

Double-Hybrid Density Functionals Provide a Balanced Description of Excited 1L_a and 1L_b States in Polycyclic Aromatic Hydrocarbons

Lars Goerigk and Stefan Grimme*

Organisch-Chemisches Institut der Universität Münster, Corrensstraße 40 D-48149, Münster, Germany

 Supporting Information

ABSTRACT: The time-dependent density functional theory (TD-DFT) double-hybrid methods TD-B2-PLYP and TD-B2GP-PLYP are applied to five linear and 12 nonlinear polycyclic aromatic hydrocarbons. The absolute errors compared to experiment for the two lowest-lying 1L_a and 1L_b excited states are evaluated and it is also tested whether the energetic order of those states and their energy difference is reproduced correctly. The results are compared to published CC2, global hybrid, and long-range corrected hybrid TD-DFT results. The two double-hybrids outmatch the other methods in terms of absolute and relative accuracy without an empirical adjustment of parameters. Although of different electronic character, both types of states are described on an equal footing by the double-hybrids. Particularly, the B2GP-PLYP functional yields very good results, which is in accordance with previous benchmarks.

1. INTRODUCTION

The theoretical description of the two lowest lying $\pi \rightarrow \pi^*$ (1L_a and 1L_b)¹ transitions in polycyclic aromatic hydrocarbons (PAHs) has sporadically gained particular interest in the past eight years. They are considered as being prototypical for low-lying excited states in practically important organic dyes. In 2003, Grimme and Parac showed^{2,3} that conventional time-dependent density functional theory (TD-DFT)^{4–7} methods severely fail in correctly describing the 1L_a states in linear² and nonlinear³ PAHs. Not only were the absolute errors larger than usually expected for valence excitation energies obtained with TD-DFT (1L_a excitations were highly underestimated), but also the molecule size-dependence of the errors was larger than found for wave function based approaches. Moreover, the energy difference between the 1L_a and 1L_b states and their relative order was very often wrong. On the basis of a semiempirical TD-PPP treatment,³ these errors were related to a theoretically estimated ionicity measure of the 1L_a states, which is higher for more delocalized π -systems. It is expected that a certain amount of ionicity may generally play a role in extended organic chromophores. As a first remedy of this problem, one could increase the amount of Fock exchange in global hybrid functionals, which generally leads to a blue-shift and smaller errors for 1L_a type states; however, more covalent (nonionic) states are also affected, and consequently, their energies are overestimated. Several studies showed that empirically about 40% nonlocal Fock exchange for larger and about 25% for smaller chromophores represents a good compromise.^{8–10} Another possibility to increase the results for extended conjugated π -chromophores is the DFT/MRCI approach,¹¹ as shown by Marian and Gilka (among others also for the series of linear acenes).¹² However, for large systems with many states, applying DFT/MRCI becomes quickly unfeasible, and one wishes a robust single-reference TD-DFT method to do the same good job.

Range-separated or long-range corrected (LRC) functionals were also thoroughly assessed for valence excitations and showed

promising results.^{9,13,14} In 2010, Wong and Hsieh evaluated LRC functionals for the same series of linear oligoacenes as Grimme and Parac in 2003 and observed a substantial improvement for the 1L_a states compared to global hybrids.¹⁵ Very recently, Richard and Herbert also investigated nonlinear PAHs with LRC functionals and furthermore analyzed the nature of the 1L_a states by various theoretical methods.¹⁶ Those studies revealed that LRC functionals indeed showed smaller errors than global hybrids for the 1L_a states. However, 1L_b states were not computed more accurately; in fact, their description sometimes worsened. Moreover, the results depended strongly on the long-range correction parameter used for the range-separated exchange-operator. Its optimal value for 1L_a states in PAHs is not necessarily the best for other chromophore classes (or state types). Richard and Herbert suggested that 1L_a excitations have a partial charge-transfer (CT) character. However, standard diagnosis tools did not show conclusive evidence for it. Furthermore, the extent of ionicity was shown to be dependent on the method with which it was estimated. Thus, the nature of 1L_a states in PAHs is still not fully revealed.

As mentioned above, also excited states of other extended chromophores can have some kind of 1L_a or 1L_b character. From a practical and also theoretical point of view we regard it as rather tedious and questionable to adjust the range-separation factor of an LRC functional for a certain class of chromophores. Particularly for the application to hitherto unknown systems, this procedure would be difficult to apply without additional computational effort (for recent advances in determining system-dependent range-separation factors in a nonempirical way, see refs 17–19). It seems desirable to have a method that could describe states with varying $^1L_a/^1L_b$ character equally well.

Time-dependent double-hybrid density functionals (TD-DHDFs) proved to be promising candidates for a balanced

Received: June 7, 2011

Published: September 02, 2011

and accurate description of low-lying excited states.²⁰ It was shown that the TD-B2-PLYP^{20,21} and TD-B2GP-PLYP^{22,23} methods can outmatch LRC functionals and the (SCS-)CC2 methods for large dyes and that they are the most accurate TD-DFT methods in excited state benchmarks.^{8,9,23} In 2009, TD-B2-PLYP was successfully applied to theoretical electronic circular dichroism spectroscopy.²⁴ In one case, a chirally substituted phenyl chromophore was examined and TD-B2-PLYP could not only reproduce the excitation energies of the 1L_a and 1L_b states but also their energy difference very well.

Herein, we will further investigate how well double-hybrid density functionals (DHDFs) can describe the 1L_a and 1L_b transitions in PAHs. First, five acenes from naphthalene to hexacene will be examined, followed by 12 nonlinear PAHs. The TD-B2-PLYP and TD-B2GP-PLYP methods will be tested and compared with previously published TD-DFT, DFT/MRCI, and CC2 values. We will not only assess the error in the excitation energies compared to experiment but will also see how well the 1L_a – 1L_b splitting and the state order is described.

2. COMPUTATIONAL DETAILS AND THEORY

Double-hybrid density functionals (DHDFs) consist of two parts: a hybrid-GGA-like portion and a perturbative correction (see ref 20 for a thorough introduction). First, a standard linear response TD-DFT treatment is carried out for the hybrid part of the functional. In the following, we will denote these portions as B2-LYP or B2GP-LYP, respectively. B2-LYP has 53% Fock exchange, and the latter has 65%. On the basis of the resulting TD-DFT excitation energies and the ground state orbitals, a perturbative CIS(D)²⁵ type treatment is then carried out. The resulting correlation energies are scaled as for the ground state by 0.27 (B2-PLYP) and 0.36 (B2GP-PLYP), respectively, and combined with the hybrid result, yielding the final DHDF excitation energy. In the following discussions, both the resulting energies from the hybrid portions and the full DHDF energies will be considered to separately evaluate the influence of Fock exchange and perturbative correlation on the excitation energies.

For the present work, BH-LYP,²⁶ B2-PLYP, and B2GP-PLYP calculations were performed with a modified version of TURBOMOLE 5.9.^{27–30} The perturbative CIS(D)-type corrections for the double-hybrids were obtained with our group's own program, RICC,³¹ by making use of the resolution of the identity (RI) approach.³² For all calculations, Dunning's cc-pVTZ basis set was applied,³³ which yields results close to the basis set limit for the investigated property. Auxiliary basis functions for the RI approximation were taken from the TURBOMOLE library.³⁴ Geometries for all systems will be taken from the work by Richard and Herbert,¹⁶ and excitation energies generally refer to vertical excitations. Results for other methods were also taken from previous studies based on the cc-pVTZ basis set (except for DFT/MRCI results, which are based on TZVP calculations).^{2,12,16} The prefix "TD" in front of a functional's name will be skipped in the following. The SCF/TD steps were performed with the TURBOMOLE grid m4³⁴ and an SCF energy convergence criterion of $10^{-7} E_h$.

Before continuing with the discussion of the results, we want to make a comment on the application of DHDFs with standard program codes. Even though many programs allow double-hybrid calculations for electronic ground states, they do not necessarily also provide a combination with the CIS(D) type correction, when excited states are calculated. During recent

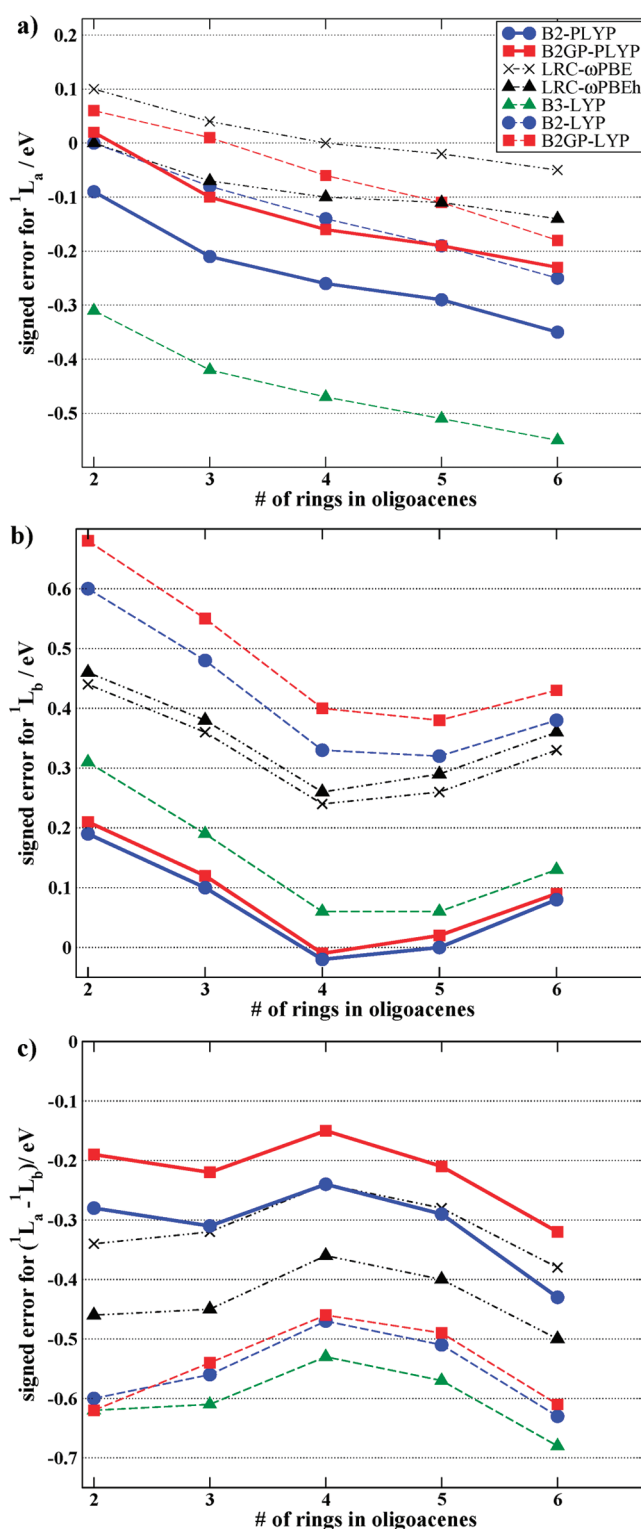


Figure 1. Signed errors (difference between theory and experiment) for various functionals for the 1L_a states (a), the 1L_b states (b), and the energy splittings between both states (c) of five polyacenes (from naphthalene to hexacene). All results are based on calculations with the cc-pVTZ basis. The results for B3-LYP and the two LRC methods were taken from ref 16. Theoretically corrected, experimental reference values were taken from ref 2.

activities as reviewers we became aware that allegedly the TD-B2PLYP method was applied, but in fact, the CIS(D) correction

seemed to have been excluded. However, usage of the perturbative CIS(D) correction as outlined in the first TD-B2-PLYP publication²⁰ is crucial. We encourage users and developers of standard quantum chemical software to take this fact into account in the future in order to prevent confusion and wrong usage.

3. RESULTS AND DISCUSSION

3.1. Linear Polyacenes. In the following discussion, results for the five acenes from naphthalene to hexacene will be considered, first. Theoretically corrected (i.e., back-corrected for vibrational effects) experimental reference values were taken from ref 2. Figure 1a shows the signed errors for various methods for the 1L_a states. The B3-LYP and LRC functionals' values were taken from ref 16. All curves show a similar behavior with system size, i.e., increasing errors for larger acenes. B3-LYP suffers from a severe underestimation from about -0.3 to -0.55 eV (see also Table S1 in the Supporting Information for the excitation energies of all tested methods). Increasing the amount of Fock exchange leads to a blue-shift, as can be seen for B2-LYP and B2GP-LYP. The errors for the latter range between 0.1 and -0.05 eV. Adding the perturbative correlation contribution leads to a red-shift of the results compared to the hybrid-GGA parts. B2-PLYP errors now range between -0.1 and -0.35 eV. B2GP-PLYP yields very good results within the accuracy of the reference values with an error range from about 0 to -0.2 eV. The LRC- ω PBEh method, as tested by Richard and Herbert, performs similarly to B2GP-PLYP; LRC- ω PBE has the smallest error range of the methods in Figure 1a, confirming previous conclusions on LRC functionals applied to 1L_a states.^{15,16} Note, that during the review process another work on range-separated functionals on PAHs was published, in which also LRC methods worked well for linear acenes.¹⁹

The picture given above changes when analyzing the errors for the 1L_b states (Figure 1b and Table S2 in the Supporting Information). All methods on average overestimate the excitation energies. Hybrid-functionals show larger errors with increasing amounts of nonlocal exchange. The long-range corrected methods are not much better than B2-LYP and worse than B3-LYP. The smallest errors are observed for the two DHDFs. This finding indicates that DHDFs more adequately describe correlation effects for the more multiconfigurational 1L_b states because the CIS(D) correction accounts for higher than single excitations which are formally absent in TDDFT and which are more important for 1L_b than for 1L_a states. Both DHDFs yield very similar results and have an error range between 0.2 and 0 eV.

Finally, the energy difference between the 1L_a and 1L_b states is considered and compared to the experimental values (Figure 1c). Even if both states had rather large absolute errors, their splitting could be still acceptable due to systematic errors. This finding would be particularly important for theoretical spectroscopy, for which it is sometimes sufficient to apply constant shifts to the spectra. Note that (opposed to all other tested methods) B3-LYP does not reproduce the correct order of states for naphthalene. All methods underestimate the splitting. However, the error range is usually smaller than for the individual states, indicating at least some error compensation. DHDFs yield here the smallest errors, closely followed by LRC- ω PBE. The other methods show larger deviations, and global hybrids perform worst.

The results were further analyzed statistically. For all three energies analyzed in Figure 1, the mean (MDs) and mean absolute deviations from experiment (MADs) were calculated

Table 1. Mean (MD) and Mean Absolute Deviations (MAD) for Vertical Gas-Phase Excitation Energies into the 1L_a and 1L_b States for Five Linear Acenes (from naphthalene to hexacene) ^a

method		$\Delta E(^1L_a)$	$\Delta E(^1L_b)$	$\Delta E(^1L_a) - \Delta E(^1L_b)$
B2-PLYP	MD	-0.24	0.07	-0.31
	MAD	0.24	0.08	0.31
B2GP-PLYP	MD	-0.13	0.09	-0.22
	MAD	0.14	0.09	0.22
CC2 ^b	MD	0.05	0.22	-0.17
	MAD	0.08	0.22	0.17
LRC- ω PBE ^c	MD	0.01	0.33	-0.31
	MAD	0.04	0.33	0.31
LRC- ω PBEh ^c	MD	-0.08	0.35	-0.43
	MAD	0.08	0.35	0.43
LRC- μ BLYP ^{c,d}	MD	-0.3	0.18	-0.49
	MAD	0.3	0.18	0.49
LRC- μ BLYP ^{c,e}	MD	-0.01	0.31	-0.32
	MAD	0.04	0.31	0.32
B3-LYP ^c	MD	-0.45	0.15	-0.60 ^f
	MAD	0.45	0.15	0.60
BH-LYP	MD	-0.15	0.40	-0.56
	MAD	0.15	0.40	0.56
B2-LYP	MD	-0.13	0.42	-0.55
	MAD	0.13	0.42	0.55
B2GP-LYP	MD	-0.06	0.49	-0.54
	MAD	0.08	0.49	0.54
DFT/MRCI ^g	MD	-0.11	-0.09	-0.02
	MAD	0.11	0.10	0.03

^a Also the MDs and MADs for the state splittings [$\Delta E(^1L_a) - \Delta E(^1L_b)$] are given. All results are based on calculations with the cc-pVTZ basis. Theoretically corrected, experimental reference values were taken from ref 2. ^b Values taken from ref 2 ^c Values taken from ref 16 ^d With a long-range correction parameter of $\mu = 0.17$ a₀⁻¹. ^e With a long-range correction parameter of $\mu = 0.30$ a₀⁻¹. ^f The order of the two states is wrong for naphthalene. ^g On the basis of calculations with the TZVP basis; values taken from ref 12.

(see Table 1). Additionally, results for the BH-LYP functional (this work), for CC2 (taken from ref 2), for DFT/MRCI (taken from ref 12), and for LRC- μ BLYP with two different values for the long-range correction parameter μ (taken from ref 16) are also shown. The values reflect the conclusions drawn above. Global hybrid functionals benefit from higher amounts of Fock exchange regarding the 1L_a states (MAD = 0.45 eV for B3-LYP and MAD = 0.08 eV for B2GP-LYP), but the results become worse for the 1L_b states (MAD = 0.15 eV for B3-LYP and MAD = 0.49 eV for B2GP-LYP). The MADs for the state splittings range between 0.60 and 0.54 eV for the global hybrids. The results for the LRC functionals indicate the influence of the range-separation parameter. This can be particularly seen for the LRC- μ BLYP method, which gives reasonable 1L_b but only modest 1L_a excitation energies for a smaller μ , but shows worse (1L_b) or better agreement (1L_a) with a larger value. The remaining two LRC functionals reproduce 1L_a excitations very well; 1L_b states are similarly described as by global hybrids, though. DHDFs yield similar or even better results than the LRC functionals. B2GP-PLYP yields improved values compared to B2-PLYP, which is in accordance with previous benchmarks.^{9,23} Its MAD for the 1L_a

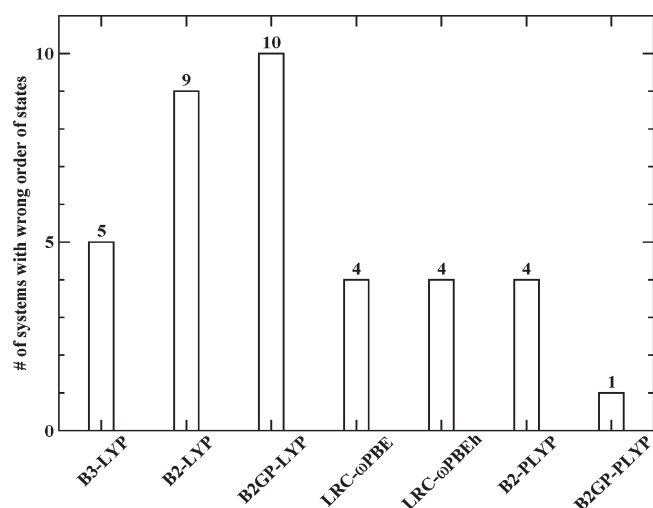


Figure 2. The number of polycyclic aromatic hydrocarbons (PAHs), for which the order of the 1L_a and 1L_b states is wrong. In total, 12 PAHs were tested. The results for B3-LYP and the two LRC methods, which were used for this analysis, were taken from ref 16.

states is slightly higher than for CC2 and the LRC functionals (MAD = 0.14 eV), but at the same time it can also describe the 1L_b states very well with an MAD of 0.09 eV, which is better than for CC2. B2-PLYP yields a higher MAD for 1L_a transitions (0.24 eV), but also a very low one for 1L_b (0.08 eV). DHDFs come closest to the very excellent results of the DFT/MRCI method, whose statistical values lie already within the estimated accuracy of the reference.

3.2. Nonlinear PAHs. Finally, the DHDFs are examined for nonlinear PAHs and compared to the B3-LYP, LRC- ω PBE, and LRC- ω PBEh functionals (results for those are again taken from ref 16). We took the investigated structures from the test set by Richard and Herbert. This set originally comprised 15 systems; however, not for every system were reference values available for both types of states. As we also always wanted to evaluate the state splittings and the energetic order of the states, we only took those 12 systems, for which all data were available (see Tables S3 and S4, Supporting Information for details on the systems). Reference values are based on measured absorption band maxima in solution;³⁵ however, as Richard and Herbert argued, those values should suffice to give a reliable estimate on a method's accuracy. Figure 2 depicts how many times a functional cannot reproduce the order of the two states correctly. For global hybrids with large amounts of nonlocal exchange, the results are unacceptable. B2-LYP predicts a wrong order in nine cases and B2GP-LYP in ten cases. Note, that it is expected that the BH-LYP functional, which is also popular in excited states applications, would not do a good job, either. As shown in Table 1 and also discussed in ref 23, BH-LYP results are practically identical to B2-LYP ones, due to similar amounts of Fock exchange. B3-LYP predicts a wrong order in five cases. The two LRC hybrids perform much better than the global ones and give wrong orders in only four cases. B2-PLYP performs similarly to the LRC methods (four cases). The best functional is B2GP-PLYP, which only gives the wrong order for one system (benzo[*b*]chrysene).

Richard and Herbert observed that whenever the B3-LYP functional performed well for the 1L_a states, the long-range corrected approaches yielded worse results and vice versa. Figure 3 shows similar plots like in ref 16. Part a shows the

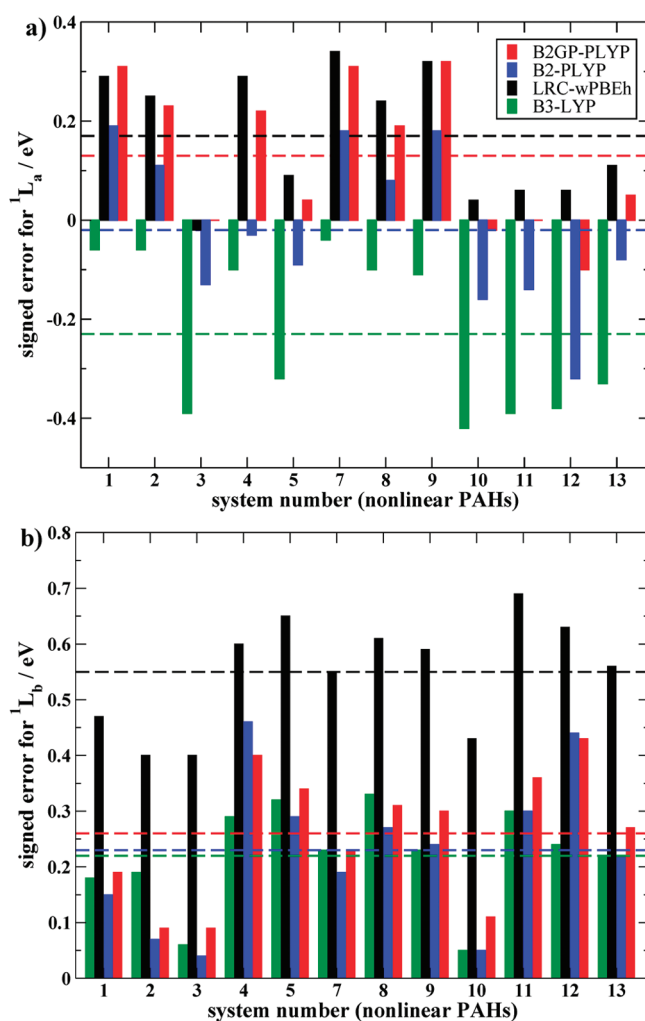


Figure 3. Signed errors (difference between theory and experiment) for various functionals for the 1L_a states (a) and the 1L_b states (b) for 12 nonlinear PAHs. All results are based on calculations with the cc-pVTZ basis. The results for B3-LYP and the LRC method were taken from ref 16. Experimental reference values were taken from ref 35. The numbers on the x-axes refer to the numbers given in ref 16; a full list of those systems is given in the Tables S3 and S4, Supporting Information.

signed errors for all tested nonlinear PAHs for B3-LYP, LRC- ω PBEh, and the two double-hybrids and compares them with their respective MDs. Like for the linear acenes, B3-LYP constantly underestimates the excitation energies, whereas LRC- ω PBEh tends to overestimate them; the DHDFs show a more balanced behavior and sometimes yield blue- or red-shifted energies, with usually smaller absolute errors. One clearly observes the behavior mentioned by Richard and Herbert when comparing B3-LYP to LRC- ω PBEh. Such a clear correlation between B3-LYP and the DHDFs is not seen; e.g., when the B3-LYP error is in an absolute range of 0.1 eV or less, B2-PLYP errors are often of the same order of magnitude. At first glance, there seems to be a correlation between the errors for LRC- ω PBEh and B2GP-PLYP. When sometimes the latter gives worse results than B2-PLYP, also the range-separated functional is worse and vice versa. However, there are also systems for which this is not the case (e.g., systems 5 and 13; see the Supporting Information for a description of these systems). Figure 3b shows the same analysis for the 1L_b states. All functionals overestimate

Table 2. Mean (MD) and Mean Absolute Deviations (MAD) for Vertical Excitation Energies into the 1L_a and 1L_b States of 12 Polycyclic Aromatic Hydrocarbons^a

method		$\Delta E(^1L_a)$	$\Delta E(^1L_b)$	$\Delta E(^1L_a) - \Delta E(^1L_b)$
B2-PLYP	MD	−0.02	0.23	−0.24 ^b
	MAD	0.14	0.23	0.26
B2GP-PLYP	MD	0.13	0.26	−0.13 ^c
	MAD	0.15	0.26	0.19
LRC- ω PBE ^d	MD	0.28	0.58	−0.30 ^b
	MAD	0.28	0.58	0.30
LRC- ω PBEh ^d	MD	0.17	0.55	−0.38 ^b
	MAD	0.18	0.55	0.38
B3-LYP ^d	MD	−0.23	0.22	−0.45 ^e
	MAD	0.23	0.22	0.45
B2-LYP	MD	0.13	0.65	−0.52 ^f
	MAD	0.16	0.65	0.52
B2GP-LYP	MD	0.20	0.77	−0.57 ^g
	MAD	0.21	0.77	0.57

^a Also the MDs and MADs for the state splittings [$\Delta E(^1L_a) - \Delta E(^1L_b)$] are given. All results are based on calculations with the cc-pVTZ basis. Experimental reference values were taken from ref 35. ^b The order of the two states is wrong in four cases. ^c The order of the two states is wrong in one case. ^d Values taken from ref 16. ^e The order of the two states is wrong in five cases. ^f The order of the two states is wrong in nine cases. ^g The order of the two states is wrong in 10 cases.

the excitation energies, with LRC- ω PBEh yielding the highest errors. Compared to the 1L_a states, the two DHDFs are more alike in this case and have overall the smallest errors.

The MDs and additionally the MADs are also shown in Table 2 (see Tables S3 and S4 of the Supporting Information for all calculated excitation energies). In all cases, the DHDFs show the best results. The MADs for the 1L_a transitions are 0.14 eV (B2-PLYP) and 0.15 eV (B2GP-PLYP). The MADs for the 1L_b transitions are more than halved compared to the LRC functionals (0.23 eV for B2-PLYP and 0.26 eV for B2GP-PLYP). Also the energy difference between the two states is better described by DHDFs. Considering the uncertainties due to, for example, solvent effects, it is expected that the errors would even be smaller, when considering a possible red-shift of about 0.1 eV to the calculated results (as also already noted in ref 16).

Note, that DHDFs do not contain any long-range corrections. It was shown that the description of CT transitions is better than for global hybrids but that they are clearly outmatched by range-separated methods for “true” CT states.⁹ On the other hand, DHDFs are not problematic for the 1L_a states, which is a further indication that they seem not to have large CT character.

4. SUMMARY

In this study, we have assessed the TD-B2-PLYP and TD-B2GP-PLYP methods on five linear and 12 nonlinear polycyclic aromatic hydrocarbons. We examined the errors for the two lowest lying states and also checked whether their energetic orders and differences were reproduced correctly. The two double-hybrids outmatched global hybrid and long-range corrected functionals and also the CC2 method in terms of accuracy and balanced distribution of the errors. This means that both 1L_a and 1L_b states are described on an equal footing, although their electronic character is rather different. Particularly, the B2GP-

PLYP functional with 65% Fock exchange and 36% nonlocal perturbative correlation yields very good results and also reproduces the order of the states best. Our findings are in accordance with previous benchmarks and good results found in a few recent applications.^{9,20,23,24,36} The advantage of the time-dependent double-hybrid methodology is the equally good description of different types of systems [for ground (see e.g. ref 37) and excited states] without an additional, system-dependent adjustment of parameters. The DHDFs perform better than exchange-only hybrids because they avoid self-interaction (overdelocalization) related errors by inclusion of a very high amount of Fock exchange and account for higher excitations by the nonlocal [i.e., (D)-type] correction for the excited state. We therefore again recommend double-hybrids for future applications to excited state problems but note that the theory in its present form is limited to low-lying states due to its perturbative character.

■ ASSOCIATED CONTENT

S Supporting Information. All excitation energies for all systems and methods evaluated. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: grimmes@uni-muenster.de. Phone: (+49)-251-8336512.

■ ACKNOWLEDGMENT

L.G. was supported with a postdoctoral scholarship by the “Research School NRW—Molecules and Materials—A Common Design Principle” within the framework of the “NRW Graduate School of Chemistry”. We thank C. Mück-Lichtenfeld for his technical assistance.

■ REFERENCES

- Platt, J. R. *J. Chem. Phys.* **1949**, *17*, 484–496.
- Grimme, S.; Parac, M. *Chem. Phys. Chem.* **2003**, *4*, 292–295.
- Parac, M.; Grimme, S. *Chem. Phys.* **2003**, *292*, 11–21.
- Casida, M. E. Time-Dependent Density Functional Response Theory for Molecules. In *Recent Advances in Density Functional Methods*; D. P. Chong, Ed.; World Scientific: Singapore, 1995; Vol. 1, pp 155–192.
- Gross, E. K. U.; Dobson, J. F.; Petersilka, M. *Top. Curr. Chem.* **1996**, *181*, 81–172.
- Bauernschmitt, R.; Ahlrichs, R. *Chem. Phys. Lett.* **1996**, *256*, 454–464.
- Time-Dependent Density Functional Theory, Lecture Notes Physics* 706; Marques, M. A. L., Ulrich, C. A., Nogueira, F., Rubio, A., Burke, K., Gross, E. K. U., Eds.; Springer: Berlin-Heidelberg, 2006.
- Jacquemin, D.; Wathelot, V.; Perpète, E. A.; Adamo, C. *J. Chem. Theory Comput.* **2009**, *5*, 2420–2435.
- Goerigk, L.; Grimme, S. *J. Chem. Phys.* **2010**, *132*, 184103.
- Dierksen, M.; Grimme, S. *J. Phys. Chem. A* **2004**, *108*, 10225–10237.
- Grimme, S.; Waletzke, M. *J. Chem. Phys.* **1999**, *111*, 5645–5655.
- Marian, C.; Gilka, N. *J. Chem. Theory Comput.* **2008**, *4*, 1501–1515.
- Jacquemin, D.; Perpète, E. A.; Scuseria, G. E.; Ciofini, I.; Adamo, C. *J. Chem. Theory Comput.* **2008**, *4*, 123–135.
- Jacquemin, D.; Perpète, E. A.; Ciofini, I.; Adamo, C. *Theor. Chem. Acc.* **2011**, *128*, 127–136.

- (15) Wong, B. M.; Hsieh, T. H. *J. Chem. Theory Comput.* **2010**, *6*, 3704–3712.
- (16) Richard, R. M.; Herbert, J. M. *J. Chem. Theory Comput.* **2011**, *7*, 1296–1306.
- (17) Stein, T.; Kronik, L.; Baer, R. *J. Am. Chem. Soc.* **2009**, *131*, 2818–2820.
- (18) Stein, T.; Kronik, L.; Baer, R. *J. Chem. Phys.* **2009**, *131*, 244119.
- (19) Kuritz, N.; Stein, T.; Kronik, R. B. L. *J. Chem. Theory Comput.* **2011**, *7*, 2408–2415.
- (20) Grimme, S.; Neese, F. *J. Chem. Phys.* **2007**, *127*, 154116.
- (21) Grimme, S. *J. Chem. Phys.* **2006**, *124*, 034108.
- (22) Karton, A.; Tarnopolsky, A.; Lamère, J. F.; Schatz, G. C.; Martin, J. M. L. *J. Phys. Chem. A* **2008**, *112*, 12868–12886.
- (23) Goerigk, L.; Moellmann, J.; Grimme, S. *Phys. Chem. Chem. Phys.* **2009**, *11*, 4611–4620.
- (24) Goerigk, L.; Grimme, S. *J. Phys. Chem. A* **2009**, *113*, 767–776.
- (25) Head-Gordon, M.; Rico, R. J.; Oumi, M.; Lee, T. J. *Chem. Phys. Lett.* **1994**, *219*, 21–29.
- (26) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372–1377.
- (27) Ahlrichs, R.; et al. *TURBOMOLE, version 5.9*; Universität Karlsruhe, 2008. See <http://www.turbomole.com>.
- (28) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165–169.
- (29) Häser, M.; Ahlrichs, R. *J. Comput. Chem.* **1989**, *10*, 104–111.
- (30) Furche, F.; Rappoport, D. In *Theoretical and Computational Chemistry*; Olivucci, M., Ed.; Elsevier: Amsterdam, 2005; Vol. 16.
- (31) Grimme, S. *RICC: A coupled-cluster program using the RI approximation*; University of Münster, 2007.
- (32) Weigend, F.; Häser, M. *Theor. Chem. Acc.* **1997**, *97*, 331–340.
- (33) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007–1023.
- (34) Eichkorn, K.; Weigend, F.; Treutler, O.; Ahlrichs, R. *Theor. Chem. Acc.* **1997**, *97*, 119–124.
- (35) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: London, 1970.
- (36) Vintonyak, V.; Warburg, K.; Kruse, H.; Grimme, S.; Huebel, K.; Rauh, D.; Waldmann, H. *Angew. Chem., Int. Ed.* **2010**, *49*, S902–S905.
- (37) Goerigk, L.; Grimme, S. *Phys. Chem. Chem. Phys.* **2011**, *13*, 6670–6688.