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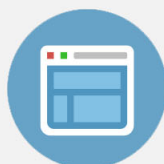
Application of recent double-hybrid density functionals to low-lying singlet-singlet excitation energies of large organic compounds

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The present work assesses some recently developed double-hybrid density functionals (B2π-PLYP, PBE0-DH, and PBE0-2) using linear-response Tamm-Dancoff Time-Dependent Density Functional Theory. This assessment is achieved against experimentally derived low-lying excitation energies of large organic dyes of recent interest, including some excitations dominated by charge-transfer transitions. Comparisons are made with some of the best-performing methods established from the literature, such as PBE0 or B3LYP hybrid or the recently proposed B2-PLYP and B2GP-PLYP double-hybrid models, to ascertain their quality and robustness on equal footing. The accuracy of parameter-free or empirical forms of double-hybrid functionals is also briefly discussed. Generally speaking, it turns out that double-hybrid expressions always provide more accurate estimates than corresponding hybrid methods. Double-hybrid functionals actually reach averaged accuracies of 0.2 eV, that can be admittedly considered close to any intended accuracy limit within the present theoretical framework. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4825359]

I. INTRODUCTION

The Time-Dependent (TD) treatment is probably the most popular extension of (ground-state oriented) Density Functional Theory (DFT) to calculate transition energies and other excited-states properties. In TD-DFT, one searches the response of the system after applying a weak electric field; current calculations are mostly based on the linear-response regime: the response of the system after perturbing the external potential leads to poles in the density response function (susceptibility) corresponding to the excitation energies $\Omega = E_m - E_n$, where E_n and E_m are the energies of the ground- and excited-state, respectively. More detailed information can be found in Refs. 1–5.

In the last years, and as it happens for ground-state DFT, extensive calibration of more and more exchange-correlation models has been performed in pursuit of the greatest possible robustness. And this is so because TD-DFT delivers a clear compromise between accuracy and computational time, although a straightforward recommendation about the use of an unique functional is not always possible. The drawbacks for it are also known, and among other, we emphasize: (i) the poor description of charge-transfer states and high-energy transitions; (ii) large errors in valence states of extended conjugated systems; and (iii) the difficulties to deal with conical intersections.

From a more fundamental point of view, it should be noted that TD-DFT in its present formulation inherits all the advantages and disadvantages of DFT,[6] including performances which are strongly functional-dependent.[7] Moreover, some of these inaccuracies are partially attributed to the poor description of non-local effects. Besides errors due to forgetfulness (due to use of local approximations in time for phenomena requiring non-locality in $t - t'$), the near-sightedness (due to use of local or semi-local approximations to the exchange-correlation kernel $f_{xc}(\mathbf{r}, \mathbf{r}')$ for phenomena requiring non-locality in $\mathbf{r} - \mathbf{r}'$) is of major importance. This effect is inherent to the choice of the functional, which actually determines the final quality of the TD-DFT excited-states properties. Over the past years, numerous successful (mainly with organic compounds) benchmarking studies[8–19] were carried out providing relevant guidelines to reach accuracy for many molecular systems and various physico-chemical properties.

In this context, and very recently, a database of challenging compounds (large organic dyes with different chemical nature) was compiled for neatly assessing theoretical methods for excitation energies of π-conjugated systems.[20,21] This set of molecules **1–12** (see Figure 1) comprises chromophores featuring low-lying bright transitions of mainly $\pi \rightarrow \pi^\star$ nature. The reference values were derived from experimental 0-0 transitions in solution after carefully correcting for solvent and vibrational effects,[22] the latter being a measure of the differences between 0-0 and vertical transitions. This constitutes a set of gas-phase excitation energies with an estimated accuracy of ± 0.1 eV (see further details in Refs. 20 and 21). In the present work, we use this set for establishing the accuracy of some recent expressions belonging to the last rung
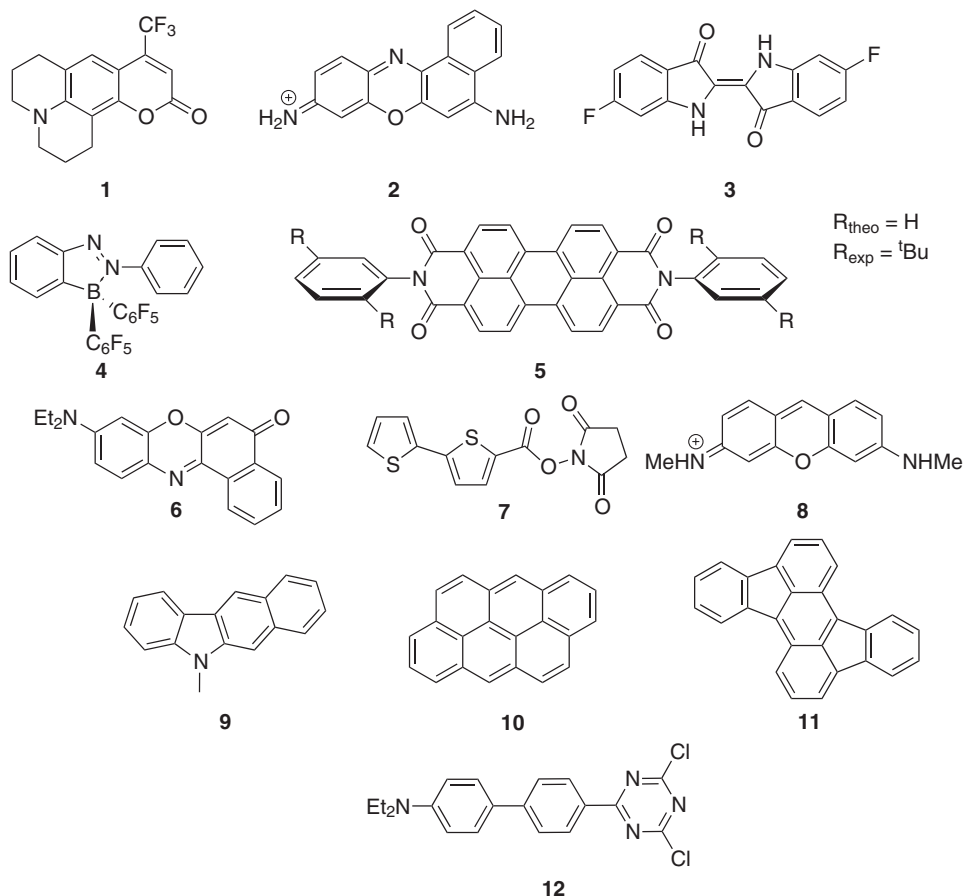
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FIG. 1. Chemical structure of the investigated compounds (**1–12**). The hydrogen atoms and corresponding C–H bonds have been omitted for clarity.

of the hypothesized hierarchy of existing methods:[23] Double-Hybrid (DH) density functionals. Two families of this kind of functionals are considered, namely PBE- and BLYP-based. Both PBE and BLYP functionals were chosen because their performances have been extensively investigated over the past decades, mainly in their hybrid forms (PBE0 and B3LYP, respectively). The excitation energies obtained with the double-hybrid models (PBE0-DH, PBE0-2, B2-PLYP, B2GP-PLYP, and B2π-PLYP) will be systematically compared to their pure DFT and hybrid counterpart models. Note that the calculations were performed under strictly the same technical conditions (*vide infra*) and that we aim at establishing useful guidelines for future safe applications in optical properties of π-conjugated compounds.

II. THEORETICAL CONSIDERATIONS

A. Double-hybrid models

This class of orbital-dependent forms[24–26] combines correlation energy (E_c) arising from second-order Perturbation Theory (PT2) together with a correlation energy functional, $E_c[\rho]$, in addition to the well-known hybrid combination of orbital-dependent (ϕ) EXact-like Exchange (EXX) energy (E_x) and an exchange energy functional $E_x[\rho]$, as it happens in older yet widely applied "hybrid" models as B3LYP[27–29] or PBE0.[30,31] The final form is thus given by a weighted combi-

nation of all these terms,

$$E_{xc}^{DH} = w_{EXX} E_x^{EXX}[\phi] + (1 - w_{EXX}) E_x[\rho] + w_{PT2} E_c^{PT2} + w_c E_c[\rho], \quad (1)$$

where w_c is usually defined as $(1 - w_{PT2})$ to reduce the number of linearly independent parameters. A relatively free choice of the exchange or correlation functionals entering into Eq. (1) is allowed, which of course compromises the underlying w_{EXX} and w_{PT2} weights. When some empiricism is allowed (e.g., employing the widely used B88[32] and LYP[33] expressions for modelling exchange and correlation effects, respectively, together with optimized weights based on training sets) one deals with non-parameter-free (or empirical) forms[34,35] (see Table I). Furthermore, under proper theoretical considerations, the expression can be recast into a one-parameter (λ) form,

$$E_{xc}^{DH} = \lambda E_x^{EXX}[\phi] + (1-\lambda)E_x[\rho] + (1-\lambda^3)E_c[\rho] + \lambda^3 E_c^{PT2}. \quad (2)$$

If one employs exclusively parameter-free functionals (e.g., the PBE exchange-correlation model,[36] and defines the value of λ after some arguments based on theory too) we arguably obtain parameter-free double-hybrid functionals[37,38] (see Table I). We also note that some authors assume that the correlation does not scale with λ,[39] or that the scaling is simply linear,[40] which will change the λ^3 dependence on the above equation to λ^2.

TABLE I. Summary of the parameters entering into all the assessed double-hybrid functionals.

Category	Acronym	Year	w_{EXX}	w_{PT2}	w_c	Reference
Empirical forms	B2-PLYP	2006	0.53	0.27	$1 - w_{PT2}$	24
	B2GP-PLYP	2008	0.65	0.36	$1 - w_{PT2}$	34
	B2π-PLYP	2009	0.6025	0.2731	0.7950	35
Category	Acronym	Year	λ	Reference		
Parameter-free	PBE0-DH	2011	1/2	37		
	PBE0-2	2012	$(1/2)^{1/3}$	38		

Note that it is still a matter of close scrutiny if the performance of both families remains the same when tackling Vertical Singlet Excitation Energies (VSEE). These energies will be calculated for a database formed by compounds **1-12**, starting from both families of double-hybrid methods ($w_{EXX} \neq 0$ and $w_{PT2} \neq 0$; or $\lambda \neq 0$), and compared with those achieved by corresponding hybrid ($w_{EXX} \neq 0$ but $w_{PT2} = 0$) and non-hybrid or pure ($w_{EXX} = w_{PT2} = \lambda = 0$) variants.

1. Time-dependent applications

Double-hybrid density functionals have been recently extended to deal with excited electronic states in a time-dependent fashion.[41] The final excitation energy Ω_{DH} is given by

$$\Omega_{DH} = \Omega + w_{PT2}\Delta_{(D)}, \tag{3}$$

or alternatively as

$$\Omega_{DH} = \Omega + \lambda^3 \Delta_{(D)}, \tag{4}$$

where Ω is the excitation energy provided by a hybrid functional composed *ad hoc* along the treatment, and $\Delta_{(D)}$ is a correction based on the CIS(D) method[42] scaled by the specific w_{PT2} weight or λ^3 value. Note thus that both Ω and $\Delta_{(D)}$ are calculated with the resulting amplitudes and eigenvalues of the converged self-consistent calculations done with the hybrid formed after neglecting the term E_c^{PT2} in Eqs. (1) and (2).

Within any TD-based formalism, the Tamm-Dancoff Approximation (TDA)[43,44] can be used to reduce the associated computational time, and further advances into this direction are highly promising to tackle large real-world systems.[45] Shortly, the pole structure of the linear-response function gives energies in pairs (Ω_i, $-\Omega_i$) corresponding to excitations and de-excitations of the system. Neglecting all de-excitation processes simplifies notably the treatment of equations, which is particularly true for hybrid and double-hybrid methods, although is not expected to significantly change the conclusion drawn here. We also note a recent study of 0-0 transitions and band shapes of a set of oligoacenes and perylenediimide molecules employing TDA and full TD-DFT methods,[46] where TDA behaved as reliable as full TD-DFT in reproducing position of the major bands and corresponding vibrational signatures in both absorption and fluorescence spectra.

B. Technical details

Structures and reference data of all the compounds were taken from Ref. 21 and used without further modifications. All the calculations were performed with the ORCA 2.9.0 quantum-chemical package.[47] We emphasize again that we employ strictly the same technical conditions for all calculations, in order to evaluate the performance of the different methods on a equal footing. These technical details are summarized next. First, the numerical thresholds were systematically increased (TightSCF, Grid6, NoFinalGrid) with respect to the defaults. We also employ the "resolution-of-the-identity" (RI) and "chain-of-spheres" (COSX) techniques[48,49] leading to large speedup of the calculations without any lack of accuracy (actually, less than 0.01 eV for excitation energies). Second, the large def2-TZVPP basis set was used with the corresponding auxiliary functions (def2-TZVPP/JK and def2-TZVPP/C) taken from the hardwired library. Note that going from the moderate TZVP to the definitive (additional diffuse and polarization functions) def2-TZVPP basis set only slightly changed excitation energies by up to 0.03 eV; thus, the results are not expected to vary upon further basis set extension. Third, and most importantly, TDA was imposed in all calculations, which may result in differences with respect to previously published values.[21] Note that we have successfully reproduced (within an accuracy of 0.01 eV) earlier PBE-based published values for VSEE[21] once the TDA was discarded (data not shown).

As a metric for the relative performance of the methods,[50] Mean Deviation (MD), Mean Absolute Deviation (MAD), and Root-Mean-Square Deviation (RMSD) functions were used, which are defined respectively as

$$MD = \frac{1}{n}\sum_i^n x_i, \tag{5}$$

$$MAD = \frac{1}{n}\sum_i^n |x_i|, \tag{6}$$

$$RMSD = \sqrt{\frac{1}{n}\sum_i^n |x_i|^2}, \tag{7}$$

for which $x_i = \Omega_i^{calculated} - \Omega_i^{reference}$, being Ω the corresponding excitation energies, and $\Omega_i^{reference}$ the experimentally obtained values as described above.

TABLE II. Calculated vertical singlet excitation energies (in eV) of compounds **1–12** with the def2-TZVPP basis set.

Method	1	2	3	4	5	6	7	8	9	10	11	12	MD	MAD	RMSD
Reference[a]	3.51	2.41	2.48	3.11	2.68	2.66	3.66	2.52	3.37	3.15	2.60	3.60			
PBE	2.97	2.62	2.24	2.88	2.23	2.66	3.47	2.98	2.94	2.77	2.17	2.27	− 0.202	0.408	0.515
PBE0	3.49	2.89	2.63	2.85	2.61	2.95	3.77	3.22	3.44	3.05	2.60	2.97	0.122	0.240	0.332
PB0-DH	3.59	2.84	2.86	3.24	2.68	2.97	3.89	3.15	3.61	3.16	2.65	3.26	0.225	0.235	0.298
BE0-2	3.60	2.65	3.08	3.30	2.73	2.95	4.01	2.94	3.71	3.25	2.75	3.51	0.256	0.243	0.290
BLYP	2.97	2.60	2.23	2.85	2.20	2.65	3.44	2.97	2.94	2.76	2.15	2.27	− 0.217	0.417	0.520
B3LYP	3.39	2.83	2.54	2.70	2.54	2.89	3.68	3.16	3.34	2.99	2.43	2.83	0.031	0.266	0.354
B2-PLYP	3.33	2.64	2.76	3.07	2.54	2.78	3.79	2.88	3.41	3.05	2.55	2.99	0.067	0.191	0.247
B2GP-PLYP	3.46	2.65	2.91	3.18	2.62	2.86	3.88	2.92	3.54	3.14	2.64	3.25	0.149	0.187	0.233
B2π-PLYP	3.50	2.70	2.88	3.20	2.63	2.89	3.87	2.99	3.56	3.14	2.65	3.25	0.170	0.196	0.239

[a]Taken from Ref. 21.

III. RESULTS AND DISCUSSION

Table II gathers all calculated values, including the MD, MAD, and RMSD for the various functionals investigated. The performance of pure density functionals (e.g., PBE and BLYP) will not be longer discussed since their drawbacks have been widely described before.[21] Briefly speaking, they (i) yield systematically spurious states having small but non negligible oscillator strengths corresponding to $n \rightarrow \pi^{\star}$ transitions; (ii) provide the worst errors with large deviations (0.4–0.5 eV) with respect to reference results; and (iii) systematically underestimate charge-transfer excitations occurring when charge density is transferred from one to another region of the molecule upon excitation. However, they can not be excluded from the analysis since they constitute the baseline for further discussing the relative performance across the conjectured hierarchy (pure, hybrid, and double-hybrid) of methods.

In this section, the evaluation of VSEE is analyzed first for the subset given by compounds **1–5**. These compounds were recently investigated by some of the most modern existing methods: the families of highly-parameterized Minnesota (e.g., M06)[13] or range-separated (e.g., ωB97)[51] functionals. It must be underlined here that subtle differences in technical details preclude the direct (quantitative) comparison of values, although the statistical data may nonetheless serve for qualitative discussions. Our results show that PBE and BLYP provide both a MAD of 0.34 eV, and the use of PBE0 or B3LYP considerably reduces this deviation (0.20 and 0.23 eV, respectively). The best results are however obtained with B2-PLYP, B2GP-PLYP, and B2π-PLYP, giving all a MAD of only 0.17 eV, which can be roughly compared with M06-2X (0.14 eV) and the sophisticated ωB97XD (0.17 eV) model.

Inspecting now the entire set of molecules (Figure 1) with the exception of compound **12**, a special case as we will see next; PBE and BLYP systematically appear to underestimate the VSEE providing a MD of –0.20 and –0.22 eV, respectively. The corresponding hybrid extensions (PBE0 and B3LYP) exhibit MD values of 0.12 and 0.03 eV, such a result arising to some compensation between under- and over-estimation VSEE. Interestingly, all the double-hybrid forms overestimate the excitation energies leading to MD values ranging from 0.26 (PBE0-2) to 0.06 (B2-PLYP) eV. It must be

stressed that no optimal values has been elucidated yet for calculations of VSEE, since the functionals employed here heritage the same w_i or λ values normally derived from ground-state calculations, which might require further investigations on a more complete dye database.

Additionally, what we would like to highlight the most here, the MAD or RMSD is largely reduced or even approximately halved when going from pure to hybrid and from hybrid to double-hybrid functionals (see Figure 2). Furthermore, all double-hybrids remedy the appearance of intruder states:
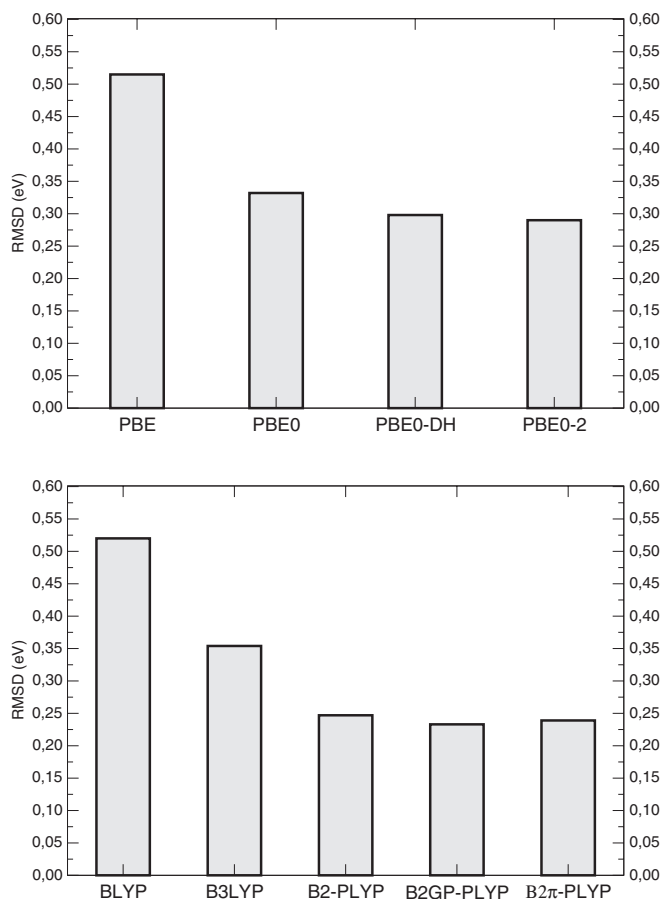

FIG. 2. Evolution of the RMSD (in eV) for the two families of functionals considered.
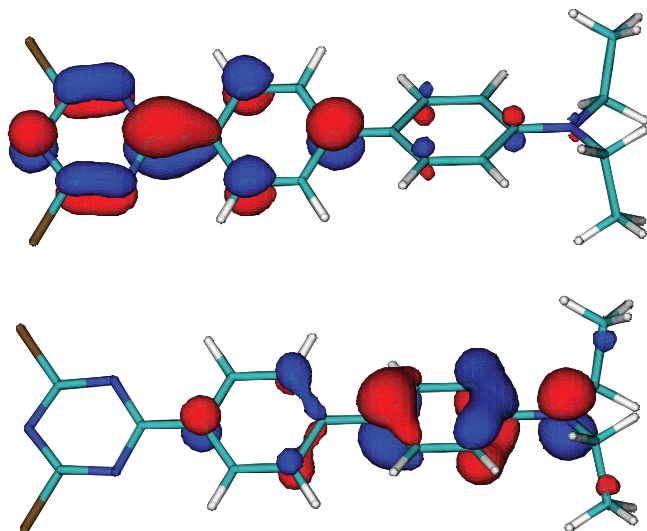
FIG. 3. Isocontour plots of the lowest unoccupied (top) and highest occupied (bottom) molecular orbitals for compound **12**.
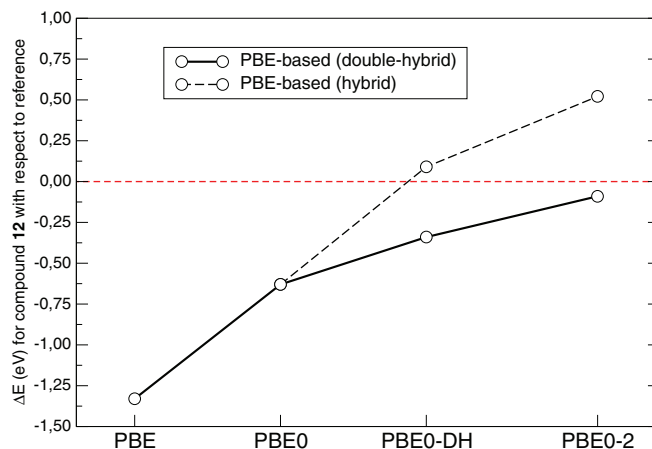

FIG. 4. Deviation (in eV) of excitation energies of compound **12**, as a function of the exact-like exchange weight for the PBE-based family of functionals.

the first singlet excited state is truly characterized as a real $\pi \rightarrow \pi^\star$ transition having a large oscillator strength and a pronounced contribution from the Highest Occupied (HO-) to the Lowest Unoccupied (LU-) Molecular Orbital (MO). These results are in agreement with previous studies (see for example Ref. 21) and confirm how higher robustness and less uncertainty in blind applications (complicated or not-yet-synthesized chromophores) is consistently achieved through the hierarchy (i.e., pure, hybrid, and double-hybrid) of methods. These results are in agreement with other recent studies (although mainly done with only B2-PLYP) reaching similar conclusions, when dealing with increasingly longer cyanine dyes[52] or with excited ^1L_a and ^1L_b states in large polycyclic aromatic hydrocarbons.[53]

The case of molecule **12** conceals a particular challenge as the excited state possesses substantial Charge-Transfer (CT) character. This is easily observed from the location, in different parts of the backbone, of the frontier molecular orbitals (HOMO and LUMO) involved in the transition (Figure 3). It is well-known that routine TD-DFT calculations with standard functionals, completely missing the correct long-range asymptotic behavior needed to describe qualitatively these excitations, might dramatically underestimate the values up to 1–2 eV.[54] Note how this is indeed the case for PBE and BLYP, underestimating the VSEE by 1.33 eV (Table II). This underestimation is further reduced to 0.63 and 0.77 eV with the corresponding hybrid versions, PBE0 and B3LYP, respectively. Interestingly, the use of double-hybrid functionals largely improves the results, specially for the PBE-based case: whereas PBE0-DH yields an underestimation of 0.34 eV (Table II) with respect to the reference value, and thus comparable to B2GP-PLYP or B2π-PLYP, the use of PBE0-2 allows to reach the accuracy limits (an underestimation of only 0.09 eV). Figure 4 represents how this deviation (ΔE) between experimental and calculated values evolves with the weight of the exact-like exchange energy entering into the formulation of the PBE-based functionals. Furthermore, from Eqs. (1) and (2), a double-hybrid func-

tional can be simplified into its hybrid form after discarding the perturbative term, giving thus the excitation energy Ω entering into Eq. (4). These values are also depicted in Figure 4 to show the influence of both weights on final values. Although the improvement might be naively related only with the amount of exact-like exchange energy, it is also known that functional with high weights (e.g., the resulting hybrid obtained from PBE0-2 having 79 % of EXX) are not recommended for common applications. In the case of compound **12**, this indeed overestimates the excitation energy by more than 0.5 eV (Figure 4). The explicit inclusion of the PT2-type contribution significantly decreases this deviation, being of −0.09 (−0.34 eV) for PBE0-2 (PBE0-DH), respectively. Hence, the particular compromise found for both w_{EXX} and w_{PT2} weights, or for the value of λ, in each of the investigated double-hybrid functionals is a key to its prominent accuracy, showing that the scaled $\Delta_{(D)}$ correction cannot be never omitted.

IV. CONCLUSIONS

We have assessed in this study the performance of some of the newest double-hybrid functionals (PBE0-DH, PBE0-2 and B2π-PLYP) on a set of specially challenging π-conjugated systems. We have systematically compared their results with related pure and hybrid models, as well as with B2-PLYP and B2GP-PLYP, in order to ascertain their accuracy across the hypothesized hierarchy of methods. All comparisons were given with respect to reference values derived from experiments. The errors provided by each functional have been closely examined strictly under the same technical conditions. According to the MAD values, the following classification is established (from lower to higher errors): B2GP-PLYP $\approx$ B2-PLYP $\approx$ B2π-PLYP < PBE0-DH $\approx$ PBE0-2 $\approx$ PBE0 < B3LYP << PBE $\approx$ BLYP, where the symbol "$\approx$" means an almost negligible deviation of $\pm$ 0.01 eV and "<<" indicates a significant deviation (> 0.1 eV). The equivalent classification provided by the RMSD values appears similar: B2GP-PLYP $\approx$ B2-PLYP $\approx$ B2π-PLYP < PBE0-2 $\approx$ PBE0-DH < PBE0 < B3LYP << PBE

$\approx$ BLYP. Furthermore, we can conclude that (i) the B2π-PLYP functional performs equally well than B2-PLYP or B2GP-PLYP do for excited-states, which motivates its further application on π-conjugated systems independently if ground- or excited-states properties need to be tackled; (ii) PBE0-DH and PBE0-2 are affected of slightly larger errors, although they also behave very well taking into account that its ancestor (PBE0) is almost universally considered as the most accurate hybrid method in use within the TD-DFT framework, and that they are able to improve it; and (iii) independently of the family of double-hybrid methods considered (i.e., parameter-free or empirical), they can be also more safely applied to CT transitions than previous versions.

In short, we can affirm from this and other previously published results[20,21] that double-hybrid density functionals have unquestionably entered into the field of TD-DFT calculations purposefully too, as they did in the past for ground-state properties. The degree of accuracy obtained for both ground and excited-states is large, and normally overtakes older models, which can thus be considered superseded as long as the slightly higher computational cost of double-hybrids does not become a serious bottleneck for real-world applications to large systems.

ACKNOWLEDGMENTS

[1] M. A. L. Marques and E. K. U. Gross, Annu. Rev. Phys. Chem. **55**, 427 (2004).
[2] K. Burke, J. Werschnik, and E. K. U. Gross, J. Chem. Phys. **123**, 062206 (2005).
[3] S. Botti, A. Schindlmayr, R. Del Sole, and L. Reining, Rep. Prog. Phys. **70**, 357 (2007).
[4] M. E. Casida, J. Mol. Struct.: THEOCHEM **914**, 3 (2009).
[5] M. E. Casida and M. Huix-Rotllant, Annu. Rev. Phys. Chem. **63**, 287 (2012).
[6] J. R. Reimers, Z.-L. Cai, A. Bilić, and N. S. Hush, Ann. N.Y. Acad. Sci. **1006**, 235 (2003).
[7] J. C. Sancho-García, Chem. Phys. Lett. **439**, 236 (2007).
[8] J. Tao, S. Tretiak, and J.-X. Zhu, Phys. Rev. B **80**, 235110 (2009).
[9] D. Jacquemin, V. Wathelet, E. A. Perpète, and C. Adamo, J. Chem. Theory Comput. **5**, 2420 (2009).
[10] D. Jacquemin, E. A. Perpète, I. Ciofini, and C. Adamo, Acc. Chem. Res. **42**, 326 (2009).
[11] M. Caricato, G. W. Trucks, M. J. Frisch, and K. B. Wiberg, J. Chem. Theory Comput. **6**, 370 (2010).
[12] D. Jacquemin, E. A. Perpète, I. Ciofini, and C. Adamo, J. Chem. Theory Comput. **6**, 1532 (2010).
[13] D. Jacquemin, E. A. Perpète, I. Ciofini, C. Adamo, R. Valero, Y. Zhao, and D. G. Truhlar, J. Chem. Theory Comput. **6**, 2071 (2010).
[14] D. Jacquemin, B. Mennucci, and C. Adamo, Phys. Chem. Chem. Phys. **13**, 16987 (2011).
[15] R. Send, M. Kühn, and F. Furche, J. Chem. Theory Comput. **7**, 2376 (2011).
[16] S. S. Leang, F. Zahariev, and M. S. Gordon, J. Chem. Phys. **136**, 104101 (2012).
[17] M. Isegawa, R. Peverati, and D. G. Truhlar, J. Chem. Phys. **137**, 244104 (2012).
[18] D. Jacquemin, A. Planchat, C. Adamo, and B. Mennucci, J. Chem. Theory Comput. **8**, 2359 (2012).
[19] P. Dev, S. Agrawal, and N. J. English, J. Chem. Phys. **136**, 224301 (2012).
[20] L. Goerigk, J. Moellmann, and S. Grimme, Phys. Chem. Chem. Phys. **11**, 4611 (2009).
[21] L. Goerigk and S. Grimme, J. Chem. Phys. **132**, 184103 (2010).
[22] J. Gierschner and J. Cornil, Adv. Mater. **19**, 173 (2007).
[23] S. Kümmel and L. Kronik, Rev. Mod. Phys. **80**, 3 (2008).
[24] S. Grimme, J. Chem. Phys. **124**, 034108 (2006).
[25] T. Schwabe and S. Grimme, Phys. Chem. Chem. Phys. **8**, 4398 (2006).
[26] I. Y. Zhang and X. Xu, Int. Rev. Phys. Chem. **30**, 115 (2011).
[27] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).
[28] V. Barone and C. Adamo, Chem. Phys. Lett. **224**, 432 (1994).
[29] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, J. Phys. Chem. **98**, 11623 (1994).
[30] J. P. Perdew, M. Ernzerhof, and K. Burke, J. Chem. Phys. **105**, 9982 (1996).
[31] C. Adamo and V. Barone, J. Chem. Phys. **110**, 6158 (1999).
[32] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).
[33] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).
[34] A. Karton, A. Tarnopolsky, J.-F. Lamère, G. C. Schatz, and J. M. L. Martin, J. Phys. Chem. A **112**, 12868 (2008).
[35] J. C. Sancho-García and A. J. Pérez-Jiménez, J. Chem. Phys. **131**, 084108 (2009).
[36] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[37] E. Brémond and C. Adamo, J. Chem. Phys. **135**, 024106 (2011).
[38] J.-D. Chai and S.-P. Mao, Chem. Phys. Lett. **538**, 121 (2012).
[39] K. Sharkas, J. Toulouse, and A. Savin, J. Chem. Phys. **134**, 064113 (2011).
[40] J. Toulouse, K. Sharkas, E. Brémond, and C. Adamo, J. Chem. Phys. **135**, 101102 (2011).
[41] S. Grimme and F. Neese, J. Chem. Phys. **127**, 154116 (2007).
[42] M. Head-Gordon, R. J. Rico, M. Oumi, and T. J. Lee, Chem. Phys. Lett. **219**, 21 (1994).
[43] S. Grimme, Chem. Phys. Lett. **259**, 128 (1996).
[44] S. Hirata and M. Head-Gordon, Chem. Phys. Lett. **314**, 291 (1999).
[45] S. Grimme, J. Chem. Phys. **138**, 244104 (2013).
[46] A. Chantzis, A. D. Laurent, C. Adamo, and D. Jacquemin, J. Chem. Theory Comput. **9**, 4517 (2013).
[47] F. Neese, WIREs Comput. Mol. Sci. **2**, 73 (2012).
[48] F. Neese, J. Comput. Chem. **24**, 1740 (2003).
[49] F. Neese, F. Wennmohs, A. Hansen, and U. Becker, Chem. Phys. **356**, 98 (2009).
[50] B. Civalleri, D. Presti, R. Dovesi, and A. Savin, Chem. Model. **9**, 168 (2012).
[51] D. Jacquemin, E. A. Perpète, I. Ciofini, and C. Adamo, Theor. Chem. Acc. **128**, 127 (2011).
[52] R. Send, O. Valsson, and C. Filippi, J. Chem. Theory Comput. **7**, 444 (2011).
[53] L. Goerigk and S. Grimme, J. Chem. Theory Comput. **7**, 3272 (2011).
[54] A. Dreuw and M. Head-Gordon, Chem. Rev. **105**, 4009 (2005).