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Cite as: J. Chem. Phys. (in press) (2021); <https://doi.org/10.1063/5.0076545>

Submitted: 26 October 2021 • Accepted: 02 December 2021 • Accepted Manuscript Online: 02 December 2021

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Violation of Hund’s Rule in Molecules: Predicting the Excited-State Energy Inversion by TD-DFT with Double-Hybrid Methods

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November 27, 2021

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Abstract

The energy difference (ΔE_{ST}) between the lowest singlet (S_1) and triplet (T_1) excited state of a set of azaphenylene compounds, which is theoretically and experimentally known to violate Hund’s rule giving rise to the inversion of the order of those states, is calculated here with a family of double-hybrid density functionals. That excited-state inversion is known to be very challenging to reproduce for TD-DFT employing common functionals, e.g. hybrid or range-separated expressions, but not for wavefunction methods due to the inclusion of higher-than-single excitations. Therefore, we explore here if the last developed family of density functional expressions (i.e., double-hybrid models) is able to provide not only the right excited-state energy order but also accurate ΔE_{ST} values, thanks to the approximate inclusion of double excitations within these models. We herein employ standard double-hybrid (B2-PLYP, PBE-QIDH, and PBE0-2), range-separated (ω B2-PLYP and RSX-QIDH), spin-scaled (SCS/SOS-B2PLYP21, SCS-PBE-QIDH, and SOS-PBE-QIDH), and range-separated spin-scaled (SCS/SOS- ω B2-PLYP, SCS-RSX-QIDH, and SOS-RSX-QIDH) expressions, to systematically assess the influence of the ingredients entering into the formulation while concomitantly providing insights for their accuracy.

1 Introduction

In the vast majority of organic chromophores, the lowest singlet excited state (S_1) lies energetically above the lowest triplet excited state (T_1) due to the fact that the exchange energy is known to be positive, and so it is the corresponding singlet-triplet energy difference or ΔE_{ST} . In a **first-order** approximation (i.e., a single-particle excitation framework) the energy difference between both excited states equals $2K_{ia}$, which is twice the exchange energy (K_{ia}) depending on the corresponding occupied (ϕ_i) and virtual (ϕ_a) orbitals involved in the spin-dependent formation of the excited-states. If ΔE_{0S} (ΔE_{0T}) corresponds to the energy difference between the ground- (S_0) and the S_1 (T_1) excited-state, then $\Delta E_{0S} \approx \Delta E_{0T} + 2K_{ia}$. The last term is known to be of the order of 0.5–1.0 eV for conjugated polymers,^{1–3} but smaller for finite-size molecules as polycyclic conjugated hydrocarbons. That Hund’s rule for molecules is also expected to hold⁴ within Density Functional Theory (DFT). However, if correlation effects are taken into account, ~~the zeroth-order approximation is not completely valid and that~~ singlet-triplet energy difference can decrease^{5,6} and thus affects many photophysical processes.⁷ Therefore, the degree of excited-states correlation effects, and how theoretical methods are able to deal with it, is a topic of utmost importance for further materials design.

Actually, and generally speaking, if the singlet-triplet energy difference $\Delta E_{ST} = \Delta E_{0S} - \Delta E_{0T}$ becomes low enough (e.g. in the order of 100–200 meV) it could be expected to foster a Reverse Intersystem Crossing Process (RISC), thus appreciably populating the S_1 state above the spin statistics limit (a 1:3 ratio for the singlet:triplet exciton formation). This mechanism has already found promising applications in last years for light-emitting devices^{8–14} since it could recover a significant portion of the dark (triplet) excitons naturally formed upon electroluminescence. This recovery could ideally enhance the

quantum yield, contributing to more efficient Organic Light-Emitting Diodes (OLEDs) through a mechanism known as Thermally Activated Delayed Fluorescence (TADF) process. The conditions under which a chemical compound could behave as a TADF emitter are being thoroughly investigated theoretically and experimentally.^{15–19} The first attempts relied on the smart combination of chemical fragments acting as a donor or as an acceptor, giving rise upon excitation to intra-molecular charge-transfer excitations with small exchange energies²⁰ and thus correspondingly displaying low ΔE_{ST} values. A step further was later achieved after the discovery of compounds holding almost isoenergetic S_1 and T_1 excited-state energies, promoting very small (of the order of 100 meV, but still positive) ΔE_{ST} values.^{21–23} Theoretical investigations also helped to isolate the reasons for such small values, which it was not only due to small exchange energies but mostly to correlation effects further contributing to the decrease of ΔE_{ST} .^{24,25}

The next step which could be envisioned would be the existence of compounds displaying negative ΔE_{ST} values after the inversion of the S_1 and T_1 excited states, which could thus foster the barrierless downconversion of triplet to singlet excitons to achieve the promise of a 100 % of quantum efficiency. This is not a so rare effect as it could be initially thought, since some old studies by Leupin *et al.* in the 80s already found solid evidences of that energy inversion for a set of chemical systems known as azaphenalenenes.^{26,27} A recent review²⁸ by Audebert *et al.* reports on the synthetic versatility and different achievements realized from that kind of molecules, be monomeric or not, which includes many fields of applications (photocatalysts, light-emitting diodes, covalent organic frameworks, liquid crystals, etc.) The advances in the synthesis of those compounds, together with the possibility of that excited-state energy inversion, clearly opens a wide area of research still not fully explored.²⁹ If that excited-state energy inversion is possible and favourable, it must be theoretically explored by correlated methods beyond the single-excitation pic-

ture^{30,31} which is however not possible within the linear-response (adiabatic) Time-Dependent Density Functional Theory (TD-DFT) method as recently shown.³²

Unsurprisingly, wavefunction methods for excited states can predict that excited-state energy inversion if at least double excitations are allowed into the excited-state wavefunction,^{33–35} although at a normally more demanding cost than TD-DFT. A way to reconcile these two extremes; i.e., the need to introduce double excitations, together with the vast implementation of TD-DFT in the most used computational codes, could be the use of double-hybrid density functionals^{36–42} for which a double correction is added to the zeroth-order excitation energies. We will thus systematically explore here the accuracy of this family of methods, which are recognized to considerably improve the performance of the well-known hybrid functionals for many properties,⁴³ for that set of azaphenalenenes compounds known to display the excited-state energy inversion. We will also aim at contributing to better understand the performance of these expressions as a function of their composition, since many approaches and variants bloomed in the last years, and try to rationalize previous applications of double-hybrid density functionals to this challenging issue.³³

2 Justification of the choice of target systems

We have started the selection of the target systems with the prototypical set of azaphenalene molecules (~~cyclazine, tetrazine, and heptazine~~) largely tackled in previous studies, see Figure 1, and for which a negative ΔE_{ST} value is robustly predicted and vastly reproduced by wavefunction methods from some pioneering works^{33–35} to more recent ones.^{32,44,45} The conclusions of the study by Ehrmaier *et al.*³⁴ also found that substitution of the heptazine core $-\text{C}_6\text{H}_7\text{H}_3-$ with chlorine $-\text{C}_6\text{H}_7\text{Cl}_3-$, cyano $-\text{C}_6\text{H}_7(\text{CN})_3-$, or p-

methoxyphenylene $-C_6N_7(p-C_6H_4OCH_3)_3-$ groups also preserved the negative ΔE_{ST} value. However, these compounds are known to display negligible, or very small in the best of the cases, transition dipole moments and associated oscillator strengths, which disqualify them for efficient light-emitting applications. On the other hand, the controlled chemical modification of these systems, by increasing the size of the triangular-shaped core and/or by introducing N or B atoms into specific positions of the structure, leads also to systems showing $\Delta E_{ST} < 0$ values and non-negligible oscillator strengths,⁴⁶ which indicates the vast possibilities still unexplored for these unique structures.

Motivated by all these previous findings, a massive yet robust screening⁴⁷ of thousands of potential azaphenylene candidates was recently accomplished by Pollice *et al.*⁴⁸ The systems were allowed to vary their topology (i.e., fusing aromatic rings to the triangular-shaped core), their N content (i.e., the number of C-substituted sites) and their peripheral groups to allow for the computationally smart data-driven design of dyes with negative ΔE_{ST} values together with reasonably non-negligible (and often large) oscillator strengths, normally found to be antagonistic properties. That pioneering study motivated us to complete our investigation with some of the most promising molecules presented in Figure 2 from the study of Pollice *et al.*, still not-yet-synthesized but having sufficiently negative ΔE_{ST} values.

Finally, we have also included a real-world heptazine-based organic dye recently incorporated into an OLED^{49,50} (see its chemical structure in Figure 3). The device uses the 2,5,8-tris(4-fluoro-3-methylphenyl)-1,3,4,6,7,9,9b-heptaazaphenylene (HAP-3MF) system: a dye based on the 2T-7N (or heptazine core) incorporating the fluorotoluene substituent to enhance the solubility and the electron accepting character of pristine heptazine. This device exhibits an exceptionally high quantum efficiency, which is explained by the

large recovery of dark triplet excitons since prompt and delayed emissions are found nearly identical for an exciplex consisting of HAP-3MF (acceptor) and 1,3-bis(N-carbazolyl)benzene or mCP (donor).⁵¹ This system was also recently studied by Domcke and Sobolewski, finding a $\Delta E_{ST} < 0$ by wave-function methods⁵² and thus confirming the excited-state energy inversion.

3 Theoretical methods and associated details

3.1 Generalities about double-hybrid density functionals

To fully understand the performance of a Double-Hybrid (DH) density functional for excited states, which is the main goal of the present study, we recall here their (simplified) general expression:

$$E_{xc}^{\text{DH}}[\rho] = a_x E_x^{\text{EXX}}[\phi_i] + (1 - a_x) E_x[\rho] + a_c E_c^{\text{PT2}}[\phi_i, \phi_a] + (1 - a_c) E_c[\rho], \quad (1)$$

whose exchange contribution is a combination of EXact-eXchange (EXX) E_x^{EXX} and exchange functional $E_x[\rho]$, a_x being the coefficient of the former term, and the correlation contribution is also a combination of a second-order Perturbation Theory (PT2) term E_c^{PT2} and the correlation functional $E_c[\rho]$, with a_c being the weight given to the former term. Note that ϕ_i (ϕ_a) are the occupied (unoccupied) orbitals self-consistently obtained from the underlying single-hybrid functional, which neglects the PT2 contribution: that is, $E_{xc}[\rho] = a_x E_x^{\text{EXX}}[\phi_i] + (1 - a_x) E_x[\rho] + (1 - a_c) E_c[\rho]$. The latter hybrid expression would give an excitation energy (Ω) if applied with the linear-response formalism, as any other hybrid functional, from which one could better understand the key role played by the a_c weight for excitation energies: the final excitation energies obtained from the corresponding double-hybrid expression (Ω') are given by

$$\Omega' = \Omega + a_c \Delta(\text{D}), \quad (2)$$

with $\Delta(\text{D})$ the corresponding correction for excited states⁵³ leading thus to the (D)-corrected excitation energy Ω' .^{54,55} We would like to emphasize here

that the values of a_x and a_c can be found following roughly two different strategies: after their fitting to some training dataset, and thus necessarily introducing some parameterization,^{56,57} or by imposing a set of known exact constraints and known theoretical limits, with the corresponding expressions being considered as minimally empirical models.^{58–60}

Some other routes, such as the range-separation of the exchange term, are also deeply investigated to improve the previous expressions, be for ground- or excited-states properties. This strategy is based on the splitting of the electron-repulsion operator r_{ij}^{-1} using the error function:

$$\frac{1}{r_{ij}} = \frac{1 - [\alpha + \beta \operatorname{erf}(\omega r_{ij})]}{r_{ij}} + \frac{\alpha + \beta \operatorname{erf}(\omega r_{ij})}{r_{ij}}, \quad (3)$$

where α and $\alpha + \beta$ are coefficients used to weight the short- and long-range EXX, respectively, with the range-separation parameter ω governing the separation between the two regimes. This extension borrows the same argument than that previously one used for hybrid functionals; i.e., improving long-range electronic properties by gradually allowing the recovery of the correct asymptotic behaviour.^{61–63} The ω value can be again tuned for ground- or excited-state properties,⁶⁴ or fitted from first-principle approaches,^{65–67} again consistently with parameterized or minimally empirical models strategies, respectively. **Despite being the most often used approach,** there are also some recent examples for which the long-range correction is applied to both exchange and correlation terms.⁶⁸ **Additionally, we also mention specifically here the lrc-XYG3 functional,⁶⁹ where range-separation applies to the correlation part with increasing PT2 contribution at the long range, to show the diversity of existing choices.**

Finally, since the PT2 contribution could be seen as a too crude truncation of the perturbative series,⁷⁰ it is also common to scale differently the same- and opposite-spin energy contribution of that term, giving rise to Spin-

Component-Scaled (SCS) double-hybrid models, be range-separated or not. This strategy has been recently pursued for both set of functionals, parameterized⁷¹ or minimally empirical,⁷² mostly for ground-state properties^{73–76} unless some recent contributions for excited states too.^{77,78} Note that any spin-scaled method can be also done to depend only on the Scaling of the Opposite-Spin (SOS) term, thus neglecting same-spin correlation and rerunning the parameterization. Due to the particularities of this electron correlation correction for excited-states, up to four additional parameters need to be determined for these applications:⁷⁹ same-spin indirect term (c_T^{SS}), opposite-spin indirect term (c_T^{OS}), same-spin direct term (c_U^{SS}), and opposite-spin direct term (c_U^{OS}).

3.2 Justification of the choice of the expressions

Having explained the different routes followed to develop (most of the existing) double-hybrid density functionals, we will thus employ here the following set of methods to systematically assess the effect of each of the methodological contributions so far presented:

- Configuration Interactions (CI) with Singles (S) and partially introduced Doubles (D) substitutions: CIS, CIS(D),⁷⁹ SCS-CIS(D),⁸⁰ and SOS-CIS(D).⁸⁰
- Standard double-hybrid density functionals: B2-PLYP,⁸¹ PBE-QIDH,⁶⁰ and PBE0-2.⁸²
- Spin-scaled double-hybrid density functionals: SCS/SOS-B2PLYP21,⁷⁸ SCS-PBE-QIDH⁷⁸ and SOS-PBE-QIDH.⁷⁸
- Range-separated double-hybrid density functionals: ω B2-PLYP⁶⁴ and RSX-QIDH.⁶⁵
- Spin-scaled range-separated double-hybrid density functionals: SCS/SOS- ω B2PLYP,⁷⁸ SCS-RSX-QIDH,⁷⁸ and SOS-RSX-QIDH.⁷⁸

Hybrid density functionals will not be explored, since it is well-known from previous studies how these expression in any of their forms are unable to provide negative ΔE_{ST} values for these compounds.^{32,33} The reason is the lack of explicit double excitations, as it happens for CIS too, which would need to go beyond standard TD-DFT treatments.^{83–86} Note also the existing similarities between CIS(D) and any double-hybrid extension for excited states, with the latter depending critically on the a_c weight, once electron correlation effects beyond single-excitations are introduced even approximately. We will also explore the SCS-CIS(D) and SOS-CIS(D) variants, to see if some improvements are also found with respect to CIS(D).

We also provide some additional explanation to better understand this choice of double-hybrid functionals, with specific information about the set of functionals gathered in Table 1. There is not a SCS-B2PLYP or SCS- ω B2-PLYP version since the SCS fit collapsed to the SOS variant,⁷⁸ and thus the original authors consequently dubbed them as SCS/SOS-B2PLYP or SCS/SOS- ω B2-PLYP. Additionally, the reparameterization of the original B2-PLYP functional for excited states led to a version renamed now as SCS/SOS-B2PLYP21⁷⁸ to distinguish from a previously developed one. We have not considered other related double-hybrid functionals with a_c values close to the ones explored here (e.g. B2GP-PLYP⁵⁷ has a $a_c = 0.35$ value, close to that of PBE-QIDH) neither other models with low a_c values (*vide infra*) such as e.g. PBE0-DH⁵⁹ for which $a_c = 1/8$.

3.3 Computational details

The ground-state (S_0) geometry of all the compounds was optimized with the B97-3c method,⁸⁷ with all-real $3N - 6$ vibrational frequencies obtained in all cases. The vertical excitation energies are thus calculated at those global minimum geometries, and for the lowest excited states of singlet (S_1) and

triplet (T_1) multiplicity, denoted respectively as $S_1 \leftarrow S_0$ and $T_1 \leftarrow S_0$. Due to the rigidity of these systems, the difference between vertical and adiabatic excitation energies is known to be minimal.²⁴ The singlet-triplet energy difference is always calculated as $\Delta E_{ST} = E(S_1 \leftarrow S_0) - E(T_1 \leftarrow S_0)$, normally being $\Delta E_{ST} > 0$ unless an inversion of S_1 and T_1 excited-state energies is found for which ΔE_{ST} will be found negative. The double-hybrid methods are employed within the standard linear-response full TD-DFT method and under the Tamm-Dancoff approximation⁸⁸ or TDA-DFT. Note that the TDA-DFT was found before to give slightly more accurate $T_1 \leftarrow S_0$ excitation energies for locally-excited excitations,¹⁵ but its use was restricted to hybrid expressions in the linear-response regime, so that we will also assess if some difference arises here. The def2-TZVP basis set⁸⁹ was used for all the calculations unless otherwise noticed, with the auxiliary def2/JK and def2-TZVP/C basis sets.⁹⁰ Note that for double-hybrid TD(A)-DFT applications, e.g with the B2-PLYP functional, a previous study⁷⁷ found a difference of only 0.01 eV for excitation energies calculated with the def2-TZVP compared with the larger def2-QZVP basis set, which is thus not expected to significantly alter the conclusions to be reached here at least qualitatively. However, we will also complementarily study if some difference significant arises here with smaller (e.g. def2-SVP) and larger (e.g. def2-QZVP) basis sets. All the CIS(D) and double-hybrid density functional calculations are done with the ORCA 5.0 package.⁹¹ Finally, some SCS-CC2 values, considered here to be a single-reference method to allow a more homogeneous comparison, were also calculated in this work with the TURBOMOLE 7.4 package.⁹²

4 Analysis of the results

4.1 2T-N, 2T-4N, and 2T-7N systems

4.1.1 Wavefunction methods

Table 2 presents first the results for the set of 2T-N, 2T-4N, and 2T-7N systems, for which a large number of reference values by previously applied wavefunction methods are available. Note that some studies [DLPNO-STEOM-CCSD, NEVPT2, SCS-CC2, and SCS-ADC(2)] used the def2-TZVP basis set, as done here, but others [EOM-CCSD, ADC(2), and ADC(3)] employed the cc-pVDZ basis set instead. However, we have preferred to consider all of these values as a guide, to clearly show that in all cases a $\Delta E_{ST} < 0$ value was obtained by any combination of method and basis set. Comparing all of these wavefunction results, we note an overestimation of values (at least for 2T-N and 2T-7N) by the DLPNO-STEOM-CCSD method compared with EOM-CCSD, ADC(3), or NEVPT2. If we thus discard those DLPNO-STEOM-CCSD values, we could obtain the averaged value (simply as a qualitative rule-of-thumb) of all the other methods mentioned. This brackets the ΔE_{ST} values (in eV) as -0.14 (between -0.04 and -0.23), -0.16 (between -0.08 and -0.18), and -0.24 (between -0.11 and -0.38) for 2T-N, 2T-4N, and 2T-7N systems, respectively. Note that, roughly speaking, the ΔE_{ST} becomes slightly more negative as the number of N atoms increases.

First of all, looking at the CIS-based methods, the simplest CIS treatment is unable to predict the excited-state energy inversion, as also reported previously, while CIS(D) does it although providing larger ΔE_{ST} values (-0.28 , -0.29 , and -0.52 eV for 2T-N, 2T-4N, and 2T-7N, respectively, see Table 2) than most of the other wavefunction methods included in Table 2 and taken as reference values. The SCS-CIS(D) [SOS-CIS(D)] correction still decreases the latter ΔE_{ST} value by -0.12 , -0.11 , and -0.17 eV (-0.34 , -0.27 , and -0.38 eV) for 2T-N, 2T-4N, and 2T-7N systems, respectively. This discrep-

ancy, with respect to the set of values included as references, can be attributed to a too pronounced stabilization of the S_1 state of these systems: note that the large underestimation of the $S_1 \leftarrow S_0$ excitation energy compared with the $T_1 \leftarrow S_0$ seems to indicate for the systems tackled here displayed an unbalanced description of correlation effects by spin-scaled CIS(D) under their current parameterization.

4.1.2 Double-hybrid density functionals

We will first comment on the B2-PLYP and PBE-QIDH results, inspecting again Table 2, for which very similar $\Delta E_{ST} > 0$ ($\Delta E_{ST} < 0$) values are found for 2T-N and 2T-4N (2T-7N) systems: These two methods are thus not able to give the excited-state energy inversion for 2T-N and 2T-4N. Note that the corresponding range-separation extension, ω B2-PLYP and RSX-QIDH, respectively, still keeps the wrong sign of ΔE_{ST} for 2T-N and 2T-4N, and reverse it for 2T-7N. Therefore, range-separation alone does not help here, since long-range exchange effects do not drive this excited-state energy inversion.⁴⁶ On the other hand, the PBE0-2 model is able to predict the correct $\Delta E_{ST} < 0$ values for the three molecules selected, thanks to its higher a_c value (compared to that of B2-PLYP and PBE-QIDH) weighing the second-order perturbation term, whose application to excited states is highly beneficial here. If we analyze next the set of SCS- or SOS-based functionals, we can see how $\Delta E_{ST} < 0$ values are predicted for 2T-N at the SCS/SOS-B2PLYP21, SCS/SOS- ω B2PLYP, SCS-PBE-QIDH, SOS-PBE-QIDH, and SOS-RSX-QIDH levels (and thus with all the variants with the exception of SCS-RSX-QIDH). However, for 2T-4N only SOS-PBE-QIDH gives a $\Delta E_{ST} < 0$ value (apparently too low) with all other methods wrongly providing $\Delta E_{ST} > 0$, which clearly shows how challenging is to calculate this excited-state energy inversion typical of this system. We thus recommend to include it on any benchmark study to be further performed.

4.2 2T-3N, 2T-4_{bis}N, 2T-5N, and 2T-5_{bis}N systems

4.2.1 Wavefunction methods

We will describe next the CIS, CIS(D), SCS-CIS(D), and SOS-CIS(D) results gathered in Table 3 for the new set of *in silico* discovered but not-yet-synthesized azaphenylene systems. For this set of molecules, only EOM-CCSD results are available from the original study, but consistently showing again $\Delta E_{ST} < 0$ values between -0.03 and -0.08 eV, and thus slightly lower than those found for the previous 2T-N, 2T-4N, and 2T-7N systems at the same level of theory. Correspondingly, CIS(D) overestimates the values by $0.3 - 0.4$ with respect to EOM-CCSD, leading thus to too negative ΔE_{ST} energy difference, with a more pronounced overestimation upon application of the SCS or SOS scaling. Once again, we find a large underestimation of the $S_1 \leftarrow S_0$ excitation energies which translates to those too negative ΔE_{ST} values.

4.2.2 Double-hybrid density functionals

The results of all the assessed double-hybrid density functionals are also presented in Table 3. Strikingly, none of BLYP-based functionals (be B2-PLYP, ω B2-PLYP or the spin-scaled SCS/SOS-B2PLYP21 or SCS/SOS- ω B2PLYP versions) was able to provide now the correct $\Delta E_{ST} < 0$ value, although SCS/SOS-B2PLYP21 or SCS/SOS- ω B2PLYP led to very low ΔE_{ST} values from quasi-isoenergetic S_1 and T_1 excited states. On the other hand, some members of the PBE-based family of functionals (SCS-PBE-QIDH, SOS-PBE-QIDH, SOS-RSX-QIDH, and PBE0-2) agree qualitatively and quantitatively with EOM-CCSD results, as it also happened for the previous 2T-N, 2T-4N, and 2T-7N systems.

4.3 The case of HAP-3MF

We finally discuss the case of the real-world dye dubbed as HAP-3MF, for which the ADC(2) and SCS-CC2 calculations predicted a $\Delta E_{ST} < 0$ value in agreement with experimental findings. Although results with a large (def2-TZVP) and a moderate (def2-SVP) basis set are calculated here, we will analyze first those obtained with the def2-TZVP one accordingly to previous systems. The effect of using another basis set will be later analyzed. As we can easily see from Table 4, all the (D)-corrected methods now led to an excited-state energy inversion, with SCS/SOS- ω B2PLYP, SCS-PBE-QIDH, SOS-PBE-QIDH, SCS-RSX-QIDH, and PBE0-2 agreeing within 0.1 eV with respect to the SCS-CC2 values. The ω B2-PLYP and RSX-QIDH methods still predicted a very small but positive value. Note also that the good results obtained by SCS-PBE-QIDH, SOS-PBE-QIDH, and PBE0-2 double-hybrid functionals are not due to some error compensation, since both $S_1 \leftarrow S_0$ and $T_1 \leftarrow S_0$ excitation energies reasonably agree well between them and with respect to SCS-CC2 results although slightly underestimated.

5 Discussion of the results

5.1 Basis set effects

Before continuing with the detailed analysis of the results, we would also like to analyze if basis set effects could bring any qualitative difference to alter the overall performance of the methods. First, the basis set effect is not very pronounced going from the def2-TZVP to the larger def2-QZVP, which it was assessed with the PBE-QIDH functional as a test case for the molecular set of 2T-N, 2T-3N, 2T-4N, 2T-4_{bis}N, 2T-5N, 2T-5_{bis}N, and 2T-7N systems. Interestingly, the $S_1 \leftarrow S_0$ and $T_1 \leftarrow S_0$ excitation energies changed as much as 0.06 and 0.05 eV, respectively, with a completely negligible influence on the corresponding ΔE_{ST} values up to 0.01 eV. Therefore, extending the basis set

is not expected to significantly influence the conclusions reached here about the performance of a double-hybrid density functional.

Additionally, note that the cost-effective def2-SVP basis set was also used for the large HAP-3MF dye. We did that taking into account its possible use in data-driven massive studies of real-world dyes, for which a less costly basis set than def2-TZVP could be needed for methods scaling with system size (N) as $O(N^5)$ (or beyond). We can see in Table 4 how $|\Delta E_{ST}|$ is modified by up to 0.05 eV but with most of the assessed methods still giving negative values. However, its impact on the SCS-CC2 method is rather significant on $S_1 \leftarrow S_0$ excitation energies. Therefore, for preliminary or screening studies using double-hybrid methods, the use of this basis set should not be discarded since it is not expected to significantly modify the conclusions if a recommended functional (*vide infra*) is used with it.

5.2 TDA-DFT vs. TD-DFT results

Since the Tamm-Dancoff approximation has been extensively used for excited-state studies with great success,^{93,94} and particularly for TADF emitters to also improve (even slightly) the $T_1 \leftarrow S_0$ excitation energy calculated by hybrid density functionals,¹⁵ we have repeated the whole set of TD-DFT calculations with this approximation (TDA-DFT). The results are presented in Tables 5-7, analogously to Tables 2-4. The use of TDA-DFT increases both the $S_1 \leftarrow S_0$ and $T_1 \leftarrow S_0$ excitation energies, but not in the same amount which translates into some variations of the corresponding ΔE_{ST} values. Generally speaking, $T_1 \leftarrow S_0$ are slightly more affected than $S_1 \leftarrow S_0$ excitation energies, with spin-scaling functionals more prone to feel that effect. $S_1 \leftarrow S_0$ values can vary up to 0.15 eV (e.g. with the SCS-RSX-QIDH or SOS-RSX-QIDH functionals and for all the set of molecules) while $T_1 \leftarrow S_0$ can differ up to 0.20 eV (again for the same SCS-RSX-QIDH and SOS-RSX-

QIDH cases taken as example). The variations of ΔE_{ST} values span a range of up to 0.3 eV, meaning that the maximum decrease (increase) was -0.16 (0.12) eV, again with SCS-RSX-QIDH and SOS-RSX-QIDH, but with some functionals like B2-PLYP, PBE-QIDH, SCS-PBE-QIDH or SOS-PBE-QIDH less affected, showing variations (in eV) comprised between $-0.01/0.03$, $-0.05/0.00$, $-0.01/0.04$, and $0.00/0.05$, respectively.

5.3 Global overall performances

Since it is clear that for all the systems selected a $\Delta E_{ST} < 0$ value is predicted by wavefunction methods, consistently with other experimental evidences,^{26,27,34} we consider whether a double-hybrid density functional could reproduce that excited-state energy inversion or not, independently of the final numerical values. Figure 4 thus presents the number of double-hybrid expressions able to behave correctly (at least qualitatively) with respect to the total number of molecules, and with the full TD-DFT scheme: PBE0-2, SCS-PBE-QIDH, and SOS-PBE-QIDH are able to do it for all the systems, closely followed by the SOS-RSX-QIDH method. On the other hand, Figure 4 also displays the number of double-hybrid expressions able to predict the excited-state energy inversion under the Tamm-Dancoff approximation, to graphically appreciate better the differences with respect to the full TD-DFT treatment: SOS-PBE-QIDH and SOS-RSX-QIDH are now the best performers, closely followed by PBE0-2 and SCS-PBE-QIDH.

Overall, spin-scaled PBE-QIDH-based methods seem to behave more accurately than B2-PLYP-based ones, independently if we invoke the TDA-DFT or the full TD-DFT treatment. A notable exception is PBE0-2 for which no scaling is needed in any case. We relate (*vide infra*) this behaviour with the large a_c weight of its perturbative term, compared with B2-PLYP or PBE-QIDH expressions, which in the case of PBE-QIDH is compensated by the spin-scaling

done. Additionally, these methods are more accurate than spin-scaled CIS(D), which led to larger deviations not only for ΔE_{ST} but also for individual excitation energies. On the other hand, range-separation is therefore not needed for this kind of molecules, contrarily to other truly charge-transfer systems.^{95,96}

5.4 Individual overall performances

We analyze next, after establishing a rule-of-thumb for the selection of a double-hybrid density functional, the accuracy of each method for the $S_1 \leftarrow S_0$, $T_1 \leftarrow S_0$, and ΔE_{ST} energies. The 'Mean-Signed Deviation' (MSD), the 'Mean Absolute Deviation' (MAD), and the 'Root Mean-Squared Deviation' (RMSD) will be obtained for all the methods assessed as: $\text{MSD} = \frac{1}{N} \sum_i^N x_i$, $\text{MAD} = \frac{1}{N} \sum_i^N |x_i|$, and $\text{RMSD} = \sqrt{\frac{1}{N} \sum_i^N x_i^2}$, with $N = 8$, $x_i = \Omega_i^{\text{calculated}} - \Omega_i^{\text{SCS-CC2}}$, all values obtained with the def2-TZVP basis set considered as accurate enough for all the systems. Table 8 presents these values at the full TD-DFT level. For the $S_1 \leftarrow S_0$ excitation energies, the best performer is SCS/SOS- ω B2PLYP with a RMSD of only 0.06 eV, closely followed by PBE-QIDH and PBE0-2 with a value of 0.09 eV. However, the accuracy of SCS/SOS- ω B2PLYP and PBE-QIDH methods for the $T_1 \leftarrow S_0$ excitation energies is not so good, with RMSD values of 0.26 and 0.22 eV, respectively, thus explaining their ranking in the global assessment done in the previous section. PBE0-2 does it well again, with a RMSD of 0.13 eV and thus comparable to that achieved for $S_1 \leftarrow S_0$ excitation energies. The best performer here is the SCS/SOS-B2PLYP21 method with a value as small as 0.05 eV, smaller than that obtained at this level for the $S_1 \leftarrow S_0$ excitation energies (0.25 eV) which is somehow atypical and should be further investigated. Finally, when looking at the ΔE_{ST} energy differences, a RMSD around 0.1 eV is obtained by SCS-PBE-QIDH, SOS-PBE-QIDH, SOS-RSX-QIDH, and PBE0-2 methods, those behaving globally more accurately in the sense of providing a $\Delta E_{ST} < 0$ value for all the systems. In this regard, it is therefore highly

advised to select a functional able to perform equally well on both $S_1 \leftarrow S_0$ and $T_1 \leftarrow S_0$ excitation energies, which would translate into accurate ΔE_{ST} predictions. This statement can be observed e.g. looking at the SOS-PBE-QIDH values: a RMSD of 0.09 eV for ΔE_{ST} (and actually the lowest found among all the methods) arises from reasonably low RMSD values for both $S_1 \leftarrow S_0$ (0.18 eV) and $T_1 \leftarrow S_0$ (0.22 eV) excitation energies, thus showing a robust performance.

6 On the decisive role of a_c

We remind that the $a_c\Delta(\text{D})$ term is in fact crucial to correct the excitation energies (Ω) obtained by any hybrid density functional in the form $\Omega' = \Omega + a_c\Delta(\text{D})$, which are known to not always lead to $\Delta E_{ST} > 0$ (wrong) values. We will denote in the following as B2-PLYP(SCF), PBE-QIDH(SCF), and PBE0-2(SCF) the underlying hybrid functionals giving the Ω excitation energies, to distinguish from the full B2-PLYP, PBE-QIDH, and PBE0-2 double-hybrid expressions. Actually, given the accuracy of the PBE0-2 model, we exemplify next the ΔE_{ST} values obtained from the Ω -only $S_1 \leftarrow S_0$ and $T_1 \leftarrow S_0$ excitation energies by PBE0-2(SCF): 0.48, 1.06, 0.46, 0.62, 0.83, 0.72, 0.74, and 0.31 eV, for the 2T-N, 2T-4N, 2T-7N, 2T-3N, 2T-4_{bis}N, 2T-5N, and 2T-5_{bis}N systems, respectively. One can easily see that all of them are positive and largely overestimated. This is not exclusive of PBE0-2, since for PBE-QIDH(SCF) one would now find: 0.42, 0.86, 0.41, 0.54, 0.68, 0.62, 0.64, and 0.28 eV, respectively, and thus slightly lower values but still all being positive. Finally, for the B2-PLYP(SCF) functional, these values are: 0.32, 0.61, 0.33, 0.42, 0.50, 0.47, 0.49, and 0.24 eV. Note that this pitfall is known to affect any hybrid functionals of those existing, independently if they are range-separated or not, their composition in terms of exchange and correlation functionals, etc. due to the lack of (D)-like excitations as it has been extensively demon-

strated before.^{32,33} Figure S1 shows the quantity $\Delta(\text{D}) = \frac{\Delta E_{ST}(\Omega') - \Delta E_{ST}(\Omega)}{a_c}$ which spans between 1–2 eV among the compounds, although not significantly differing between the three models (B2-PLYP, PBE-QIDH, and PBE0-2) selected for this analysis.

Indeed, that leads the responsibility of final values to the marked influence of the $a_c\Delta(\text{D})$ contribution, or more particularly speaking the value of a_c , which makes the difference from (wrong) $\Delta E_{ST} > 0$ to (right) $\Delta E_{ST} < 0$ values in these systems. That contribution is known to be an individual quantity for each functional, molecule, and excited state, which in fact determines the final quality of an excitation energy calculated by a double-hybrid density functional.^{97–99} Figure 5 presents the magnitude of that term for the standard B2-PLYP, PBE-QIDH, and PBE0-2 expressions, which differ in their a_c weight ($a_c = 0.27$, $a_c = 1/3$, and $a_c = 1/2$, respectively) and for both excitation energies ($S_1 \leftarrow S_0$ and $T_1 \leftarrow S_0$) for the whole set of systems. The first observation is how the magnitude of the correction for $S_1 \leftarrow S_0$ excitation energies increase with a_c , as expected, ranging from -0.24 to -0.71 eV for B2-PLYP, from -0.26 to -0.76 eV for PBE-QIDH, and from -0.38 to -1.09 eV for PBE0-2. Note that: (i) a_c values for B2-PLYP and PBE-QIDH are close and smaller than that of PBE0-2, thus explaining the similar range of values found, and why is larger for PBE0-2; and (ii) double excitations contributions are always negative for the $S_1 \leftarrow S_0$ excitation energies, significantly contributing thus to the stabilization of the S_1 state due to correlation effects.¹⁰⁰ Turning now to $T_1 \leftarrow S_0$ excitation energies, the variation ranges from 0.06 to -0.40 eV for B2-PLYP, from 0.22 to -0.41 eV for PBE-QIDH, and from 0.48 to -0.57 eV for PBE0-2. These findings are also preserved for each molecule and not only globally.

Let us take the 2T-N case as example to further clarify the impact on this

correction on the final ΔE_{ST} values. This was calculated from the Ω excitation energies by PBE-QIDH(SCF) to be 0.415 eV, that is without the $a_c\Delta(\text{D})$ correction. Since that correction decreases the $S_1 \leftarrow S_0$ excitation energy by -0.263 eV while the $T_1 \leftarrow S_0$ excitation energy increased by 0.114 eV, the new (D)-corrected ΔE_{ST} value changes to 0.038 eV, which is the value entering into Table 2. If we repeat the same calculation for PBE0-2, for which the pristine ΔE_{ST} value obtained from the Ω excitation energies was 0.478 eV by PBE0-2(SCF), the (D)-like correction decreases the $S_1 \leftarrow S_0$ excitation energy by -0.383 eV while the $T_1 \leftarrow S_0$ excitation energy increased by 0.197 eV, leading now to a (D)-corrected ΔE_{ST} value of -0.102 eV. Finally, taken the B2-PLYP(SCF) expression, the Ω excitation energies led to a ΔE_{ST} value of 0.318 eV, which is changed with a decrease of the $S_1 \leftarrow S_0$ excitation energy by -0.239 eV and an increase of the $T_1 \leftarrow S_0$ excitation energy by 0.063 eV, leading to the final value of 0.02 eV gathered in Table 2. Table 9 shows the magnitude of the $a_c\Delta(\text{D})$ correction for all the molecules, and for both excitation energies, for which it can be corroborated its key importance for this challenging situation. That strong dependence on the $a_c\Delta(\text{D})$ correction also explains why (exchange) range-separation leads to similar results to standard double-hybrid models.

Table 10 finally gathers the magnitude of the $a_c\Delta(\text{D})$ correction for all the molecules, and again for both excitation energies, but now considering the spin-scaled SCS-PBE-QIDH and SOS-PBE-QIDH functionals. If we define the ratio between the magnitude of that correction for spin-scaled and spin-unscaled functionals as:

$$\text{ratio} = \frac{a_c\Delta(\text{D}) [\text{SCS-PBE-QIDH}]}{a_c\Delta(\text{D}) [\text{PBE-QIDH}]}, \quad (4)$$

we find a value between 1.3–1.6 for the $S_1 \leftarrow S_0$ excitation energy in the case of SCS-PBE-QIDH. In the case of SOS-PBE-QIDH, that ratio slightly increases to 1.4–1.7, thus showing in both cases a significant impact on the stabilization

of the S_1 state since that contribution is always negative for the $S_1 \leftarrow S_0$ excitation energy. Calculating the same ratio now for the $T_1 \leftarrow S_0$ excitation energy, this becomes 0.8–1.2 (0.9–1.3) for SCS-PBE-QIDH (SOS-PBE-QIDH), being thus not pronounced as for the $S_1 \leftarrow S_0$ excitation energy. The interplay between this asymmetry, in the right direction of stabilizing the S_1 state by correlation effects, causes the excited-state energy inversion of all the systems in agreement with wavefunction and experimental reference results.

7 Conclusions

We have elucidated the reasons for the performance of different double-hybrid exchange-correlation functionals to predict the energy inversion of the lowest singlet (S_1) and triplet (T_1) excited states of organic molecules with envisioned optoelectronic or photocatalytic applications. That violation of Hund’s rule manifests in a negative singlet-triplet energy difference, ΔE_{ST} , contrarily to most conjugated systems, which could foster a mechanism to recover the triplet excitons after their formation by spin statistics. That recovery could lead to the design of most efficient electroluminescent organic devices, after a molecular-driven design with predictive nature. However, the lack of explicit double excitations into standard TD-DFT calculations precluded up to now the systematic use of this methodology for that purpose, and thus double-hybrid exchange-correlation functionals incorporating (partially) those double excitations could become a solid alternative to wavefunction methods for this purpose.

To investigate this performance in more detail, we have systematically applied a set of methods to disentangle if a standard double-hybrid expression (i.e., B2-PLYP, PBE-QIDH, PBE0-2) could lead to negative ΔE_{ST} values, as well as if exchange range-separation (i.e., ω B2-PLYP, RSX-QIDH) and/or

spin-scaling for standard (SCS/SOS-B2PLYP21, SCS-PBE-QIDH, SOS-PBE-QIDH) or range-separated (SCS/SOS- ω B2PLYP, SCS-RSX-QIDH, and SOS-RSX-QIDH) expressions could help. Not surprisingly, the key aspect of those exchange-correlation methods assessed was the weight given to the double excitations into the calculations, which is known to be mediated by a coefficient a_c . The minimum weight needed to obtain negative ΔE_{ST} values is believed to be at least $a_c \geq 0.5$. Complementarily, since correlation and not exchange effects are the reason for that excited-state energy inversion, exchange range-separation did not bring any advantage with respect to standard double-hybrid expressions. Finally, spin-scaling was able to recover the negative ΔE_{ST} values, even for some of those functionals unable initially to do it, after scaling the correlation contribution by a factor sufficiently high (e.g. C_T^{OS} and $C_U^{OS} \geq 0.5$).

As a computational recipe to choose one or another double-hybrid functional among all the existing expressions, we recommend to use PBE0-2, SOS-PBE-QIDH, SCS-PBE-QIDH, and SOS-RSX-QIDH (or some other comparable) methods, which fit with the recommendations about the a_c and C_T^{OS} and C_U^{OS} values needed. If at least two of these expressions are able to predict a negative ΔE_{ST} value, it could be robustly inferred that the molecule thus exhibits the excited-state energy inversion. The use of a cost-effective basis set (def2-SVP) with respect to a nearly-converged one (def2-TZVP) did not alter the conclusion reached about which method was able to give that negative ΔE_{ST} values. Additionally, the use or not of the Tamm-Dancoff approximation does not change significantly the list of methods with an acceptable performance. Overall, we hope this study will contribute to accurately tackle the data-driven design of this challenging systems.

Acknowledgements

The work in Alicante is supported by the “Ministerio de Ciencia e Innovación” of Spain (Grant No. PID2019-106114GB-I00). Y.O. acknowledges funding by the “Fonds de la Recherche Scientifique-FNRS” under Grant n. F.4534.21 (MIS-IMAGINE). E.B. thanks ANR (Agence Nationale de la Recherche) and CGI (Commissariat à l’Investissement d’Avenir) for their financial support to this work through Labex SEAM (Science and Engineering for Advanced Materials and devices), Grant Nos. ANR-10-LABX-096 and ANR-18-IDEX-0001. G.R. acknowledges a grant from the “Fonds pour la formation a la Recherche dans l’Industrie et dans l’Agriculture” (F.R.I.A.) of the F.R.S.-F.N.R.S. We acknowledge useful discussions with E. Zysman-Colman (U. St.-Andrews, U.K.), S. Ghosh (Max Planck Institute for Coal Research, Germany), and R. Pollice and A. Aspuru-Guzik (U. Toronto, Canada)

Supplementary Material

In the Supplementary Material we include: (i) Cartesian (XYZ) atomic coordinates (in Å) of all the systems considered; (ii) Representation of the quantity $\Delta(D) = \frac{\Delta E_{ST}(\Omega') - \Delta E_{ST}(\Omega)}{a_c}$

Data Availability

The data that supports the findings of this study are available within the article [and its supplementary material] or are available from the corresponding authors upon reasonable request.

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Figure 1: Chemical structures of the first set of studied molecules: 2T-N (or cyclazine), 2T-4N, and 2T-7N (or heptazine). Hydrogen atoms are omitted for clarity. 2T denotes the core and xN refers to the number of C sites substituted by N atoms.

Figure 2: Chemical structures of the second set of studied molecules: 2T-3N, 2T-4_{bis}N, 2T-5N, and 2T-5_{bis}N. Hydrogen atoms are omitted for clarity. 2T denotes the core and xN refers to the number of C sites substituted by N atoms.

Figure 3: Chemical structure of the real-world HAP-3MF molecule. Hydrogen atoms are omitted for clarity.

Figure 4: Number of $\Delta E_{ST} < 0$ values correctly predicted by each method at the full TD-DFT (left) and TDA-DFT (right) levels with respect to the total number of molecules (red line).

Figure 5: Magnitude (in eV) of the $a_c \Delta(D)$ term for the $S_1 \leftarrow S_0$ (left) and $T_1 \leftarrow S_0$ (right) as calculated by the standard functionals B2-PLYP ($a_c = 0.27$), PBE-QIDH ($a_c = 1/3$), and PBE0-2 ($a_c = 1/2$). For each of the functionals, the values for each molecule (circles) for $S_1 \leftarrow S_0$ are ordered from low to high values, while the values for $T_1 \leftarrow S_0$ correspond to that of the $S_1 \leftarrow S_0$. The vertical bars denotes the maximum variation between the values for each functional and excitation.

Table 1: Values of the coefficients weighting the different terms of the double-hybrid density functionals considered.

Functional	a_x	a_c	ω	c_T^{SS}	c_T^{OS}	c_U^{SS}	c_U^{OS}
B2-PLYP	0.53	0.27	–	–	–	–	–
SCS/SOS-B2PLYP21	0.53	0.27	–	0.000	0.334	0.000	0.283
ω B2-PLYP	0.53	0.27	0.30	–	–	–	–
SCS/SOS- ω B2PLYP	0.53	0.27	0.30	0.000	0.433	0.000	0.460
PBE-QIDH	$3^{-1/3}$	$1/3$	–	–	–	–	–
SCS-PBE-QIDH	$3^{-1/3}$	$1/3$	–	0.070	0.515	0.096	0.524
SOS-PBE-QIDH	$3^{-1/3}$	$1/3$	–	0.000	0.547	0.000	0.573
RSX-QIDH	$3^{-1/3}$	$1/3$	0.27	–	–	–	–
SCS-RSX-QIDH	$3^{-1/3}$	$1/3$	0.27	0.174	0.541	0.586	0.424
SOS-RSX-QIDH	$3^{-1/3}$	$1/3$	0.27	0.000	0.632	0.000	0.714
PBE0-2	$2^{-1/3}$	$1/2$	–	–	–	–	–

Table 2: Vertical excitation energies (full TD-DFT) and associated ΔE_{ST} energy difference (all in eV) calculated with different methods, and with the def2-TZVP basis set unless otherwise noticed.

Method	2T-N			2T-4N			2T-7N		
	$S_1 \leftarrow S_0$	$T_1 \leftarrow S_0$	ΔE_{ST}	$S_1 \leftarrow S_0$	$T_1 \leftarrow S_0$	ΔE_{ST}	$S_1 \leftarrow S_0$	$T_1 \leftarrow S_0$	ΔE_{ST}
CIS	1.795	1.458	0.34	3.208	2.522	0.69	4.238	3.918	0.32
CIS(D)	1.042	1.322	-0.28	2.109	2.396	-0.29	2.632	3.154	-0.52
SCS-CIS(D)	0.804	1.201	-0.40	1.900	2.298	-0.40	2.385	3.077	-0.69
SOS-CIS(D)	0.383	0.922	-0.54	1.478	2.043	-0.56	1.895	2.795	-0.90
B2-PLYP	1.123	1.107	0.02	2.109	1.972	0.14	2.736	2.773	-0.04
SCS/SOS-B2PLYP21	1.401	1.453	-0.05	2.450	2.328	0.12	3.131	3.184	-0.05
ω B2-PLYP	1.217	1.101	0.12	2.373	2.037	0.34	3.092	3.027	0.06
SCS/SOS- ω B2PLYP	1.054	1.074	-0.02	2.217	2.029	0.19	2.871	2.988	-0.12
PBE-QIDH	1.183	1.145	0.04	2.277	2.070	0.21	2.975	2.990	-0.02
SCS-PBE-QIDH	1.037	1.162	-0.12	2.125	2.133	-0.01	2.742	2.962	-0.22
SOS-PBE-QIDH	1.006	1.170	-0.16	2.100	2.124	-0.02	2.704	2.973	-0.27
RSX-QIDH	1.246	1.136	0.11	2.438	2.085	0.35	3.191	3.137	0.05
SCS-RSX-QIDH	0.896	0.785	0.11	2.045	1.777	0.27	2.693	2.729	-0.04
SOS-RSX-QIDH	0.782	0.908	-0.13	1.957	1.923	0.03	2.546	2.857	-0.31
PBE0-2	1.122	1.223	-0.10	2.222	2.254	-0.03	2.863	3.029	-0.17
EOM-CCSD/cc-pVDZ ^a	1.09	1.19	-0.10	—	—	—	2.79	2.97	-0.18
ADC(2)/cc-pVDZ ^b	1.02	1.18	-0.16	—	—	—	2.57	2.85	-0.28
ADC(3)/cc-pVDZ ^c	0.78	0.87	-0.09	—	—	—	2.66	2.77	-0.11
DLPNO-STEOM-CCSD ^d	0.61	1.04	-0.43	1.92	2.11	-0.19	2.35	3.01	-0.66
NEVPT2(12,12) ^e	1.244	1.288	-0.04	1.980	2.159	-0.18	3.259	3.398	-0.14
SCS-CC2 ^e	1.110	1.334	-0.22	2.258	2.342	-0.08	2.847	3.226	-0.38
SCS-ADC(2) ^e	1.080	1.308	-0.23	2.125	2.303	-0.18	2.790	3.174	-0.38

^a Taken from Refs. 33,34,48^b Taken from Ref. 44^c Taken from Ref. 48^d Taken from Ref. 45^e Taken from Ref. 32

Table 3: Vertical excitation energies (full TD-DFT) and associated ΔE_{ST} energy difference (all in eV) calculated with different methods, and with the def2-TZVP basis set unless otherwise noticed.

Method	2T-3N			2T-4 _{bis} N			2T-5N			2T-5 _{bis} N		
	$S_1 \leftarrow S_0$	$T_1 \leftarrow S_0$	ΔE_{ST}	$S_1 \leftarrow S_0$	$T_1 \leftarrow S_0$	ΔE_{ST}	$S_1 \leftarrow S_0$	$T_1 \leftarrow S_0$	ΔE_{ST}	$S_1 \leftarrow S_0$	$T_1 \leftarrow S_0$	ΔE_{ST}
CIS	2.617	2.102	0.52	3.056	2.405	0.65	3.442	2.772	0.67	3.427	2.759	0.67
CIS(D)	1.592	1.921	-0.33	1.946	2.305	-0.36	2.193	2.663	-0.47	2.122	2.549	-0.43
SCS-CIS(D)	1.356	1.798	-0.44	1.709	2.172	-0.46	1.948	2.520	-0.57	1.882	2.420	-0.54
SOS-CIS(D)	0.918	1.516	-0.60	1.264	1.891	-0.64	1.489	2.230	-0.74	1.423	2.136	-0.71
B2-PLYP	1.657	1.602	0.06	1.978	1.907	0.07	2.227	2.194	0.03	2.188	2.134	0.05
SCS/SOS-B2PLYP21	1.973	1.952	0.02	2.310	2.252	0.06	2.575	2.545	0.03	2.538	2.488	0.05
ω B2-PLYP	1.843	1.655	0.19	2.205	1.972	0.23	2.489	2.302	0.19	2.452	2.232	0.22
SCS/SOS- ω B2PLYP	1.669	1.622	0.05	2.028	1.940	0.09	2.298	2.262	0.04	2.260	2.190	0.07
PBE-QIDH	1.778	1.680	0.10	2.130	2.021	0.11	2.404	2.329	0.08	2.364	2.252	0.11
SCS-PBE-QIDH	1.611	1.683	-0.07	1.956	2.029	-0.07	2.213	2.321	-0.11	2.170	2.238	-0.07
SOS-PBE-QIDH	1.580	1.689	-0.11	1.924	2.034	-0.11	2.180	2.325	-0.14	2.136	2.242	-0.11
RSX-QIDH	1.894	1.703	0.19	2.269	2.044	0.22	2.564	2.375	0.19	2.526	2.296	0.23
SCS-RSX-QIDH	1.506	1.355	0.15	1.867	1.709	0.16	2.138	2.033	0.10	2.095	1.940	0.16
SOS-RSX-QIDH	1.389	1.471	-0.08	1.749	1.830	-0.08	2.008	2.139	-0.13	1.965	2.047	-0.08
PBE0-2	1.706	1.758	-0.05	2.059	2.192	-0.13	2.326	2.433	-0.11	2.278	2.331	-0.05
EOM-CCSD/cc-pVDZ ^a	1.66	1.73	-0.07	2.01	2.04	-0.03	2.25	2.33	-0.08	2.21	2.28	-0.07
SCS-CC2	1.690	1.891	-0.20	2.050	2.225	-0.17	2.308	2.541	-0.23	2.258	2.477	-0.22

^a Taken from Ref. 48

Table 4: Vertical excitation energies (full TD-DFT) and associated ΔE_{ST} energy difference (all in eV) calculated with different methods and basis sets.

Method	HAP-3MF					
	def2-SVP			def2-TZVP		
	$S_1 \leftarrow S_0$	$T_1 \leftarrow S_0$	ΔE_{ST}	$S_1 \leftarrow S_0$	$T_1 \leftarrow S_0$	ΔE_{ST}
CIS	4.377	3.243	1.13	4.446	3.227	1.22
CIS(D)	2.487	3.040	-0.55	2.557	3.092	-0.54
SCS-CIS(D)	2.248	2.966	-0.72	2.325	3.014	-0.69
SOS-CIS(D)	1.799	2.695	-0.90	1.839	2.716	-0.88
B2-PLYP	2.657	2.730	-0.07	2.705	2.753	-0.05
SCS/SOS-B2PLYP21	3.042	3.143	-0.10	3.144	3.209	-0.06
ω B2-PLYP	3.073	3.077	-0.00	3.153	3.122	0.03
SCS/SOS- ω B2PLYP	2.847	3.023	-0.18	2.936	3.070	-0.13
PBE-QIDH	2.907	2.978	-0.07	2.961	2.997	-0.04
SCS-PBE-QIDH	2.666	2.921	-0.26	2.731	2.946	-0.22
SOS-PBE-QIDH	2.631	2.932	-0.30	2.701	2.958	-0.26
RSX-QIDH	3.173	3.186	-0.01	3.232	3.213	0.02
SCS-RSX-QIDH	2.627	2.726	-0.10	2.667	2.725	-0.06
SOS-RSX-QIDH	2.508	2.869	-0.36	2.574	2.880	-0.31
PBE0-2	2.783	2.991	-0.21	2.841	3.014	-0.17
ADC(2)/cc-pVDZ ^a	2.58	2.82	-0.24			
SCS-CC2/cc-pVDZ	2.82	3.18	-0.36			
SCS-CC2	2.773	3.170	-0.40	3.082	3.237	-0.16

^a Taken from Ref. 52

Table 5: Vertical excitation energies (under the Tamm-Dancoff approximation or TDA-DFT) and associated ΔE_{ST} energy difference (all in eV) calculated with different methods, and with the def2-TZVP basis set unless otherwise noticed.

Method	2T-N			2T-4N			2T-7N		
	$S_1 \leftarrow S_0$	$T_1 \leftarrow S_0$	ΔE_{ST}	$S_1 \leftarrow S_0$	$T_1 \leftarrow S_0$	ΔE_{ST}	$S_1 \leftarrow S_0$	$T_1 \leftarrow S_0$	ΔE_{ST}
B2-PLYP	1.155	1.132	0.02	2.139	2.028	0.11	2.768	2.813	-0.04
SCS/SOS-B2PLYP21	1.444	1.416	0.03	2.493	2.343	0.15	3.169	3.202	-0.03
ω B2-PLYP	1.310	1.219	0.09	2.449	2.213	0.24	3.170	3.124	0.05
SCS/SOS- ω B2PLYP	1.176	1.193	-0.02	2.313	2.197	0.12	2.974	3.087	-0.11
PBE-QIDH	1.241	1.203	0.04	2.327	2.173	0.15	3.031	3.065	-0.03
SCS-PBE-QIDH	1.112	1.198	-0.09	2.186	2.173	0.01	2.817	3.030	-0.21
SOS-PBE-QIDH	1.089	1.204	-0.12	2.167	2.183	-0.02	2.786	3.041	-0.26
RSX-QIDH	1.345	1.263	0.08	2.520	2.283	0.24	3.278	3.252	0.03
SCS-RSX-QIDH	1.007	0.997	0.01	2.126	2.013	0.11	2.793	2.872	-0.08
SOS-RSX-QIDH	0.943	1.084	-0.14	2.076	2.114	-0.04	2.687	2.990	-0.30
PBE0-2	1.194	1.241	-0.05	2.281	2.237	0.04	2.863	3.029	-0.17

Table 6: Vertical excitation energies (under the Tamm-Dancoff approximation or TDA-DFT) and associated ΔE_{ST} energy difference (all in eV) calculated with different methods, and with the def2-TZVP basis set unless otherwise noticed.

Method	2T-3N			2T-4 _{bis} N			2T-5N			2T-5 _{bis} N		
	$S_1 \leftarrow S_0$	$T_1 \leftarrow S_0$	ΔE_{ST}	$S_1 \leftarrow S_0$	$T_1 \leftarrow S_0$	ΔE_{ST}	$S_1 \leftarrow S_0$	$T_1 \leftarrow S_0$	ΔE_{ST}	$S_1 \leftarrow S_0$	$T_1 \leftarrow S_0$	ΔE_{ST}
B2-PLYP	1.693	1.640	0.05	2.017	1.943	0.07	2.263	2.231	0.03	2.224	2.179	0.04
SCS/SOS-B2PLYP21	2.021	1.942	0.08	2.362	2.248	0.11	2.624	2.548	0.08	2.586	2.496	0.09
ω B2-PLYP	1.933	1.782	0.15	2.296	2.103	0.19	2.579	2.421	0.16	2.540	2.366	0.17
SCS/SOS- ω B2PLYP	1.784	1.753	0.03	2.143	2.074	0.07	2.413	2.388	0.02	2.372	2.332	0.04
PBE-QIDH	1.838	1.757	0.08	2.192	2.082	0.11	2.466	2.403	0.06	2.425	2.343	0.08
SCS-PBE-QIDH	1.687	1.745	-0.06	2.033	2.070	-0.04	2.292	2.385	-0.09	2.247	2.322	-0.08
SOS-PBE-QIDH	1.662	1.751	-0.09	2.009	2.076	-0.07	2.265	2.391	-0.13	2.219	2.328	-0.11
RSX-QIDH	1.992	1.847	0.14	2.367	2.177	0.19	2.662	2.512	0.15	2.622	2.452	0.17
SCS-RSX-QIDH	1.609	1.563	0.05	1.969	1.897	0.07	2.240	2.221	0.02	2.196	2.155	0.04
SOS-RSX-QIDH	1.538	1.654	-0.12	1.895	1.987	-0.09	2.156	2.311	-0.16	2.109	2.245	-0.14
PBE0-2	1.781	1.808	-0.03	2.136	2.147	-0.01	2.403	2.479	-0.08	2.355	2.406	-0.05

Table 7: Vertical excitation energies (under the Tamm-Dancoff approximation or TDA-DFT) and associated ΔE_{ST} energy difference (all in eV) calculated with different methods and basis sets.

Method	HAP-3MF					
	def2-SVP			def2-TZVP		
	$S_1 \leftarrow S_0$	$T_1 \leftarrow S_0$	ΔE_{ST}	$S_1 \leftarrow S_0$	$T_1 \leftarrow S_0$	ΔE_{ST}
B2-PLYP	2.684	2.764	-0.08	2.730	2.793	-0.06
SCS/SOS-B2PLYP21	3.084	3.159	-0.08	3.175	3.227	-0.05
ω B2-PLYP	3.143	3.278	-0.14	3.220	3.209	0.01
SCS/SOS- ω B2PLYP	2.941	3.235	-0.29	3.027	3.161	-0.13
PBE-QIDH	2.956	3.042	-0.09	3.008	3.065	-0.06
SCS-PBE-QIDH	2.732	2.984	-0.25	2.795	3.012	-0.22
SOS-PBE-QIDH	2.702	2.995	-0.29	2.771	3.025	-0.25
RSX-QIDH	3.240	3.275	-0.04	3.307	3.312	-0.00
SCS-RSX-QIDH	2.719	2.844	-0.12	2.757	2.855	-0.10
SOS-RSX-QIDH	2.636	2.978	-0.34	2.699	3.002	-0.30
PBE0-2	2.853	3.059	-0.21	2.908	3.085	-0.18

Table 8: MSD, MAD, and RMSD values (in eV) for the double-hybrid density functionals selected, calculated with the with the def2-TZVP basis set and with respect to the SCS-CC2 values taken as reference.

Method	$S_1 \leftarrow S_0$			$T_1 \leftarrow S_0$			ΔE_{ST}		
	MSD	MAD	RMSD	MSD	MAD	RMSD	MSD	MAD	RMSD
B2-PLYP	-0.11	0.11	0.16	-0.35	0.35	0.36	0.24	0.24	0.25
SCS/SOS-B2PLYP21	0.24	0.24	0.25	0.02	0.04	0.05	0.22	0.22	0.23
ω B2-PLYP	0.15	0.15	0.16	-0.23	0.23	0.23	0.38	0.38	0.39
SCS/SOS- ω B2PLYP	-0.03	0.04	0.06	-0.26	0.26	0.27	0.23	0.23	0.24
PBE-QIDH	0.06	0.09	0.09	-0.22	0.22	0.22	0.28	0.28	0.29
SCS-PBE-QIDH	-0.13	0.13	0.15	-0.22	0.22	0.23	0.10	0.10	0.12
SOS-PBE-QIDH	-0.16	0.16	0.18	-0.22	0.22	0.22	0.06	0.06	0.09
RSX-QIDH	0.22	0.22	0.23	-0.16	0.16	0.17	0.38	0.38	0.39
SCS-RSX-QIDH	-0.21	0.21	0.23	-0.53	0.53	0.53	0.32	0.32	0.33
SOS-RSX-QIDH	-0.33	0.33	0.34	-0.40	0.40	0.40	0.07	0.07	0.11
PBE0-2	-0.02	0.05	0.09	-0.13	0.13	0.14	0.11	0.11	0.13

Table 9: Magnitude (in eV) of the $a_c\Delta(\text{D})$ term, as calculated by various (standard) double-hybrid functionals at the full TD-DFT level.

Molecule	B2-PLYP		PBE-QIDH		PBE0-2	
	$S_1 \leftarrow S_0$	$T_1 \leftarrow S_0$	$S_1 \leftarrow S_0$	$T_1 \leftarrow S_0$	$S_1 \leftarrow S_0$	$T_1 \leftarrow S_0$
2T-N	-0.239	0.063	-0.263	0.114	-0.383	0.197
2T-4N	-0.408	0.062	-0.433	0.220	-0.607	0.484
2T-7N	-0.656	-0.288	-0.702	-0.275	-0.989	-0.363
2T-3N	-0.366	-0.001	-0.394	0.054	-0.559	0.119
2T-4 _{bis} N	-0.416	0.018	-0.422	0.134	-0.620	0.340
2T-5N	-0.481	-0.044	-0.510	0.034	-0.712	0.117
2T-5 _{bis} N	-0.493	-0.056	-0.526	0.005	-0.741	0.056
HAP-3MF	-0.707	-0.399	-0.765	-0.411	-1.088	-0.569

Table 10: Magnitude (in eV) of the $a_c\Delta(\text{D})$ term, as calculated by various (spin-scaled) double-hybrid functionals at the full TD-DFT level.

Molecule	SCS-PBE-QIDH		SOS-PBE-QIDH	
	$S_1 \leftarrow S_0$	$T_1 \leftarrow S_0$	$S_1 \leftarrow S_0$	$T_1 \leftarrow S_0$
2T-N	-0.409	0.131	-0.440	0.139
2T-4N	-0.585	0.264	-0.610	0.275
2T-7N	-0.935	-0.303	-0.972	-0.292
2T-3N	-0.560	0.056	-0.591	0.063
2T-4 _{bis} N	-0.616	0.143	-0.647	0.148
2T-5N	-0.701	0.026	-0.734	0.030
2T-5 _{bis} N	-0.720	-0.009	-0.754	-0.005
HAP-3MF	-1.006	-0.468	-1.041	-0.457

2T-N

2T-4N

2T-7N

2T-3N

2T-4_{bis}N

2T-5N

2T-5_{bis}N

$\Delta E_{\text{ST}} < 0$ (correct number of times)

8
7
6
5
4
3
2
1
0

SOS-PBE-QIDH

SOS-RSX-QIDH

PBE0-2

SCS-PBE-QIDH

SCS/SOS- ω B2PLYP

SCS/SOS-B2PLYP21

PBE-QIDH

B2-PLYP

SCS-RSX-QIDH

RSX-QIDH

ω B2-PLYP