more strongly bound systems with shorter intermolecular distances (e.g., entries 80 and 81). This view is further supported, firstly, by the results for the strongly bound Watson-Crick base pair of guanine and cytosine (entry 89) where (as noted recently²⁷) dispersion is also important and thus B2-PLYP is better than B3-LYP by about 2 kcal/mol and, secondly, by the more consistent description of the series of dimers from ammonia to hydrogen fluoride (entries 85–87).

There are further systems that deserve a comment. For the (hypothetical) formation reaction of fullerene C_{60} from C_3 all functionals except of B3-LYP provide surprisingly accurate results that are within the experimental uncertainties (the range of experimental values^{58,59} for ΔH_f^0 is 30 kcal/mol). A huge π system such as C_{60} has significant metallic character which poses a problem for standard (MP2) perturbation theory.¹³ However, the B2-PLYP error for this system is not larger than usual (0.5 kcal/mol/atom) which may be attributed to the KS orbitals and the reduced PT2 contribution. The other metallic system (Be_4 , entry 13) is

TABLE III. Mean absolute (MAD), maximum (max), and minimum (min) deviations (kcal/mol) from experiment for the heats of formations ΔH_f^0 (298 K) of the G2/97 neutral data set (148 entries) as obtained from different density functionals and Gn theory.

Method	Max	Min	MAD
B-LYP ^a	24.8	-28.4	7.3
PBE0 ^b	16.2	-24.0	4.8
TPSSh ^c	16.2	-22.6	4.6
BMK ^c	13.0	-12.0	3.4
B3-LYP ^c	8.6	-20.4	3.6
B3-LYP ^a	8.2	-20.1	3.1
X3-LYP ^d	7.9	-18.5	2.8
B97-3 ^e	7.2	-22.4	2.3
B2-PLYP ^c	6.8	-9.4	1.8
G2 ^f	8.2	-7.1	1.6
G3 ^f	4.9	-4.8	0.9

^aReference 56.

^bReference 62.

^cThis work.

^dReference 57.

^eReference 40.

^fReference 11.

significantly overbound, but considering the similar or even much larger errors of B3-LYP and TPSSh, this does not seem alarming.

The proton affinities of ammonia, water, and hydrogen fluoride (entries 32–34) seem at first sight relatively accurate with all functionals (deviations of +1.3 to -1.8 kcal/mol) but a closer look reveals this not to be true. For a chemist, very often the trends in a series of molecules are more important than accurate absolute values and in this sense a good functional should provide similar errors for the isoelectronic series. As can be seen from the values in Table IV this does not hold for BMK which yields errors between -0.5 and 0.7 kcal/mol (range of 1.2 kcal/mol) while the other three yield much smaller ranges of 0.2 (B2-PLYP), 0.3 (B3LYP), and 0.4 (TPSSh) kcal/mol. This finding may be attributed to some kind of overfitting in BMK.

C. Bond lengths and potential-energy curves

It is clear that the performance of the proposed model must be also evaluated on properties other than energies. Because analytical gradients have not yet been implemented, only preliminary tests could be performed. In Table V, equilibrium bond distances and harmonic vibrational frequencies obtained by the calculation of the potential-energy curves for 18 diatomic molecules are presented. Table VI shows results for the FOOF molecule and transition-metal complexes in comparisons with MP2 and B3-LYP.

Inspection of the data in Table V shows that already the r_e values calculated by B3-LYP compare favorably with experiment (MAD=0.016 Å). Nonetheless, B2-PLYP provides also here uniform improvements (MAD=0.010 Å) and also the maximum error is reduced. Particular noteworthy are the more consistent B2-PLYP results for the heavier molecules Cl_2 , Br_2 , and Cu_2 where the B3-LYP errors are relatively large. Furthermore, also the difficult molecules with spin/spatial-symmetry breaking in the KS determinant (N_2^+ , O_2^+ ,

TABLE IV. Deviations for energetic data (ΔE , ZPVE exclusive, in kcal/mol) from reference values for the second data set. (If not mentioned otherwise, it is derived from experimental ΔH_f° values that have been taken from Refs. 10, 63, and 64. The experimental values of the transition-metal complexes 60–66 are from Ref. 45 and for the barrier heights 75–80 from Ref. 55. The (theoretical) reference values for most of the weakly bound systems are from Ref. 27 (from which also the DFT-D-BLYP geometries used were taken). The IP of the transition-metal atoms refer to a $d^n s^1$ configuration of the ion; the experimental values are from Ref. 65.)

Entry	Species	ΔE Reference value	Deviation ^a			
			B3-LYP	TPSSH	BMK	B2-PLYP
Main-group reactions						
1	$20C_3 \rightarrow C_{60}^b$	-3367 ^c	-173.0	-15.0	-32.9	-33.0
2	$P_4 + 5O_2 \rightarrow P_4O_{10}$	-653.5	-21.4	-28.7	44.3	10.2
3	$SF_6 + O_2 \rightarrow SO_2 + 3F_2$	-223.7	-8.2	-5.2	10.8	-1.3
4	$^3CH_2 + 3\text{ethyne} \rightarrow \text{quadricyclane}$	-187.8	-16.0	4.9	18.2	-6.6
5	$3\text{ethene} + 2\text{ethyne} \rightarrow \text{adamantane}$	-177.7	-17.7	4.6	23.4	2.9
6	$^1CH_2 + H_2 \rightarrow CH_4$	-128.2	1.6	3.5	5.1	3.4
7	$3\text{ethene} + \text{ethyne} \rightarrow \text{bicyclo}[2.2.2]\text{octane}$	-127.2	-25.6	-9.8	4.2	-10.4
8	$3\text{ethyne} \rightarrow$	-151.1	-0.3	10.0	10.4	0.7
9	$F_2 + H_2 \rightarrow 2HF$	-132.9	-2.5	-10.4	3.6	0.9
10	$6Cl_2 + \text{benzene} \rightarrow C_6Cl_6 + 6HCl$	-149.4	-24.5	-22.3	-21.6	-3.5
11	$4S_2 \rightarrow S_8^d$	-101.0	-30.2	-16.9	4.2	-18.5
12	$CH_3 + SO_2 \rightarrow (CH_3)_2SO_2$	-96.2	-13.2	-11.0	-1.6	-8.0
13	$4Be \rightarrow Be_4(T_d)$	-86.4 ^e	7.7	22.9	-0.5	11.2
14	$\text{benzene} + 3H_2 \rightarrow \text{cyclohexane}$	-67.8	-11.2	-8.2	4.1	-6.5
15	$CO + 3H_2 \rightarrow CH_4 + H_2O$	-62.3	2.5	0.7	2.8	2.1
16	$2P_2 \rightarrow P_4$	-55.6	-9.4	10.0	10.4	-5.3
17	$\text{ethyne} + H_2 \rightarrow \text{ethene}$	-48.8	0.8	2.4	3.4	-0.3
18	$\text{butadiene} + \text{ethene} \rightarrow \text{cyclohexene}$	-38.7	-5.3	0.2	7.1	0.1
19	$N_2 + 3H_2 \rightarrow 2NH_3$	-36.7	4.1	0.8	9.8	2.2
20	$\text{diphenylethyne} \rightarrow \text{anthracene}^b$	-36.2	2.2	5.5	7.5	4.7
21	$BH_3 + CO \rightarrow BH_3CO$	-25.0 ^f	3.3	7.6	6.3	2.2
22	$\text{anthracene} + H_2 \rightarrow 9, 10\text{-dihydroanthracene}^b$	-20.0	-3.2	-2.7	3.8	-1.1
23	$OH + H_2 \rightarrow H + H_2O$	-16.1	-4.2	-7.9	-0.2	-1.2
24	$SO_3 + H_2O \rightarrow H_2SO_4$	-15.5	2.7	3.8	7.6	3.5
25	$CH_2O + H_2O \rightarrow CH_2(OH)_2$	-13.7	-1.7	0.9	1.1	-0.8
26	$HCN + H_2O \rightarrow CH_4 + NH_3$	-12.7	-0.5	-0.1	3.4	-1.3
27	$\text{endiyne} \rightarrow ^1p\text{-benzyne}^b$	10.1 ^g	-23.6	-15.4	-26.5	-7.6
28	$CO + H_2O \rightarrow CO_2 + H_2$	-6.7	5.5	11.2	3.5	4.9
29	$O + CH_4 \rightarrow OH + CH_3$	5.6	2.4	0.0	-0.3	1.1
30	$\text{allene} \rightarrow \text{propyne}$	-1.5	-3.3	-3.7	-2.0	-0.6
31	$\text{pyridone} \rightarrow 2\text{-hydroxypyridine}^b$	-1.0 ^h	-1.6	-1.8	-1.8	-0.9
Ionic systems						
32	$NH_3 + H^+ \rightarrow NH_4^+$	212.5 ⁱ	1.0	-1.8	-0.5	1.1
33	$H_2O + H^+ \rightarrow H_3O^+$	172.3 ⁱ	0.8	-1.6	-0.1	1.1
34	$HF + H^+ \rightarrow H_2F^+$	122.2 ⁱ	1.1	-1.4	0.7	1.3
35	$He_2^+ \rightarrow He + He^+$	56.9 ^j	-20.0	-20.6	-11.7	-10.8
36	$H_2^+ \rightarrow H_2^+(r=2r_e)$	36.3 ^k	14.6	13.2	10.3	8.3
37	$Li \rightarrow Li^+$	124.3	-3.7	-2.4	2.4	-2.0
38	$Be \rightarrow Be^+$	214.9	6.7	6.1	11.6	7.1
39	$B \rightarrow B^+$	191.4	-8.2	-10.3	-3.9	-4.8
40	$C \rightarrow C^+$	259.6	-4.6	-4.6	-1.6	-2.2
41	$N \rightarrow N^+$	335.3	-0.8	-2.8	0.2	0.6
42	$O \rightarrow O^+$	313.8	-9.6	-7.6	-8.8	-3.8
43	$F \rightarrow F^+$	401.7	-4.4	1.4	-3.7	-1.1

TABLE IV. (Continued.)

Entry	Species	ΔE Reference value	Deviation ^a			
			B3-LYP	TPSSh	BMK	B2-PLYP
44	Fe \rightarrow Fe ⁺	180.8	-0.2	8.4	-0.9	1.6
45	Co \rightarrow Co ⁺	189.1	-0.8	7.2	-3.0	1.6
46	Ni \rightarrow Ni ⁺	206.4	7.6	14.9	4.4	10.2
47	Cu \rightarrow Cu ⁺	249.7	1.4	3.0	15.7	-1.3
48	Zn \rightarrow Zn ⁺	212.8	-2.1	4.0	-4.6	0.9
49	F \rightarrow F ⁻	78.4	-0.7	3.0	2.2	-1.8
50	O \rightarrow O ⁻	33.7	-2.9	2.1	0.7	-1.5
51	C \rightarrow C ⁻	29.1	-0.8	-2.9	0.5	1.1
52	B \rightarrow B ⁻	6.4	-2.6	-3.2	0.4	0.0
53	Cl \rightarrow Cl ⁻	83.4	0.8	1.3	-1.5	0.1
54	S \rightarrow S ⁻	47.9	-0.8	0.4	-1.0	0.1
55	Si \rightarrow Si ⁻	31.9	2.7	-1.0	1.9	2.7
56	Al \rightarrow Al ⁻	10.2	1.2	-1.3	3.2	2.3
Transition-metal reactions						
57	CuF ₄ ⁻ \rightarrow CuF ₂ ⁻ + F ₂	91.7 ^l	0.9	-6.4	-3.2	7.2
58	Au ₂ \rightarrow 2Au	53.0 ^m	7.8	2.7	4.0	4.8
59	Cu ₂ \rightarrow 2Cu	47.2 ⁿ	6.0	2.8	2.5	3.9
60	Cr(CO) ₆ \rightarrow Cr(CO) ₅ + CO	39.0	3.4	-3.2	1.0	-6.5
61	Ni(CO) ₃ \rightarrow Ni(CO) ₂ + CO	30.0	1.0	-4.3	1.1	-7.6
62	Ni(CO) ₄ \rightarrow Ni(CO) ₃ + CO	27.0	7.4	0.2	9.7	-8.4
63	Cr(CO) ₅ (ethene) \rightarrow Cr(CO) ₅ + ethene	27.0	12.4	2.9	5.9	-2.6
64	Cr(CO) ₅ (H ₂) \rightarrow Cr(CO) ₅ + H ₂	17.5	4.6	0.0	3.2	-2.8
65	Mn ₂ (CO) ₁₀ + H ₂ \rightarrow 2Mn(CO) ₅ H	8.7	9.6	5.3	6.3	-4.9
66	Co ₂ (CO) ₈ + H ₂ \rightarrow 2Co(CO) ₄ H	3.5	10.1	1.0	8.0	-16.2
Barrier heights						
67	HCN \rightarrow CNH	47.7 ⁱ	0.2	0.2	1.9	-0.2
68	butadiene \rightarrow cyclobutene	45.4 ⁱ	-3.3	0.0	-1.8	-2.8
69	cope-rearrangement	34.8 ^o	-1.4	2.7	-4.1	0.2
70	butadiene + ethene \rightarrow cyclohexene	22.6 ^l	-4.2	1.5	-3.2	-1.1
71	CH ₂ N ₂ + ethene \rightarrow 1-pyrazoline	13.9 ^p	-4.6	-0.2	-5.3	-1.1
72	cyclopentadiene \rightarrow dicyclopentadiene	13.3 ^q	-9.1	-0.5	-3.1	-0.3
73	Cl ⁻ + CH ₃ Cl(S _N 2)	2.5 ^r	2.2	4.5	-2.0	1.8
74	F ⁻ + CH ₃ F(S _N 2)	-0.3 ^s	3.4	5.6	-0.5	2.2
75	H + HCl \rightarrow H ₂ + Cl	18.0	5.1	8.7	0.3	1.6
76	O + CH ₄ \rightarrow OH + CH ₃	13.7	6.0	5.5	1.4	2.4
77	O + HCl \rightarrow OH + Cl	9.8	8.4	8.6	2.7	3.1
78	H + H ₂ \rightarrow H ₂ + H	9.6	5.5	8.4	-0.3	2.4
79	H + CH ₃ OH \rightarrow H ₂ + CH ₂ OH	7.3	3.6	6.6	-2.5	-0.6
80	H ₂ + OH \rightarrow H ₂ O + H	5.7	4.7	5.1	1.3	2.3
Weakly bound complexes						
81	ethyne + ethene \rightarrow ethyne · ethene(C _{2v})	-1.5	-0.8	-0.6	-1.1	-0.4
82	2benzene \rightarrow (benzene) ₂ (T)	-2.8	-4.0	-3.2	-3.0	-1.6
83	2benzene \rightarrow (benzene) ₂ (PD)	-2.8	-6.0	-5.1	-4.0	-2.5
84	2Be \rightarrow Be ₂	-2.6 ^t	1.6	4.3	-0.1	-0.1
85	2NH ₃ \rightarrow (NH ₃) ₂	-3.1 ⁱ	-0.7	-0.6	-0.8	-0.3
86	2H ₂ O \rightarrow (H ₂ O) ₂	-5.2 ⁱ	-0.4	-0.4	-0.8	-0.2
87	2HF \rightarrow (HF) ₂	-4.7 ⁱ	0.0	-0.1	-0.5	0.1
88	2HCOOH \rightarrow (HCOOH) ₂	-13.9	1.2	2.0	1.4	1.8

TABLE IV. (Continued.)

Entry	Species	ΔE Reference value	Deviation ^a			
			B3-LYP	TPSSh	BMK	B2-PLYP
89	G+C → G·C (Watson-Crick)	-28.8	-3.2	-2.5	-2.5	-1.3
	Mean deviation		-1.7	0.0	1.9	-0.5
	Mean absolute deviation		5.6	5.2	4.9	3.2
	Maximum absolute deviation		30.2	28.7	44.3	18.5
	No. of times best		13	14	25	37
	No. of times worst		27	28	30	4

^aDeviation=reference-calc. Absolute deviations larger than 5 kcal/mol are indicated in bold and errors leading to wrong signs for ΔE in italic. If not mentioned otherwise, the calculated results refer to single-point calculations with QZV3P AO basis sets employing B3-LYP/TZV2P optimized geometries (see Sec. III A). The electron affinities were obtained with an aug-cc-pVQZ AO basis set (Ref. 44 and 66).

^bTZV(2df,2pd) AO basis.

^cDerived from recommend ΔH_f^0 value (Refs. 64), not included in the statistics.

^dMP2/TZV(2df) geometry.

^eQCISD(T)/QZV3P value using MP2/TZV(2df,2pd) geometry.

^fReference 67.

^gCCSD(T)/cc-pVTZ (Ref. 68).

^hQCISD(T)/TZV(2df,2pd) (Ref. 69).

ⁱQCISD(T)/QZV(3d2f,2pd) (Ref. 32).

^jCI (Ref. 26).

^kExact within the AO basis.

^lCCSD(T) (Ref. 70).

^mReference 71.

ⁿReference 72.

^oReference 73.

^pQCISD(T)/TZV(2df,2pd).

^qEndo form of product (Ref. 15).

^rCCSD(T)/aug-cc-pVTZ from Ref. 74.

^sQZV3P AO basis augmented with diffuse set of *spd* functions on fluorine atoms used for all treatments (Ref. 75).

^t r_{12} MRCI (Ref. 76).

and F_2^+), which is a problem for MP2, are described very well. On the average, also the vibrational frequencies are better than with B3-LYP (MAD of 24 vs 50 cm^{-1}).

These findings are further supported by diatomic potential-energy curves for the extreme cases N_2 (triple bond) and Be_2 (strong van der Waals bond) shown in Fig. 3. For N_2 , B3-LYP yields too high while MP2 gives too low energies as the bond is stretched. The B2-PLYP data are remarkably close to the CCSD(T) reference. For Be_2 , B2-PLYP clearly outperforms all other approaches and seems to be even more accurate than the recent OEP(2) method from Ref. 16. Note that neither geometric data nor weakly bonded complexes have been used to obtain the two empirical parameters of the method.

The theoretical description of transition-metal complexes with metals in low oxidation states is particularly difficult because MP2 and HF errors for metal-ligand distances have opposite sign, i.e., MP2 gives much too short and HF too long bonds. The complexes considered in Table VI represent thus a critical test of the two mixing parameters a_x and c for properties other than the energy. Similar problems have been observed for the structure of the FOOF molecule (as discussed in detail in Ref. 60) that is included as a challenging main-group system.

Perusing this table, one finds that B2-PLYP performs very good and is even better than B3-LYP for the carbonyl compounds and the $Cr(C_6H_6(CO)_3)$ complex. For ferrocene

both DF approaches perform almost the same with deviations between 2 and 4 pm. The problems of MP2 mentioned above are evident from deviations between 6 and 8 pm (15–20 pm for ferrocene) for metal-ligand distances. For FOOF notably good results are obtained with B2-PLYP for the critical OF distance that is too short with MP2 and B3-LYP. Although these promising results must be further verified on larger systems, they indicate that the success of the introduced PT2 part also transfers to the description of structural properties.

V. CONCLUSIONS

The success of time-dependent DFT for the excited states of molecules and solids very strongly underlines the very fundamental meaning of the virtual Kohn-Sham orbitals. It seems thus straightforward to employ these functions (even when resulting from approximate GGA functionals) as basis for a simple perturbation treatment of electron correlation. This idea has been explored empirically in the present work by considering basic energetic data of atoms and molecules. The new functional consisting of standard GGA exchange and correlation parts and the new perturbative term with two appropriate mixing factors seems to outperform all current hybrid GGAs and meta-GGAs, respectively. This conclusion is not only based on a widely used standard set of molecules ($G2/97 \Delta H_f^0$ values) but further supported by a

TABLE V. Comparison of experimental (Ref. 72) and calculated [QZV3P AO basis (see Sec. III A)] (given as deviations= $\text{expt.}-\text{calc.}$) ground-state equilibrium bond distances r_e (in Å) and harmonic vibrational frequencies ω_e (in cm^{-1}) for 18 diatomic molecules.

	r_e			ω_e		
	Expt.	B3-LYP	B2-PLYP	Expt.	B3-LYP	B2-PLYP
CH	1.120	-0.002	0.004	2859	21	-48
OH	0.970	-0.004	-0.001	3738	21	-33
HF	0.917	-0.006	-0.003	4138	40	6
B ₂	1.590	-0.022	-0.014	1051	-2	-48
C ₂	1.242	-0.004	-0.011	1855	-19	9
N ₂ ⁺	1.116	0.013	0.000	2207	-123	3
N ₂	1.098	0.008	0.000	2360	-87	9
BF	1.252	-0.009	-0.008	1402	-6	-32
O ₂ ⁺	1.116	0.011	-0.005	1905	-144	63
O ₂	1.208	0.003	-0.005	1580	-50	39
F ₂ ⁺	1.322	0.028	0.005	1073	-158	8
F ₂	1.412	0.015	0.011	917	-128	-92
P ₂	1.893	0.002	-0.009	781	-38	2
SO	1.481	-0.011	-0.014	1149	1	3
S ₂	1.889	-0.019	-0.016	726	17	24
Cl ₂	1.987	-0.033	-0.020	560	22	8
Br ₂	2.281	-0.032	-0.013	325	6	-3
Cu ₂	2.220	-0.062	-0.038	264	21	-8
Mean deviation		-0.007	-0.008		-33	-5
Mean absolute deviation		0.016	0.010		50	24
Maximum absolute deviation		0.062	0.038		158	92

second set of 87 reactions that can be regarded as mostly very difficult for electronic structure methods. For both data sets, B2-PLYP performs best with MADs of only 1.8 and 3.3 kcal/mol, respectively, compared to, e.g., 3.4 and 4.9 kcal/mol for BMK. Compared to the other density functionals tested, particularly striking are the results for oxidation reactions, strained or polyhalogenated molecules, isomerizations, and the notoriously difficult transition states. Even the electron affinities that are already good with B3-LYP or BMK are further improved, again, both on the aver-

age and also with respect to the error range. Preliminary results for bond distances and harmonic vibrational frequencies of diatomic molecules and geometries of transition-metal complexes are also very promising. The new functional furthermore provides the best results for noncovalently bound systems (including borderline cases such as Be₂) where dispersion (long-range correlation) is important. Furthermore, one of the critical questions how the perturbational part behaves in cases that are known to be problematic for standard MP2 can be positively answered. Except for the

TABLE VI. Comparison of experimental and calculated ground-state equilibrium bond distances (in Å) for FOOF (the experimental MP2 and B3-LYP values are from Ref. 60 and all calculations refer to a cc-p VQZ AO basis) and transition-metal compounds (The experimental values are from Refs. 77–80. The MP2 and B3-LYP data are from Ref. 81. For the metal atoms a [6s4p3d1f] AO basis is used. The remaining basis sets are TZV (2df) for the first two molecules and TZV (2d,2p) for the rest.)

Molecule	Parameter	Expt.	Deviation=100(expt.-calc.)		
			MP2	B3LYP	B2-PLYP
FOOF	OO	1.214	1.4	-1.3	1.2
	OF	1.571	2.9	5.0	0.8
Cr(CO) ₆	CrC	1.914	6.3	-1.2	-0.6
	CO	1.140	-1.6	0.1	-0.8
Ni(CO) ₄	NiC	1.838	6.9	-0.3	-0.8
	CO	1.141	-1.0	0.6	-0.3
Cr(C ₆ H ₆ (CO) ₃)	CrC _{ar}	2.230	6.8	-2.2	1.4
	CrC _{CO}	1.845	8.8	-1.5	-0.5
	CO	1.158	-1.7	0.8	0.2
Ferrocene	FeC	2.06	15.9	-2.0	3.5
	CC	1.44	0.0	1.7	-1.2
	FeCp	1.66	20.6	-3.2	4.0

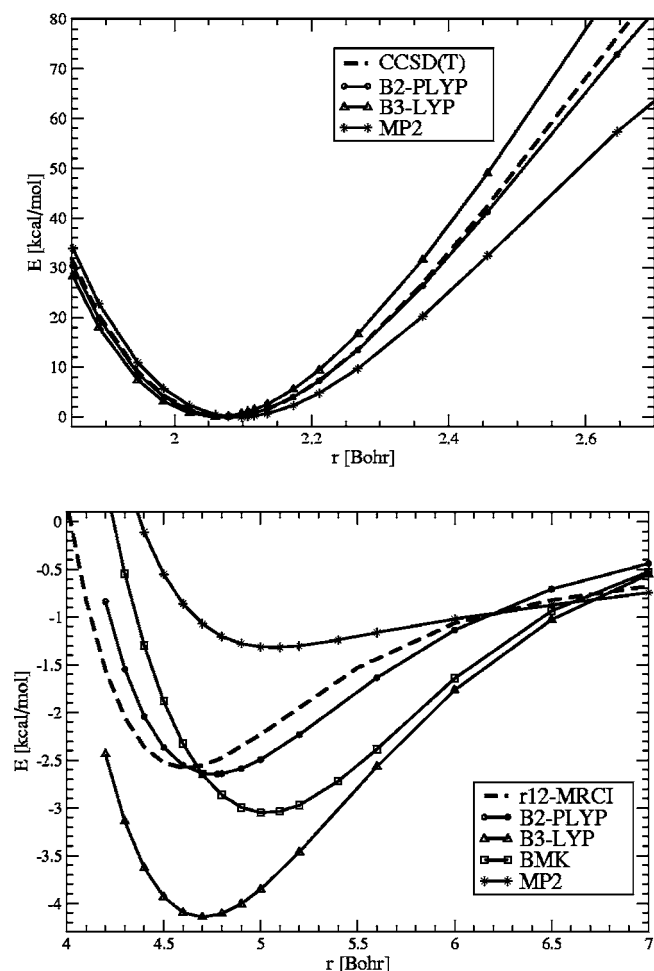


FIG. 3. Potential curves for N_2 (top, cc-pVQZ AO basis) and Be_2 (bottom, $[9s7p3d2f1g]$ AO basis). The CCSD(T) and r_{12} MRCI data (Ref. 76) are taken as accurate reference values.

carbonyl complexes of the metals, where B2-PLYP slightly overbinds the ligands, none of the typical MP2 problems show up in B2-PLYP. Tentatively, this can be attributed to the use of the KS orbitals that implicitly account for static correlation effects.

Concerning another important area of application it is noted that the description of van der Waals-type attraction is still not completely satisfactory, especially for systems with relatively large intermolecular distances. For, e.g., the π -stacked benzene dimer, only 10% of the binding energy is obtained although one should keep in mind that this system is not bound at all with most other functionals. According to our experience, a simultaneously good description of the thermochemistry of complex molecules on the one hand (including transition-metal complexes) and van der Waals binding energies on the other hand cannot be obtained with a simple perturbation theory (the former require small mixing parameters a_x and c while for the latter c should be >0.5). According to the author's opinion, this is definitely the biggest challenge for DFT in chemistry.

To this end, further shortcomings of the present approach compared to standard functionals should be mentioned. The basis set dependence of the results is of course more significant with PT2 as a two-electron property is expanded in the

one-particle basis. Preliminary investigations showed that (as expected) the basis set dependence is in between that of standard GGAs and MP2. However, as for MP2, reliable results are usually obtained with a properly polarized triple- ζ AO set that should be used anyway for accurate DFT work. Secondly, the prize to pay for the higher accuracy is the increase of the scaling behavior of the computation time with system size which is (without any "tricks" or further approximations) N_{el}^4 for hybrid functionals but N_{el}^5 when including PT2.

The quite surprising success of the present, very simple approach indicates that electron correlation can (and should) be separated into exchange-static and dynamic effects. To a large extent these can be described by a local GGA or meta-GGA ansatz. However, in order to account for the variability of the electronic structure of molecules (and the same might hold for solids as well) the inclusion of nonlocal correlations is necessary and the KS orbitals seem to provide a very good basis for that purpose already in low order of perturbation theory. Double-counting effects of electron correlation do not show up, presumably because the orbitals used in the PT2 are generated by the GGA parts and thus carry the necessary information to prevent this.

The results for energies from the other tested functionals also deserve a comment. For B3-LYP it is observed that the performance deteriorates as the molecules become larger and especially in the second data set, many outliers with large errors have been found. If the focus is on robustness, the TPSSh functional should be preferred as it provides a more uniform accuracy for small (simple) and more complex bonding situations. Due to its small HF-mixing parameter, TPSSh performs also very clearly best for transition-metal complexes although it was noted recently¹³ that a larger a_x , as, e.g., in PBE0 would increase the accuracy for many other systems. The assessment of the highly parametrized BMK meta-GGA functional with large a_x (42%) is quite difficult. For both, the G2/97 and the second test set, it performs better than B3-LYP and TPSSh and on the positive side we note very good results for some "hard" problems (e.g., entries 11, 14, and 46 in Table IV). There are, however, also serious errors for some simple systems (e.g., entries 6, 19, and 47), too many outliers in general and for the second data set, BMK yields the largest maximum absolute error. According to the author's opinion, this contradicting behavior indicates missing robustness and thus such functionals may not deserve much attention by chemists in the future. In this sense it should be mentioned that an inconsistent description of a particular functional can already be identified within the G2/97 data set if chemically reasonable reactions are considered instead of errors for individual molecules. As an example, for the valence isoelectronic halides CX_4 and SiX_4 ($X=Cl$ and F), the BMK functional seems to be an improvement with smaller errors compared to B3-LYP and TPSSh but this conclusion changes completely when, e.g., the chemically meaningful exchange reaction $CF_4 + SiCl_4 \rightarrow CCl_4 + SiF_4$ is considered [the errors for the reaction enthalpy are 5.8, 17.7, 14.6, and 8.8 kcal/mol for B2-PLYP, BMK, TPSSh, and B3-LYP; the recently proposed B97-3 density functional also fails with an even larger error of 18 kcal/mol (see supplementary material of Ref. 40)].

In summary it can be concluded that the accuracy of B2-PLYP for many important parts of chemistry is satisfactory and its limitations (strong multireference or very “metallic” cases) are also clear. Maybe, the new functional can take the succession of B3-LYP that represented one of the major steps forward in computational chemistry in the past. Any attempts for further improvement, especially for the ΔH_f^0 values, must also consider further basis set issues (core/core-valence correlation) and effects of more accurate zero-point energies and relativity. The intrinsic accuracy of virtual orbital-dependent DFT, if measured both on the average and by the number of outliers, may be further increased by using more flexible GGA expansions (empirical strategy) or by division of electron correlation in short- and long-range components,⁶¹ respectively (physical reasoning). In any case, the B2-PLYP functional represents a successful step along a not quite well-explored direction and from a more practical point of view it is suggested as a very robust and efficient quantum chemical method of general purpose.

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