Time-dependent double-hybrid density functionals with spin-component and spin-opposite scaling

Tobias Schwabe[†] and Lars Goerigk^{*,‡}

[†]*Center for Bioinformatics and Physical Chemistry Institute, University of Hamburg, Bundesstraße 43, D-20146 Hamburg, Germany*

[‡]*School of Chemistry, The University of Melbourne, Parkville, Victoria 3010, Australia*

E-mail: lars.goerigk@unimelb.edu.au

Abstract

For the first time, we combine time-dependent double-hybrid density functional approximations (TD-DHDFAs) for the calculation of electronic excitation energies with the concepts of spin-component and spin-opposite scaling (SCS/SOS) of electron-pair contributions to their non-local correlation components. Different flavors of this idea, ranging from standard SCS parameters to fully fitted parameter sets, are presented and tested on six different parent DHDFAs. For cross-validation, we assess those methods on three benchmark sets that cover small to medium-sized chromophores (up to 78 atoms) and different excitation types. For this purpose, we also introduce new CC3 reference values for the popular Gordon benchmark set that we recommend using in future studies. Our results confirm that already the (unscaled) parent TD-DHDFAs are accurate and outperform some wave-function methods. Further introduction of SCS/SOS eliminates extreme outliers, reduces deviation spans from reference values by up to 0.5 eV, aligns the performance of the Tamm-Dancoff approximation (TDA) to

that of full TD calculations, and also enables a more balanced description of different excitation types. The best-performing TD-based methods in our cross validation have MADs as low as 0.14 eV compared to the time- and resource-intensive CC3 approach. A very important finding is that we also obtained SOS variants with excellent performance, contrary to wave-function based methods. This opens a future pathway to highly efficient methods for the optimization of excited-state geometries, particularly when paired with computing strategies such as the Laplace transform. We recommend our SCS- and SOS-based variants for further testing and subsequent applications.

Keywords: TD-DFT, time-dependent double-hybrid density functionals, spin-component scaling, spin-opposite scaling, electronic excitation energies,

1 Introduction

Kohn-Sham (KS) Density Functional Theory¹ (DFT) is the workhorse for day-to-day electronic structure theory computations,^{2,3} as it offers a good compromise between computational efficiency and applicability. Nevertheless, although an exact theory in principle, the method suffers from the fact that the true energy functional is unknown and, therefore, all applications are based on density functional approximations (DFAs), which suffer to different extents from various shortcomings.²⁻⁴ Their steady improvement is therefore an ongoing research topic.⁴

Further progress towards better approximations is aggravated by the fact that a systematic approach to improve DFAs is unknown. This has led to the development of a plethora of different methods. One way to classify and hierarchically order DFAs is Perdew’s analogy of “Jacobs’s ladder”.⁵ Here, DFAs are associated with one of five “ladder rungs” that lead from the “Hartree world” to the exact theory. At the highest level are those DFAs that employ virtual KS orbitals. One representative of this rung is the double-hybrid density functional approximation (DHDFA).⁶⁻⁹ It can be formally separated into two main parts,

with the first connecting (semi-)local DFA exchange with non-local Fock exchange and the second connecting (semi-)local DFA correlation with a non-local contribution from wave-function-based electron-correlation methods. It should be noted that the general ansatz has a rigorous theoretical foundation either via Görling–Levy perturbation theory^{10,11} or the constraint search formalism with a partitioned Hamiltonian.^{12–14} DHDFAs are currently regarded as the most sophisticated and most accurate DFAs for molecular thermochemistry, surpassing popular wave-function approaches, such as Møller-Plesset perturbation theory or even the composite complete-basis-set (CBS-QB3) approach.^{8,15–19}

Due to its success for electronic ground states, the DH DFA approach has also been extended to the computation of electronic excitation energies. A first solution suggested by Grimme and Neese was to transfer the configuration interaction singles with perturbative doubles²⁰ (CIS(D)) approach to a time-dependent DFT (TD-DFT) formalism in 2007 (TD-DHDFAs).²¹ Subsequently, a derivation based on linear response²² and a second order expansion²³ of a simplified KS-DFT perturbation theory²⁴ have also been presented. However, these latter two variants have not seen widespread use so far and, herein, we focus on the original TD-DH DFA idea.

The first benchmark studies of TD-DHDFAs were based exclusively on the B2PLYP⁶ and B2GPPLYP²⁵ double hybrids. Later applications with the "non-empirical" PBE0-DH²⁶ and PBE0-2²⁷ functionals were also conducted,^{28,29} but it was also demonstrated that those were less accurate than the first two.^{8,29,30} Between 2009 and 2012, Goerigk and Grimme showed that TD-B2PLYP and TD-B2GPPLYP solve a number of problems of conventional TD-DFT methods. For instance, they are more robust and accurate for theoretical electronic circular dichroism (ECD) spectroscopy.^{31,32} The same is also true for singlet-singlet valence π - π^* excitations in large organic dyes, for which TD-B2GPPLYP has been reported to have an average absolute error of 0.16 eV compared to at least twice as large an error for hybrid DFAs.^{33,34} For the same systems, TD-DHDFAs even outperformed variants of the resource-intensive, approximate coupled-cluster singles doubles wave-function approach

CC2,^{35,36} which is often referred to as the "gold-standard" for organic chromophores (0.17-0.20 eV average absolute error).³⁴ TD-DHDFAs are also the only TD-DFT based methods that give the correct energy order of the first two excitations in polycyclic aromatic hydrocarbons, which are important in technological applications due to their optical or semi-conducting behaviors.³⁷ Additionally, TD-DHDFAs do not suffer from artificial states ("ghost states"), an often-ignored problem that makes the interpretation of excited-state calculations unreliable.^{31-34,37} Also, they are able to describe exciton-coupled ECD spectra.³² Exciton coupling is a crucial process for photochemical electronic devices, but conventional TD-DFT approaches — including range-separated hybrid DFAs — fail to describe it.^{32,38} The good performance of DHDFAs for electronic excitation energies has also been confirmed in subsequent application-oriented studies.^{29,30,39-42} Note, that most of those studies applied the related Tamm-Dancoff approximation^{43,44} for DFT (TDA-DFT).^{29,30,41,42} TD(A)-DHDFAs are, thus, a valuable option for the treatment of medium-sized chromophores of 20-30 non-hydrogen atoms, all challenging systems for wave-function approaches due to their size. However, the aforementioned absolute error of 0.16 eV is still above what some have defined as the "chemical-accuracy" threshold of 0.1 eV. In this context, it should be noted that the human eye is able to resolve photon energy differences as small as 0.01-0.02 eV, which means even seemingly small numerical improvements are significant.³⁴ Whilst reviewing the literature, it is striking to see that DH DFA development has been a very active research field for electronic ground states, but that little has been done to further develop this idea for excited states. Herein, we aim to close this gap and further explore routes to not only improve the accuracy of TD(A)-DHDFAs, but to also increase their robustness by aligning the average errors for different types of excitations, for instance, π - π^* , n - π^* , σ - π^* , or Rydberg transitions.

A successful strategy to improve DH DFA accuracy for ground-state thermochemistry was the introduction of spin-component scaling^{45,46} (SCS) to the treatment of the non-local electron-correlation component, which was independently introduced in three publications.⁴⁷⁻⁴⁹ Par-

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3 particularly, Kozuch and Martin's family of dispersion-corrected spin-component-scaled double-
4 hybrid DFAs^{16,49,50} (DSD-DFAs) were shown to be the currently most reliable DFAs for
5 molecular thermochemistry with an average accuracy of 1.3 kcal/mol.⁸
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9 A special case of SCS is the spin-opposite scaling (SOS) variant, which neglects the treatment
10 of same-spin electron pairs in the non-local correlation part.⁵¹ This concept has also been
11 applied to ground state DHDFAs on different occasions.^{16,52-55} While this does not necessarily
12 improve the accuracy of an DHdFA, it can reduce the computational cost by exploiting a
13 Laplace transform for the energy expression.^{51,56}
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17 Herein, we apply the SCS and SOS techniques for the first time to DHDFAs to calculate
18 electronic excitation energies. For this purpose, we have chosen different standard DHDFAs,
19 for which we have adjusted different variants of SCS and SOS corrections to enable a TD- or
20 TDA treatment. To support our developments, we also established a training set with very
21 sophisticated theoretical single-reference benchmark values for vertical excitations. This is in
22 contrast to other method-development studies, which rely often on a mixture of experimen-
23 tally measured 0-0 transitions and multi-reference methods as a reference. By having a more
24 consistent training set, we are able to rule out any error-compensation effects and to assess
25 whether our SCS and SOS modifications constitute a true methodological improvement over
26 conventional TD(A)-DHDFAs.
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30 In the following, we first establish the theoretical and computational background and then
31 outline our method-development procedure. The new TD(A)-DHDFAs are then applied to
32 several benchmark sets and their performance is evaluated. We conclude with a discussion
33 of the performance of the new methods and some final remarks.
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2 Theoretical background

2.1 Double-hybrid density functionals for electronic ground states

In DHDFAs, portions of (semi-local) DFT exchange (E_X^{DFT}) are replaced by non-local Fock exchange (E_X^{HF}), while (semi-)local DFT correlation is partially complemented by a non-local correlation term. While various non-local correlation contributions are conceivable for this purpose,^{57–60} a DHDA in its original sense contains a second-order Møller-Plesset-type term (E_C^{MP2}).^{6–9} The resulting DHDA energy can, thus, be described as:

$$E_{XC}^{DHDA} = (1 - a_X)E_X^{DFT} + a_X E_X^{HF} + (1 - a_C)E_C^{DFT} + a_C E_C^{MP2}, \quad (1)$$

where a_X and a_C are the scale parameters for the non-local exchange and correlation contributions, respectively. The first three components in Equation 1 are akin to a hybrid functional approximation. For DHDFAs, the self-consistent-field (SCF) equations are solved first for these three components, before the resulting orbitals and orbital energies are used to obtain the MP2 portion and the final DHDA energy. The first functional of this type was Grimme’s B2PLYP⁶ functional in 2006, which contains Becke-88⁶¹ (B88) DFT exchange and Lee-Yang-Parr^{62,63} (LYP) DFT correlation; its scale parameters are $a_X=0.53$ and $a_C=0.27$. A popular reparametrized version for ”general-purpose” applications is Martin’s B2GPPLYP functional with $a_X=0.65$ and $a_C=0.36$.²⁵ Different combinations of E_X^{DFT} and E_C^{DFT} have been employed with various values for the two scale parameters; see Ref. 8 for a detailed review. Besides the aforementioned B2PLYP and B2GPPLYP functionals, we will also focus herein on DHDFAs containing Perdew-Burke-Ernzerhof⁶⁴ (PBE) DFT exchange and correlation contributions, namely PBE0-DH²⁶ ($a_X=0.50$; $a_C=0.125$) and PBE0-2²⁷ ($a_X=0.794$; $a_C=0.50$).

In 2003, Grimme presented the spin-component-scaled (SCS) variant of MP2 theory,⁴⁵ in which electron-correlation contributions from electron pairs of same and opposite spins are scaled up or down, respectively; see Ref. 46 for an explanation of this idea. A year

later, Head-Gordon showed that by completely neglecting the same-spin components (SOS-MP2),⁵¹ one can employ a Laplace⁵⁶ transformation algorithm to bring down the formal scaling behavior of MP2 from $\mathcal{O}(N^5)$ to $\mathcal{O}(N^4)$, with N being the system size or number of orbitals. Despite a small, additional computational overhead, this technique constitutes an overall speed-up at some point; general guidelines when to apply the SOS scheme were presented in Ref. 65. The SCS and SOS ideas have also been employed in the context of DHDFAs since 2008.^{47,48,52,53} In particular, Kozuch's and Martin's DSD functionals are of interest, which have the form:^{16,49,50}

$$E_{XC}^{DSD-DFA} = (1 - a_X)E_X^{DFT} + a_X E_X^{HF} + c_C E_C^{DFT} + c_O E_C^{OS-MP2} + c_S E_C^{SS-MP2} + E_{disp}, \quad (2)$$

where the meaning of the first three terms is the same as in Equation 1 and E_C^{SS-MP2} and E_C^{OS-MP2} are the same- and opposite-spin contributions to the non-local correlation energy scaled by c_S and c_O . Here, the scale factor c_C for the DFT correlation is independent from the two MP2 parameters. Additionally, all parameters were fitted in the presence of a dispersion correction E_{disp} , which is why this approach was dubbed "DSD" (Dispersion-corrected, Spin-component-scaled Double-hybrid). Herein, we will base our study on two of those DSD-DFAs, namely DSD-BLYP⁴⁹ and DSD-PBEP86.⁵⁰ The first is based again on B88 exchange and LYP correlation with $a_X = 0.69$, $c_C = 0.54$, $c_S = 0.37$, and $c_O = 0.46$. The second is based on PBE exchange and Perdew-Wang-86^{66,67} (P86) correlation with $a_X = 0.70$, $c_C = 0.43$, $c_S = 0.25$, and $c_O = 0.53$. Note that while a dispersion correction was used for the fitting procedure to determine the various scale parameters, we will not employ such a correction, as our focus is on excitation energies to which dispersion corrections currently do not contribute. While the magnitude of London-dispersion interactions in the excited state differ from the ground state,⁶⁸ this difference should be negligible for our context, with notable exceptions being excimers.^{69,70}

2.2 Initial time-dependent formulation for double-hybrid density functionals

In 2007, Grimme and Neese proposed a time-dependent (TD) version of the B2PLYP functional.²¹ In the spirit of the ground-state B2PLYP method, two calculations are combined to yield a final excitation energy. First, the hybrid component of the DHDFAs — i.e. the first three terms in Equation 1 — is used for a standard linear-response TD-DFT^{71,72} treatment that yields excitation energies ΔE_{TD-DFT} :

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \Delta E_{TD-DFT} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}, \quad (3)$$

where $\mathbf{X}$ and $\mathbf{Y}$ are solution vectors describing single excitations and de-excitations, and $\mathbf{A}$ and $\mathbf{B}$ are related to the corresponding Hamiltonian matrices between these (de-)excitations. The hybrid-functional excitation energy ΔE_{TD-DFT} is then corrected through a second-order perturbative treatment with Head-Gordon's CIS(D)²⁰ correction ($\Delta_{CIS(D)}$) and scaled down with the same parameter a_C that is known from the ground-state DHDFAs treatment (Equation 1). The resulting expression for TD-DHDFAs excitation energies is therefore:

$$\Delta E_{TD-DHDFAs} = \Delta E_{TD-DFT} + a_C \Delta_{CIS(D)}, \quad (4)$$

where the exact nature of $\Delta_{CIS(D)}$ is discussed in the next section.

DHDFAs have also been tested in the context of the Tamm-Dancoff approximation⁴³ (TDA), in which the matrix $\mathbf{B}$ in Equation 3 is set to zero, which reduces the standard TD-DFT problem to the same formalism that defines the configuration-interaction-singles (CIS) wavefunction approach. As a KS determinant is used instead of a Slater determinant, one refers to this approach as TDA-DFT:⁴⁴

$$\mathbf{A}\mathbf{X} = \Delta E_{TDA-DFT}\mathbf{X}. \quad (5)$$

TD(A)-DHDFA calculations can be carried out with any program with TD(A)-DFT and CIS(D) algorithms, as long as it is ensured that the correct terms from the TD(A)-DFT treatment are handed over to the CIS(D) subroutine. Note, that ORCA⁷³ is currently the only program available to the researcher community that allows for TDA-DHDFA calculations despite claims⁷⁴ that full TD-DHDFA treatments were carried out with other commercially available programs.

While this manuscript focusses on excitation energies, we would like to remind the reader that minor adjustments have to be made to the standard expressions for oscillator and rotational strengths when TD(A)-DHDFA are used for the simulation of UV/Vis or ECD spectra.⁷⁵ This information is outlined in the Supporting Information (SI).

2.3 The CIS(D) correction

In this section, we first explain the original CIS(D) wave-function approach before we comment on how to use it in the context of TD(A)-DHDFA. In the spirit of MP2 being a second-order perturbative correlation correction to the Hartree-Fock (HF) ground state energy, CIS(D) introduces electron correlation to excited states by perturbatively correcting configuration interaction singles (CIS) energies. The expression for CIS(D) correlation contribution ($E_c^{CIS(D)}$) to the total energy of an excited state is:²⁰

$$E_c^{CIS(D)} = \langle \Phi_{CIS} | \hat{V} | \hat{U}_2 \Phi_0 \rangle + \langle \Phi_{CIS} | \hat{V} | \hat{T}_2 \hat{U}_1 \Phi_0 \rangle, \quad (6)$$

where $\hat{V}$ stands for the perturbation potential due to electron correlation, Φ_0 is the HF ground-state determinant, and Φ_{CIS} is the CIS wave function that one obtains from the single-excitation operator $\hat{U}_1$ according to:

$$\Phi_{CIS} = \hat{U}_1 \Phi_0 = \sum_{ia} t_i^a \Phi_i^a, \quad (7)$$

with t_i^a standing for CIS single-excitation amplitudes and Φ_i^a for the related singly excited

determinants. In Equation 7 as well as in the following, we follow the standard convention of naming orbitals that are occupied in the ground state with letters i, j, k , and virtual orbitals with letters a, b, c . Unless noted differently, these shall be in general spin-orbital form.

The first term in Equation 6 is called “direct term” and involves double excitations from the HF ground state induced by the operator $\hat{U}_2$:

$$\hat{U}_2\Phi_0 = -\frac{1}{4}\sum_{ijab}\frac{\langle\Phi_{ij}^{ab}|\hat{V}|\hat{U}_1\Phi_0\rangle}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j - \Delta E_{CIS}}\Phi_{ij}^{ab}, \quad (8)$$

where ΔE_{CIS} is the CIS excitation energy, ϵ stands for an orbital energy, and Φ_{ij}^{ab} a doubly excited determinant.

The second term in Equation 6 is dubbed “indirect term”, as it involves a single excitation of a CIS-active electron by $\hat{U}_1$ followed by double excitation of CIS-inactive electrons by the operator $\hat{T}_2$, which is defined as:

$$\hat{T}_2\Phi_0 = -\frac{1}{4}\sum_{ijab}t_{ij}^{ab}\Phi_{ij}^{ab} = -\frac{1}{4}\sum_{ijab}\frac{(ij||ab)}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}\Phi_{ij}^{ab}, \quad (9)$$

where we have used Mulliken’s notation for the anti-symmetrized two-electron integrals $(ij||ab) = (ij|ab) - (ia|jb)$. t_{ij}^{ab} is a double-excitation amplitude whose expression is also known from ground-state MP2 theory.⁷⁶

While the above equations define the CIS(D) correlation energy of an excited state, the actual CIS(D) correction $\Delta_{CIS(D)}$ to the excitation energy ΔE_{CIS} is obtained as the difference between the second-order perturbative correlation energies for the excited and the ground states:

$$\Delta_{CIS(D)} = E_c^{CIS(D)} - E_c^{MP2} = -\frac{1}{4}\sum_{ijab}\frac{(u_{ij}^{ab})^2}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j - \Delta E_{CIS}} + \sum_{ia}t_i^av_i^a, \quad (10)$$

with the direct term using:

$$u_{ij}^{ab} = \sum_c (ab || cj)t_i^c - (ab || ci)t_j^c - \sum_k (ka || ij)t_k^b - (kb || ij)t_k^a, \quad (11)$$

and indirect term using the array v_i^a :

$$v_i^a = \frac{1}{2} \sum_{jkb} (jk || bc)[t_i^b t_{jk}^{ca} + t_j^a t_{ik}^{cb} + 2t_j^b t_{ik}^{ac}]. \quad (12)$$

For details on different algorithms that speed up the evaluation of $\Delta E_{CIS(D)}$, the reader is referred to Refs. 21 and 77.

The TD(A)-DHDFAs defined in the previous section employ the correction defined in Equation 10 with KS instead of HF orbitals, and with ΔE_{TD-DFT} or $\Delta E_{TDA-DFT}$ (see Equations 3 and 5) instead of ΔE_{CIS} .²¹ As TDA-DFT is formally related to CIS, it is straightforward to use the excitation vector $\mathbf{X}$ for the single-excitation amplitudes t_i^a to obtain TDA-DH DFA excitation energies.²¹ $\mathbf{X}$ is also used as an input for TD-DH DFA excitation energies, while the vector $\mathbf{Y}$ is neglected. In practice, this poses no problem.²¹

2.4 CIS(D) with spin-component and spin-opposite scaling

In the spirit of the SCS-MP2 approach, the electron-pair contributions to the correlation energy of an excited state can be scaled differently depending on whether the electrons are of same spin (SS) or opposite spin (OS). In a first implementation of this SCS-CIS(D) idea in 2003, Grimme and Izgorodina applied the same scale parameters as SCS-MP2 ground-state theory to the indirect term only.⁷⁸ Rhee and Head-Gordon developed this idea further and applied additional scale factors to the direct term. The correlation-energy expression for SCS-CIS(D), thus, becomes:⁷⁷

$$E_c^{SCS-CIS(D)} = \left\langle \Phi_{CIS} \mid \hat{V} \mid \left(c_U^{OS} \hat{U}_2^{OS} + c_U^{SS} \hat{U}_2^{SS} \right) \Phi_0 \right\rangle \\ + \left\langle \Phi_{CIS} \mid \hat{V} \mid \left(c_T^{OS} \hat{T}_2^{OS} + c_T^{SS} \hat{T}_2^{SS} \right) \hat{U}_1 \Phi_0 \right\rangle, \quad (13)$$

where c_U^{SS} and c_U^{OS} are the same- and opposite-spin scale parameters for the direct term and c_T^{SS} and c_T^{OS} the related parameters in the indirect term. The operators $\hat{U}_2$ and $\hat{T}_2$ become spin dependent and in spin-orbital form, with a bar marking β electrons, these operators are expressed as:

$$\hat{U}_2^{OS} \Phi_0 = -\frac{1}{4} \sum_{i\bar{j}} \sum_{a\bar{b}} \frac{\langle \Phi_{i\bar{j}}^{a\bar{b}} \mid \hat{V} \mid \hat{U}_1 \Phi_0 \rangle}{\epsilon_a + \epsilon_{\bar{b}} - \epsilon_i - \epsilon_{\bar{j}} - \lambda \Delta E_{CIS}} \Phi_{i\bar{j}}^{a\bar{b}}, \quad (14)$$

$$\hat{U}_2^{SS} \Phi_0 = -\frac{1}{4} \sum_{ij} \sum_{ab} \frac{\langle \Phi_{ij}^{ab} \mid \hat{V} \mid \hat{U}_1 \Phi_0 \rangle}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j - \lambda \Delta E_{CIS}} \Phi_{ij}^{ab} \\ - \frac{1}{4} \sum_{i\bar{j}} \sum_{a\bar{b}} \frac{\langle \Phi_{i\bar{j}}^{a\bar{b}} \mid \hat{V} \mid \hat{U}_1 \Phi_0 \rangle}{\epsilon_{\bar{a}} + \epsilon_{\bar{b}} - \epsilon_{\bar{i}} - \epsilon_{\bar{j}} - \lambda \Delta E_{CIS}} \Phi_{i\bar{j}}^{a\bar{b}}, \quad (15)$$

$$\hat{T}_2^{OS} \Phi_0 = -\frac{1}{4} \sum_{i\bar{j}} \sum_{a\bar{b}} \frac{(i\bar{j} \parallel a\bar{b})}{\epsilon_a + \epsilon_{\bar{b}} - \epsilon_i - \epsilon_{\bar{j}}} \Phi_{i\bar{j}}^{a\bar{b}}, \quad (16)$$

$$\hat{T}_2^{SS} \Phi_0 = -\frac{1}{4} \sum_{ij} \sum_{ab} \frac{(ij \parallel ab)}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} \Phi_{ij}^{ab} \\ - \frac{1}{4} \sum_{i\bar{j}} \sum_{a\bar{b}} \frac{(\bar{i}\bar{j} \parallel \bar{a}\bar{b})}{\epsilon_{\bar{a}} + \epsilon_{\bar{b}} - \epsilon_{\bar{i}} - \epsilon_{\bar{j}}} \Phi_{i\bar{j}}^{a\bar{b}}. \quad (17)$$

Expressions for the SCS-CIS(D) correction to the CIS excitation energy ($\Delta_{SCS-CIS(D)}$) have the same form as for $\Delta_{CIS(D)}$ in Equation 10, only with separate scaling for SS and OS pairs in u_{ij}^{ab} (Equation 11) and the double excitation amplitudes t_{ij}^{ab} in v_i^a (Equation 12).

In Rhee and Head-Gordon's version, the scale parameters of the indirect term were set to the

same values as in SCS-MP2, while those that apply to the direct term were empirically fitted to experimental 0-0 transition energies.⁷⁷ Note that Rhee and Head-Gordon introduced a damping parameter λ for ΔE_{CIS} in $\hat{U}_2^{OS}$ and $\hat{U}_2^{SS}$ (Equations 14 and 15). Two versions of SCS-CIS(D) were developed with $\lambda=0$ and $\lambda=1$.⁷⁷ Later, no significant differences were found for medium-sized to large organic dyes,^{34,38} and we will therefore not employ this parameter in our own development of spin-component-scaled TD(A)-DHDFAs. A SCS-CIS(D) variant, in which the parameters in the direct term were chosen to be the same as in the indirect one, proved to be inefficient and had larger errors than the unscaled CIS(D) parent approach.³⁴ By setting both same-spin parameters to zero, one obtains the SOS-CIS(D) approach, which benefits from a better formal scaling behavior by employing the same Laplace transform algorithm that can be used for SOS-MP2.^{51,77}

2.5 New time-dependent double-hybrid variants with spin-component or spin-opposite scaling

Herein, we combine the TD(A)-DHDFAs idea with the SCS/SOS-CIS(D) approach presented in Section 2.4, which changes Equation 4 to:

$$\Delta E_{TD(A)-SCS/SOS-DHFA} = \Delta E_{TD(A)-DFT} + \Delta_{SCS/SOS-CIS(D)}. \quad (18)$$

As parent DHDFAs, we choose six different methods: B2PLYP, B2GPPLYP, PBE0-DH, PBE0-2, DSD-BLYP and DSD-PBEP86. To limit the number of possible scale parameters to a bare minimum, we herein only consider perturbative SCS/SOS-CIS(D)-type corrections with a damping parameter $\lambda=1$ (see Equations 14 and 15). This leaves us with the four scale parameters c_U^{SS} , c_U^{OS} , c_T^{SS} , and c_T^{OS} introduced in Equation 13. Per parent functional, we analyze five possible variants with different values for the four scale parameters, in the following labeled with A–E, which are defined as:

A) The original parametrization of the ground-state DHDFAs. For DHDFAs following Equations

tion 1 (B2PLYP, B2GPPLYP, PBE0-DH, and PBE0-2) this means variant A is the normal TD(A)-DHDF version, as $c_U^{SS} = c_T^{SS} = c_U^{OS} = c_T^{OS} = a_C$. In the case of DSD-BLYP and DSD-PBEP86, however, this variant already includes SCS with $c_U^{SS} = c_T^{SS} = c_S$ and $c_U^{OS} = c_T^{OS} = c_O$ (see Equation 2).

- B) The value for the non-local ground-state correlation contribution is scaled by the SCS parameters introduced for SCS-MP2, i.e. $c_T^{SS} = c_U^{SS} = \frac{1}{3}a_C$ and $c_T^{OS} = c_U^{OS} = \frac{6}{5}a_C$. For the two DSD functionals, we apply the same idea for consistency reasons with $c_T^{SS} = c_U^{SS} = \frac{1}{3}c_S$ and $c_T^{OS} = c_U^{OS} = \frac{6}{5}c_O$.
- C) Application of the standard parameters for the indirect term (same values as defined in variant (A)) and a free least-squares fit of the parameters in the direct term with a training set defined below in Section 4.
- D) A free fit of all four parameters.
- E) An SOS variant with $c_T^{SS} = c_U^{SS} = 0$ and a free fit for the two OS parameters.

Finally, we investigate individual fits for both a TD-DHDF and a TDA-DHDF approach. Another sixth possibility would be to fit the SS and OS parameters with the constraint that they have the same value for the direct and the indirect part. Although this would be more consistent with a linear-response approach used to derive CIS(D) in 2008,³⁶ this was not further pursued because the results were slightly less accurate as the free fit (results not shown). Herein, we are only interested in excitation energies and no technical complications arise from treating the four parameters independently. We thereby follow Head-Gordon's strategy for the SCS-CIS(D) wave-function method, in which the parameters of the direct term also differ from the indirect part. If, at a later stage, another strategy is required to derive other properties based on response theory, this sixth variant would also be a suitable approach.

3 Computational details

All computations with coupled cluster singles doubles (CCSD), coupled cluster singles doubles with perturbative triple excitation correction (CCSDR(3)), and the approximate coupled-cluster singles doubles triples model (CC3) were performed with DALTON2013 and 2015.^{79,80} For CIS(D), the algebraic diagrammatic construction through second order model (ADC(2)),⁸¹ and CC2,³⁵ the resolution-of-the-identity (RI) approximation for the Coulomb term along with corresponding auxiliary basis sets⁸² was applied for the ground state, using the RIDFT module⁸³ of TURBOMOLE, version 7.1.⁸⁴ For excitations, the RICC2 module⁸⁵ was used. Standard DFT computations were done with TURBOMOLE, version 7.1, with the DSCF module⁸⁶ for the ground state and ESCF module⁸⁷ for the excitation energies, respectively. For all DFT energies, a multi-grid approach (m5)⁸⁸ for the numerical integration of the exchange-correlation potential was chosen. DHDFa ground-state calculations were carried out with a locally modified version of TURBOMOLE, or with Turbomole versions 7.0 and 7.1 by using the XCFun library version 1.99.⁸⁹ Subsequent excitation-energy computations are based on TD-DFT or TDA-DFT results with the same TURBOMOLE packages. All (SCS/SOS)-CIS(D) corrections, including those for wave-function CIS(D), were obtained with our own modified version of the RICC program (our version is dubbed RICC 3.0).⁹⁰ Geometries that were not taken from the literature were fully optimized. For that, the def2-TZVPP⁹¹ Ahlrichs-type atomic-orbital (AO) basis set was applied, either with PW6B95⁹² including a DFT-D3(BJ)^{93,94} correction or PBE0.^{95,96} Note that in the latter case, no London-dispersion correction was necessary because of the small size of the molecules. Our training and cross-validation sets are internally consistent, as they rely on geometries derived at the same level of theory and as also all reference values are based on the same geometries within the same set. The latter is a clear advantage over test sets that rely on experimental reference values. Similarly to large ground-state benchmark databases,^{15,53} the usage of different geometries in a compilation of different benchmark sets does not distort the observed trends, as the statistics for robust methods should be geometry independent. This was already ob-

served for TD-B2PLYP and TDA-B2PLYP.^{31,33} We can already confirm at this stage that the same geometry-independence can be observed in the present study.

For the computation of electronic excitation energies, either Dunning’s aug-cc-pVDZ, aug-cc-pVTZ,^{97,98} or Ahlrich’s TZVP⁹⁹ AO basis sets were used. For the correlation contributions in ADC(2), CC2, and (SCS/SOS)-CIS(D) — including our TD(A)-DHDFAs — the corresponding auxiliary basis sets for the RI approximation were applied.¹⁰⁰

4 Fit set and parametrization of the SCS and SOS approaches

For an unbiased assessment of the SCS/SOS approach for TD(A)-DHDFAs, we decided against fitting the methods against experimental results to avoid error-compensation effects. Instead, CCSDR(3) results are taken as a reference. CCSDR(3) is based on CCSD and a non-iterative triples correction to the excitation energies. It can, thus, be seen as an excited-state equivalent to the coupled cluster singles doubles with perturbative triples (CCSD(T)) approach routinely used to generate ground-state thermochemical reference values. Although CCSDR(3) does not make use of an explicit multi-reference reference state, its triples correction provides enough flexibility to account for some multi-reference character in the excited state. For well-behaved one-electron excitations, it is correct up to fourth order in the energy. Furthermore, due to the relatively high amount of exact Fock exchange in all considered DHDFAs (50–79.4%), they have the same characteristics as other single reference approaches. Therefore, although DFAs are in general capable of accounting for some multi-reference character implicitly, it cannot be expected that the DHDFAs perform any better than CCSDR(3). Accordingly, no results from multi-reference approaches such as second-order multi-reference Møller-Plesset perturbation theory (MRMP2) or second-order complete active space perturbation theory (CASPT2) have been used for fitting. However, achieving CCSDR(3) accuracy with a TD-DFT-type approach would constitute a significant

achievement.

The training set consists of 22 molecules with a total of 38 excitations that constitute a balanced mix of representative excitation types, namely π - π^* , n - π^* , Rydberg- and σ - π^* transitions. Note that this fit set and the following benchmark study are restricted to singlet-singlet excitations, which is a consequence of current technical limitations; the extension of our study to triplet states is planned for the future. The complete fit set is compiled in Tab. 1 along with the reference data, some representative literature results and some results of representative standard methods for electronic excitations (ADC(2) results can be found in the SI in Tab. S1). The composition of our fit set was partially inspired by similar fit sets for the two previously published SCS-CIS(D) methods, with the main difference that experimental data were used for those.^{77,78} More importantly, however, the composition reflects our goal to improve a method's robustness by fitting it simultaneously to different chromophores, types of excitations, and excitation-energy ranges. This also included difficult scenarios, such as the 1L_a and 1L_b transitions in aromatic systems. All molecular geometries were optimized at the PW6B95-D3(BJ)/def2-TZVPP level of theory and all excitation energies were obtained with the aug-cc-pVTZ basis set except for the largest molecules (anthracene and norcamphor) for which the smaller aug-cc-pVDZ basis set had to be applied for CCSDR(3) due to computer-resource restrictions. Only small differences between these two basis sets were observed for the other molecules and no significant influence on the fitting procedure should be expected from this limitation.

Comparing the reference values with results from the literature, which are either experimental or very sophisticated theoretical data, a general agreement can be found. However, we note that CCSDR(3) shows a general blue shift in the excitation energies, which can be quite profound in some cases (see e.g. the values for acrolein or cyclopentenone in Tab. 1). On the other hand, the other theoretical methods show very similar trends. Many of the cases with larger differences are based on experimental results. It might well be that, for instance, vibrational and solvent effects, which are not considered here, are the reasons for these

Table 1: Literature reference data and results for various electronic structure methods for the present fit set; the literature results are theoretical unless noted otherwise. All computations are based on PW6B95-D3(BJ)/def2-TZVPP geometries. The aug-cc-pVTZ AO basis set was used, unless noted otherwise. The statistical key data are: mean deviation (MD), mean absolute deviation (MAD), root-mean-square (RMS), and deviation span (Δ_{err}). All values in eV.

molecule	exc. state	lit. ref.	from Ref.	CCSD- R(3)	CCSD	PBE0	BH- LYP	CIS(D)	SCS- CIS(D)	SOS- CIS(D)	CC2	SCS- CC2	SOS- CC2
ammonia	$1^1A'$ ($n-3s$)	6.38 ^a	77	6.55	6.57	6.17	6.59	6.36	6.46	6.52	6.37	6.48	6.53
	$1^1A''$ ($n-3p$)	7.91 ^a	77	8.11	8.11	7.45	8.00	7.84	7.98	8.04	7.83	7.96	8.03
water	1^1B_2 ($n-3s$)	7.49 ^a	77	7.61	7.61	7.19	7.69	7.19	7.32	7.39	7.25	7.40	7.47
	1^1A_2 ($n-3p$)	9.20 ^a	77	9.38	9.37	8.62	9.28	8.93	9.09	9.18	8.90	9.09	9.18
ethene	1^1B_{1u} ($\pi-\pi^*$)	7.8	101	8.00	8.12	7.61	7.04	8.05	8.10	8.12	8.02	8.08	8.11
	1^1A_2 ($n-\pi^*$)	4.38 ^a	101	4.56	4.61	4.50	4.72	4.59	4.68	4.73	4.63	4.71	4.76
acetone	1^1B_1 ($\sigma-\pi^*$)	9.1	101	9.33	8.54	7.80	8.77	9.18	9.36	9.45	9.41	9.52	9.58
	$1^1A''$ ($n-\pi^*$)	3.21 ^a	78	3.88	3.99	3.67	4.06	3.98	4.12	4.19	3.93	4.11	4.19
acrolein	1^1B_u ($\pi-\pi^*$)	6.18	101	6.28	6.42	5.76	5.87	6.31	6.41	6.47	6.23	6.35	6.42
butadiene	$1^1A''$ ($\pi-\pi^*$)	3.36 ^a	78	4.00	4.13	3.84	4.27	4.06	4.20	4.28	3.97	4.18	4.27
cyclopentenone	1^1B_2 ($\sigma-\pi^*$)	6.76	101	6.77	6.91	6.41	6.62	6.91	7.10	7.19	6.81	6.95	7.01
cyclopropene	1^1B_1 ($\pi-\pi^*$)	7.06 ^a	101	6.78	6.85	6.31	6.42	6.95	7.07	7.13	6.84	6.99	7.07
formamide	$1^1A''$ ($n-\pi^*$)	5.63	101	5.76	5.79	5.69	5.92	5.69	5.79	5.84	5.79	5.87	5.91
anthracene	1^1B_{2u} ($\pi-\pi^*$)	3.43 ^a	78	3.88 ^b	4.03	3.31	3.54	3.96	4.03	3.90	3.68	3.85	3.93
	1^1B_{3u} ($\pi-\pi^*$)	3.89	102	3.92 ^b	3.96	3.98	4.17	3.97	3.90	3.86	3.93	3.88	3.86
	$1^1A''$ ($n-\pi^*$)	3.34 ^a	78	3.93	4.02	3.72	4.12	3.96	4.10	4.18	3.92	4.10	4.18
benzaldehyde	1^1B_{3u} ($\pi-\pi^*$)	5.08	101	5.07	5.13	5.55	5.69	5.40	5.22	5.13	5.34	5.18	5.10
benzene	1^1B_{2u} ($\pi-\pi^*$)	6.54	101	6.41	6.45	6.21	6.16	6.66	6.56	6.50	6.54	6.45	6.41
	1^1B_2 ($\pi-\pi^*$)	6.32	101	6.45	6.57	6.17	6.17	6.64	6.67	6.68	6.51	6.55	6.58
furan	2^1A_1 ($\pi-\pi^*$)	6.57	101	6.77	6.94	6.87	7.21	7.16	7.23	7.26	6.86	6.89	6.91
	3^1A_1 ($\pi-\pi^*$)	8.13	101	8.27	8.44	7.88	8.01	8.26	8.32	8.36	8.33	8.42	8.46
2-nitro-ethenamine	$1^1A''$ ($n-\pi^*$)	—		4.22	4.28	4.10	4.45	4.04	4.19	4.26	4.11	4.28	4.36
	$1^1A'$ ($\pi-\pi^*$)	—		4.88	5.05	4.84	5.10	4.86	4.93	4.97	4.89	5.00	5.05
hexatriene	1^1B_u ($\pi-\pi^*$)	5.10	101	5.38	5.52	4.77	4.93	5.36	5.49	5.56	5.26	5.42	5.50
naphthalene	1^1B_{2u} ($\pi-\pi^*$)	4.24	101	4.44	4.49	4.59	4.77	4.54	4.45	4.40	4.50	4.43	4.40
	1^1B_{3u} ($\pi-\pi^*$)	4.77	101	4.98	5.09	4.49	4.68	5.19	5.18	5.17	4.86	4.96	5.00
norcamphor	1^1A ($n-\pi^*$)	4.25 ^a	31	4.39 ^b	4.42	4.32	4.56	4.37	4.49	4.54	4.41	4.52	4.58
	2^1A ($n-3s$)	6.29 ^a	31	6.17 ^b	6.24	5.82	6.69	5.80	6.28	6.52	5.79	6.26	6.50
phenol	3^1A ($n-3p$)	6.77 ^a	31	6.75 ^b	6.82	6.37	7.25	6.33	6.84	7.09	6.33	6.81	7.05
pyrazine	$1^1A'$ ($\pi-\pi^*$)	4.51 ^a	78	4.97	5.05	5.18	5.39	5.11	4.98	4.92	5.02	4.93	4.88
	1^1B_{3u} ($n-\pi^*$)	3.95	101	4.22	4.32	3.98	4.39	4.37	4.53	4.62	4.14	4.34	4.44
pyridine	1^1B_{2u} ($\pi-\pi^*$)	4.64	101	5.21	5.27	5.55	5.62	5.38	5.23	5.16	5.26	5.12	5.05
	1^1B_2 ($n-\pi^*$)	4.59	101	5.06	5.19	4.85	5.31	5.23	5.41	5.50	5.01	5.22	5.32
tetrazine	1^1B_1 ($\pi-\pi^*$)	4.85	101	5.32	5.38	5.66	5.78	5.49	5.32	5.24	5.41	5.26	5.18
	1^1B_{3u} ($n-\pi^*$)	2.25 ^a	78	2.51	2.61	2.24	2.69	2.64	2.82	2.92	2.36	2.58	2.69
triazine	1^1A_u ($\pi-\pi^*$)	3.48	101	3.70	3.89	3.46	4.24	3.80	4.09	4.23	3.48	3.79	3.95
	2^1A_2 ($n-\pi^*$)	4.60	101	4.87	5.02	4.67	5.33	4.62	4.83	4.94	4.75	4.98	5.10
	1^1B_2 ($\pi-\pi^*$)	5.79	101	5.97	6.03	6.39	6.59	5.96	5.79	5.70	6.01	5.85	5.77
				MD	0.07	-0.23	0.09	0.01	0.10	0.14	-0.05	0.05	0.11
				MAD	0.11	0.34	0.33	0.16	0.16	0.20	0.12	0.11	0.17
				RMS	0.16	0.43	0.38	0.20	0.20	0.24	0.17	0.13	0.19
				Δ_{err}	0.98	2.01	1.58	0.85	0.75	0.80	0.75	0.52	0.53

^a experimental result, ^b aug-cc-pVDZ result

deviations. Also, the often challenging task of deriving exact theoretical vertical excitation energies from experimental data can cause these differences. In general, the other theoretical methods are closer to CCSDR(3) than to the literature results, which also indicates that the herein presented reference data are consistent and suitable for fitting.

To put the fit results into context, statistical key values for the deviations of some standard methods from our benchmark values are also presented in Tab. 1. For TD-PBE0 and TD-BHLYP, standard DFAs often applied to electronic excitation energies, the mean absolute deviations (MAD) are 0.34 and 0.33 eV, respectively. With a negative mean deviation (MD) of -0.23 eV, TD-PBE0 is the only method that significantly underestimates the excitation energies with respect to the reference. The reason could be the relatively low amount of exact Fock exchange (25% instead of 50% for BHLYP), which causes more severe self-interaction problems, a well-reported trend for functionals with Fock-exchange components below 40%.^{33,34}

In addition, we note that for this fit set, SCS leads to a small improvement for CC2, reducing the MAD from 0.12 to 0.11 eV and the deviation span from 0.75 eV to only 0.52 eV, the lowest of all considered methods so far. It should also be noted that the SOS approach deteriorates results for both, CIS(D) and CC2, so that its sole advantage is its reduced computational cost.

The fitting procedure was carried out by minimizing the root-mean-square deviation to the reference results for each TD(A)-DHDFA formulation. In addition to the constraints for variants C–E (see Section 2.5), any parameter that became negative during the minimization was set to zero and no longer varied to avoid unphysical results. The effect of the SCS and SOS schemes and the outcome of the parametrization are depicted in Fig. 1, which shows the deviation probability densities computed as normal distributions based on mean and standard deviations with respect to the reference data.

Already the non-fitted TD-DHDFA variants outperform the common DFAs and most of them are competitive or even superior to the related CIS(D) approach (Tab. 2). Their MADs range

Figure 1: Deviation probability densities for the variants A–E (see text) for the DHDFAs under consideration, either based on time-dependent DFT excitation energies (TD) or those obtained within the Tamm-Dancoff approximation (TDA). A: solid black line, B: solid blue line, C: dotted blue line, D: solid red line, E: dotted red line.

from 0.09 to 0.27 eV and are significant lower than for hybrid TD-DFT (see Tabs. S2-S13 for all data). TD-PBE0-2(A) even outperforms the CC2 and SCS-CC2 approaches. In general, TDA variants give blue-shifted results with respect to their TD counterparts, and this leads to a mean deviation (MD) closer to zero for those DHDFAs that are not based on PBE. For the PBE-based ones, TD results for method A show the better performance. Actually, the best non-fitted DHDFA for the present set is TD-PBE0-2(A) with a mean deviation of -0.01 eV and a mean absolute deviation of 0.09 eV. Finally, introducing the standard SCS parameters can lead to small improvements, most pronounced for TDA-B2PLYP(B), but in general this strategy has no significant effect.

The parameter fitting results are compiled in Tab. 3. Already variant C, for which only

Table 2: Summary of the results for all TD(A)-DHDFAs with methods A–E (see text) for the present fit set. All computations are based on PW6B95-D3(BJ)/def2-TZVPP geometries. The aug-cc-pVTZ AO basis set was used in all cases. The statistical key data are: mean deviation (MD), mean absolute deviation (MAD), root-mean-square (RMS), and deviation span (Δ_{err}). All values in eV.

		TD					TDA				
functional		A	B	C	D	E	A	B	C	D	E
B2PLYP	MD	−0.25	−0.18	−0.04	−0.02	−0.02	−0.15	−0.07	−0.02	−0.03	−0.03
	MAD	0.27	0.19	0.16	0.16	0.16	0.21	0.13	0.14	0.13	0.13
	RMS	0.33	0.25	0.21	0.20	0.20	0.29	0.20	0.21	0.19	0.19
	Δ_{err}	1.05	0.82	0.94	0.93	0.93	1.15	0.94	1.01	0.90	0.90
B2GPPLYP	MD	−0.15	−0.11	−0.03	−0.02	−0.03	−0.03	0.01	−0.02	−0.01	0.02
	MAD	0.17	0.13	0.13	0.11	0.11	0.14	0.11	0.11	0.10	0.11
	RMS	0.22	0.18	0.17	0.15	0.15	0.19	0.15	0.15	0.14	0.14
	Δ_{err}	0.81	0.63	0.68	0.65	0.63	0.95	0.78	0.76	0.68	0.69
DSD-BLYP	MD	−0.16	−0.14	−0.03	−0.02	−0.02	−0.05	−0.02	−0.03	−0.01	0.00
	MAD	0.17	0.14	0.12	0.11	0.12	0.13	0.10	0.10	0.10	0.10
	RMS	0.22	0.19	0.16	0.15	0.15	0.19	0.15	0.16	0.14	0.14
	Δ_{err}	0.75	0.58	0.68	0.64	0.65	0.92	0.76	0.73	0.66	0.63
DSD-PBEP86	MD	−0.14	−0.15	−0.02	−0.01	0.01	−0.02	−0.03	0.00	−0.02	−0.01
	MAD	0.14	0.16	0.10	0.10	0.10	0.11	0.10	0.09	0.09	0.09
	RMS	0.18	0.20	0.13	0.12	0.13	0.15	0.14	0.13	0.12	0.12
	Δ_{err}	0.59	0.60	0.57	0.56	0.56	0.77	0.67	0.65	0.60	0.56
PBE0-2	MD	−0.01	0.03	−0.02	0.01	0.02	0.13	0.18	0.00	0.01	0.01
	MAD	0.09	0.12	0.09	0.08	0.13	0.14	0.18	0.09	0.08	0.10
	RMS	0.12	0.15	0.12	0.11	0.16	0.18	0.21	0.11	0.11	0.13
	Δ_{err}	0.52	0.62	0.50	0.50	0.74	0.63	0.48	0.51	0.47	0.55
PBE0-DH	MD	−0.02	−0.01	−0.06	−0.02	−0.02	0.09	0.11	−0.01	−0.01	−0.01
	MAD	0.16	0.15	0.16	0.11	0.11	0.15	0.15	0.13	0.12	0.12
	RMS	0.21	0.20	0.20	0.15	0.15	0.21	0.21	0.16	0.15	0.15
	Δ_{err}	0.91	0.85	0.80	0.75	0.75	0.83	0.76	0.71	0.72	0.72

the parameters for the direct term are fitted, leads to a considerable improvement for most DHDFAs and the MDs are shifted systematically towards zero. Consequently, the free fit of all four parameters shows only marginal improvements whenever variant C already shows good results. Exceptions are PBE-based DHDFAs in combination with the TD treatment that do not gain much from fitting only the direct term. But also in these cases, the free fit improves the results. We can, thus, conclude that the introduction of SCS and subsequent parametrization (variants C and D) allow for a more balanced description of

Table 3: (Optimized) parameters for all considered functionals and variants A–E (see text) for either the time-dependent (TD) approach or the Tamm-Dancoff approximation (TDA). Parameters for variant A and B are identical for TD and TDA.

functional	param.	TD					TDA		
		A	B	C	D	E	C	D	E
B2PLYP ^a	c_T^{SS}	0.270	0.090	0.270	0.000	0.000	0.270	0.000	0.000
	c_T^{OS}	0.270	0.324	0.270	0.407	0.407	0.270	0.251	0.251
	c_U^{SS}	0.270	0.090	0.000	0.000	0.000	0.000	0.000	0.000
	c_U^{OS}	0.270	0.324	0.329	0.350	0.350	0.351	0.258	0.258
B2GPPLYP	c_T^{SS}	0.360	0.120	0.360	0.157	0.000	0.360	0.000	0.000
	c_T^{OS}	0.360	0.432	0.360	0.502	0.578	0.360	0.445	0.440
	c_U^{SS}	0.360	0.120	0.072	0.000	0.000	0.000	0.007	0.000
	c_U^{OS}	0.360	0.432	0.446	0.524	0.539	0.504	0.457	0.448
DSD-BLYP	c_T^{SS}	0.370	0.123	0.370	0.070	0.000	0.370	0.058	0.000
	c_T^{OS}	0.460	0.552	0.460	0.615	0.626	0.460	0.461	0.486
	c_U^{SS}	0.370	0.123	0.146	0.089	0.000	0.000	0.052	0.000
	c_U^{OS}	0.460	0.552	0.513	0.566	0.591	0.607	0.489	0.512
DSD-PBEB86	c_T^{SS}	0.250	0.083	0.250	0.034	0.000	0.250	0.072	0.000
	c_T^{OS}	0.530	0.636	0.530	0.643	0.675	0.530	0.488	0.512
	c_U^{SS}	0.250	0.083	0.126	0.135	0.000	0.013	0.058	0.000
	c_U^{OS}	0.530	0.636	0.547	0.566	0.631	0.624	0.523	0.540
PBE0-2	c_T^{SS}	0.500	0.167	0.500	0.590	0.000	0.500	0.202	0.000
	c_T^{OS}	0.500	0.600	0.500	0.591	0.842	0.500	0.607	0.692
	c_U^{SS}	0.500	0.167	0.475	0.423	0.000	0.328	0.327	0.000
	c_U^{OS}	0.500	0.600	0.513	0.628	0.816	0.608	0.601	0.740
PBE0-DH ^a	c_T^{SS}	0.125	0.042	0.125	0.000	0.000	0.125	0.000	0.000
	c_T^{OS}	0.125	0.150	0.125	0.385	0.385	0.125	0.228	0.228
	c_U^{SS}	0.125	0.042	0.000	0.000	0.000	0.000	0.000	0.000
	c_U^{OS}	0.125	0.150	0.184	0.337	0.337	0.200	0.241	0.241

^a variants D are identical to E.

the excited states at hand. We additionally note that the two DSD functionals also benefit from a reparametrization, which indicates that the OS and SS parameters determined for the ground state are not necessarily the best for excitation energies. The exception are the results for the TDA versions of DSD functionals, for which the probability distributions in all variants look very similar.

Another important finding is that the SOS variants (E) perform very similarly to variant D. In fact, the free fits of variants D for TD(A)-B2PLYP and TD(A)-PBE0-DH automatically converged to variant E, as in these cases, the SS parameters would have otherwise become negative in completely unrestricted fits. Although the parameters are treated as empirical ones here, we do not allow such an unphysical result because it might severely hamper

the transferability of the methods; negative values were also avoided in all ground-state applications of the SCS idea.⁴⁶ It should also be noted that TD(A)-PBE0-2(E) performs slightly worse than its variant D.

We can, thus, confirm previous findings that already the unscaled parent TD-DHDFAs outperform other popular methods.^{21,29–34,37,39–42} We have further demonstrated that the new SCS/SOS variants show an ever better performance than their parent methods. This may come as no surprise for the fit set, and in the following section, we will carry out cross-validation analyses to verify this observation.

Before we do so, however, we would like to briefly address the expected basis-set dependence of TD(A)-DHFAs. We do so for TD-B2PLYP(A) and TD-PBE0-2(A), as they are both extremes in the sense that B2PLYP contains a relatively small fraction of non-local correlation and PBE0-2 the largest of all tested DHDFAs. In addition, we do the same analysis for the CIS(D) approach, which contains 100% of non-local correlation. Results for the aug-cc-pVQZ^{97,98} AO basis set and their differences from aug-cc-pVTZ numbers are shown in Table S14. The MAD for the quadruple- ζ results with respect to the triple- ζ ones is only 0.03 eV for CIS(D). Due to their smaller fractions of non-local correlation, the two DHDFAs show faster basis-set convergence than their wave-function counterpart — a trend that is well-known from ground-state DHDFAs.¹⁵ In fact, the MADs for both DHDFAs are only 0.01 eV, with most energy differences being zero. The largest deviation for TD-PBE0-2(A) is 0.06 eV for the high-lying 1^1B_1 state in acetone (σ - π^* transition). All other methods, including the fitted ones, have effectively smaller non-local correlation contributions than PBE0-2 and, thus, a smaller basis-set dependence. We can conclude that for the states and energy ranges considered herein, it is not necessary to go to the quadruple- ζ level with TD(A)-DHDFAs.

5 Cross validation of all methods

5.1 Results for the Thiel benchmark set

Thiel, Sauer and co-workers published a well-established benchmark set for local valence excitations in organic molecules,¹⁰¹ which they used to thoroughly assess single-reference and multi-reference wave-function as well as DFT-based methods.^{103–105} Goerigk et al. then showed for the same set that the TD-B2PLYP and TD-B2GPPLYP methods outperform conventional hybrid-DFT approaches.³³ The original paper suggested theoretical "best estimates" as reference values that had been collected from different sources and were based on different wave-function levels of theory.¹⁰¹ To be more consistent, we decided to base the present analysis on Thiel, Sauer and co-workers' presented molecular geometries and their CC3/TZVP values. CC3 is comparable to CCSDR(3), but is solved fully iteratively, whereas CCSDR(3) relies on a one-step perturbation correction. The iterative approach allows for a more flexible description of the electronic excitations and, therefore, offers even higher accuracy for complicated cases. Such values were presented for 24 molecules comprising 111 excitation energies, with 74 having π - π^* , 34 n - π^* , and 3 σ - π^* character. Thiel, Sauer and co-workers were also able to compare CC3/TZVP with CC3/aug-cc-pVTZ for a small subset of this set, and they concluded that low-lying excitations were not affected significantly by the AO basis set choice, whereas excitations above 7 eV with potential valence-Rydberg mixing may benefit from the larger basis set.¹⁰⁶ Nevertheless, the published CC3/TZVP numbers were still the best available, and due its popularity, we decided to include this set in our analysis. Moreover, our conclusions should remain relatively unaffected by this choice, as we base our comparison between the TD(A)-DHDFAs and the reference values on the same basis set.

First, we discuss the results for the π - π^* and n - π^* transitions separately, and for the TD-DHDFAs only. All relevant statistical values based on calculations with the TZVP basis set are shown in Tab. 4. For both types of transitions and for all tested functionals, introducing

the spin-based scaling leads to a general blue-shift, with the MDs becoming more positive. In the case of π - π^* excitations, this leads normally to better MDs that are closer to zero for B2PLYP and B2GPPLYP, while the PBE-based and DSD functionals after parameter optimization show MDs whose absolute values are similar to those of variant A. In the majority of cases, the original variants A seem to provide a more balanced description of n - π^* transitions than the optimized spin-scaled methods, with the exception of the two PBE-based functionals. In fact, SCS and SOS seem to have an overall larger effect on π - π^* transitions with methods D and E having lower MADs than their counterparts A. Some MADs improve by more than 0.1 eV, as in the case of TD-PBE0-DH (0.37 vs. 0.26 eV). Also the deviation spans are reduced by introducing the scaling and optimizing all parameters. The MADs for the n - π^* subset are generally very small for all functionals and variants (usually below 0.15 eV), with variants A of B2GPPLYP, DSD-BLYP, and DSD-PBEP86 having slightly lower MADs than the variants with optimized parameters. The description of these excitations improves, however, for the optimized SCS variants of B2PLYP, PBE0-2, and, PBE0-DH with the latter having an MAD below the 0.1 eV threshold.

An important aspect to investigate is, of course, whether a method is capable of providing a description of different types of transitions on an equal footing. Tab. 5 therefore lists the statistical values of all 111 excitations combined. The overall picture is also here that variants D and E, i.e. with optimized parameters, show generally better MDs and MADs with the three best methods being TD-PBE0-DH (MAD=0.20 eV for variant E), and TD-B2PLYP and TD-B2GPPLYP (MAD=0.23 eV for variant E). This finding is particularly useful, as variant E is computationally more efficient, as discussed before.

Separate statistics for π - π^* and n - π^* transitions for the TDA versions of all DFAs are shown in the SI (Tab. S15) and they exhibit the same trends as the TD versions. The statistics for TDA-DHDFAs for the complete set are shown in Tab. 5. When comparing variants A of TD and TDA with each other, one notices a general blue-shift. This is further increased by introducing SCS/SOS. The MADs however, do not differ significantly between the five

Table 4: Overview of the TD-DHDFa performance for the Thiel benchmark set with variants A–E (see text), separately analyzed for π - π^* and n - π^* transitions. The statistical key values are: mean deviation (MD), mean absolute deviation (MAD), root-mean-square (RMS), and the deviation span (Δ_{err}). All values are in eV and they are based on the TZVP AO basis set.

functional		π - π^*					n - π^*				
		A	B	C	D	E	A	B	C	D	E
TD-B2PLYP ^a	MD	-0.20	-0.17	-0.03	-0.01	-0.01	-0.16	-0.01	0.13	0.13	0.13
	MAD	0.36	0.33	0.30	0.28	0.28	0.17	0.08	0.13	0.13	0.13
	RMS	0.43	0.40	0.38	0.36	0.36	0.19	0.11	0.17	0.17	0.17
	Δ_{err}	2.07	2.02	2.06	1.94	1.94	0.43	0.60	0.61	0.53	0.53
TD-B2GPPLYP	MD	-0.08	-0.07	0.00	0.01	0.00	0.01	0.10	0.19	0.18	0.16
	MAD	0.35	0.32	0.31	0.28	0.27	0.10	0.14	0.20	0.19	0.17
	RMS	0.44	0.42	0.42	0.40	0.39	0.13	0.18	0.25	0.23	0.22
	Δ_{err}	2.37	2.33	2.39	2.27	2.21	0.59	0.72	0.76	0.64	0.65
TD-DSD-BLYP	MD	-0.06	-0.07	0.05	0.05	0.03	0.00	0.07	0.19	0.19	0.20
	MAD	0.35	0.34	0.31	0.29	0.29	0.12	0.13	0.20	0.20	0.21
	RMS	0.47	0.46	0.47	0.46	0.45	0.15	0.17	0.25	0.25	0.26
	Δ_{err}	2.46	2.50	2.50	2.47	2.49	0.59	0.69	0.66	0.70	0.74
TD-DSD-PBEP86	MD	-0.04	-0.07	0.06	0.06	0.07	0.02	0.01	0.18	0.17	0.20
	MAD	0.33	0.34	0.30	0.29	0.28	0.12	0.13	0.19	0.18	0.21
	RMS	0.47	0.46	0.47	0.46	0.46	0.16	0.16	0.24	0.23	0.26
	Δ_{err}	2.45	2.46	2.47	2.44	2.45	0.63	0.73	0.64	0.66	0.70
TD-PBE0-2	MD	0.08	0.09	0.07	0.11	0.09	0.19	0.30	0.18	0.17	0.23
	MAD	0.34	0.32	0.34	0.31	0.31	0.20	0.30	0.20	0.19	0.25
	RMS	0.52	0.52	0.52	0.52	0.51	0.28	0.38	0.28	0.26	0.32
	Δ_{err}	2.52	2.52	2.52	2.46	2.49	0.83	1.06	0.84	0.88	1.03
TD-PBE0-DH ^a	MD	-0.02	-0.01	-0.06	-0.02	-0.02	0.12	0.15	0.10	0.02	0.02
	MAD	0.37	0.36	0.36	0.26	0.26	0.13	0.16	0.13	0.07	0.07
	RMS	0.45	0.44	0.43	0.33	0.33	0.22	0.25	0.22	0.10	0.10
	Δ_{err}	2.21	2.19	2.16	1.70	1.70	1.09	1.13	1.06	0.43	0.43

^a variant D is identical to E.

variants and they are very close to those of the TD counterparts. An exception here are the two PBE-based functionals whose MADs improve by up to 0.09 eV compared to variant A. We conclude this part by comparing the SCS/SOS-based TD(A)-DHDFAs with their wavefunction-based relatives (SCS/SOS)-CIS(D). For the latter, introducing SCS/SOS interestingly induces a red-shift and MDs decrease from CIS(D) (MD=0.27 eV) to SCS-CIS(D) (0.12 eV) and SOS-CIS(D) (-0.14 eV); see Tab. S22. MADs for SCS-CIS(D) are slightly better than for CIS(D) (0.32 vs. 0.35 eV), but they increase to 0.42 eV for SOS-CIS(D). We can therefore conclude that the effect of spin-based scaling for CIS(D) is different than for TD(A)-DHDFAs, with the latter clearly benefitting from the scaling and being more

Table 5: Overview of the TD(A)-DHDFA performance for the Thiel benchmark set with variants A–E (see text). The statistical key values are: mean deviation (MD), mean absolute deviation (MAD), root-mean-square (RMS), and the deviation span (Δ_{err}). All values are in eV and they are based on the TZVP AO basis set.

functional		TD					TDA				
		A	B	C	D	E	A	B	C	D	E
B2PLYP ^a	MD	−0.19	−0.12	0.02	0.03	0.03	−0.03	0.05	0.09	0.11	0.11
	MAD	0.29	0.25	0.24	0.23	0.23	0.23	0.20	0.21	0.24	0.24
	RMS	0.37	0.34	0.33	0.31	0.31	0.30	0.28	0.29	0.32	0.32
	Δ_{err}	2.07	2.02	2.06	1.94	1.94	1.86	1.80	1.82	1.86	1.86
B2GPPLYP	MD	−0.05	−0.02	0.06	0.06	0.05	0.11	0.15	0.13	0.14	0.17
	MAD	0.27	0.26	0.27	0.24	0.23	0.24	0.24	0.23	0.24	0.25
	RMS	0.37	0.36	0.37	0.35	0.34	0.34	0.34	0.33	0.34	0.35
	Δ_{err}	2.37	2.33	2.39	2.27	2.21	2.20	2.12	2.14	2.08	2.08
DSD-BLYP	MD	−0.05	−0.03	0.09	0.09	0.08	0.11	0.13	0.13	0.15	0.15
	MAD	0.27	0.27	0.27	0.25	0.26	0.23	0.22	0.23	0.25	0.25
	RMS	0.40	0.39	0.40	0.40	0.40	0.34	0.33	0.33	0.36	0.36
	Δ_{err}	2.46	2.50	2.50	2.47	2.49	2.30	2.23	2.25	2.18	2.17
DSD-PBEP86	MD	−0.02	−0.04	0.09	0.09	0.11	0.13	0.11	0.15	0.14	0.15
	MAD	0.26	0.27	0.26	0.25	0.25	0.23	0.21	0.22	0.23	0.24
	RMS	0.39	0.39	0.40	0.40	0.40	0.34	0.32	0.34	0.35	0.36
	Δ_{err}	2.45	2.46	2.47	2.44	2.45	2.26	2.24	2.24	2.19	2.17
PBE0-2	MD	0.11	0.15	0.10	0.13	0.13	0.28	0.33	0.16	0.16	0.16
	MAD	0.29	0.31	0.29	0.26	0.29	0.33	0.36	0.25	0.24	0.25
	RMS	0.45	0.47	0.45	0.44	0.45	0.45	0.49	0.39	0.38	0.39
	Δ_{err}	2.52	2.52	2.52	2.46	2.49	2.19	2.18	2.24	2.20	2.20
PBE0-DH ^a	MD	0.02	0.03	−0.02	−0.01	−0.01	0.20	0.22	0.09	0.09	0.09
	MAD	0.29	0.29	0.28	0.20	0.20	0.30	0.30	0.25	0.22	0.22
	RMS	0.39	0.39	0.37	0.27	0.27	0.40	0.40	0.33	0.30	0.30
	Δ_{err}	2.21	2.19	2.16	1.70	1.70	1.76	1.74	1.66	1.62	1.62

^a variant D is identical to E.

accurate than the wave-function based CIS(D)-type approaches.

5.2 Results for the Gordon benchmark set

As a second test of the transferability of the results from the parametrization study, the TD(A)-DHDFA variants were applied to a popular benchmark set originally compiled by Gordon and co-workers.¹⁰⁷ Again, the evaluation is restricted to singlet-singlet excitations and includes 30 Rydberg and 33 valence excitations (15 $\pi - \pi^*$, 14 $n - \pi^*$, 3 $n - \sigma^*$, and 1 $\sigma - \pi^*$) from 14 different molecules. The molecular geometries were re-optimized with PBE0/def2-TZVPP and used for all subsequent single-point calculations. In the original

study, geometries were individually optimized with the respective DFA, which we do not find necessary here.

Instead of relying on experimental results, as done in the original benchmark study, we computed new reference values for all excitations. Because the assessed molecules are smaller in size than the largest one in our training set, we were able to obtain excitation energies at the fully iterative CC3/aug-cc-pVDZ level of theory. To increase their reliability, these values were then corrected for basis-set incompleteness by adding the difference between CCSDR(3)/aug-cc-pVTZ and CCSDR(3)/aug-cc-pVDZ results, thus providing us with estimated CC3/aug-cc-pVTZ references for this set; all coupled-cluster results are tabulated in the SI in Tab. S23.

The basis-set correction could be as large as 0.14 eV for relatively high-lying excited states. In some cases, we were also able to conduct CC3/aug-cc-pVTZ calculations. These exact values and the estimated CC3/aug-cc-pVTZ reference results did not differ by more than 0.02 eV from each other. Therefore, the new reference data used herein can be regarded as very accurate. Nevertheless, the deviations to the experimental values can be as large as 0.88 eV as for the $3p$ -Rydberg excitation (2^1B_2 excitation) in furan. Therefore, analyzing the SCS effect in TD(A)-DHDFA is more consistent when the theoretical reference results are applied.

The results for all DHDFA variants are compiled in Tab. 6. The overall trend parallels what we observed for the fit set. Already variant B with the standard (non-fitted) SCS parameters is a slight improvement over conventional B2PLYP, for which the MADs decrease from 0.35 eV to 0.25 eV (TD) and from 0.32 eV to 0.23 eV (TDA), respectively. For the other functionals, the effects are smaller. The fitted variants C-E hardly improve the MADs, but the MDs of the TD variants are shifted towards zero compared to strategies A and B. The best MAD over the entire set is obtained for TD-PBE0-DH(E) with a value of 0.14 eV. Within the accuracy of the reference data, the TD and TDA approaches show similar results.

Table 6: Overview of the TD(A)-DHDFA performance for the Gordon benchmark set with variants A–E (see text). The aug-cc-pVTZ AO basis set was used. The statistical key values are: mean deviation (MD), mean absolute deviation (MAD), root-mean-square (RMS), and the deviation span (Δ_{err}). All values are in eV.

functional		TD					TDA				
		A	B	C	D	E	A	B	C	D	E
B2PLYP ^a	MD	−0.33	−0.23	−0.10	−0.09	−0.09	−0.27	−0.17	−0.11	−0.13	−0.13
	MAD	0.35	0.25	0.23	0.21	0.21	0.32	0.23	0.24	0.24	0.24
	RMS	0.40	0.31	0.28	0.25	0.25	0.39	0.29	0.31	0.28	0.28
	Δ_{err}	1.11	0.93	1.52	1.00	1.00	1.30	1.07	1.70	1.05	1.05
B2GPPLYP	MD	−0.18	−0.12	−0.03	−0.02	−0.02	−0.12	−0.05	−0.04	−0.05	−0.03
	MAD	0.24	0.20	0.21	0.17	0.17	0.23	0.19	0.19	0.19	0.19
	RMS	0.29	0.24	0.25	0.22	0.21	0.28	0.23	0.25	0.22	0.22
	Δ_{err}	1.11	1.04	1.32	1.13	1.12	1.10	1.02	1.52	0.96	0.95
DSD-BLYP	MD	−0.18	−0.12	−0.03	−0.01	0.00	−0.11	−0.05	−0.04	−0.04	−0.03
	MAD	0.23	0.20	0.19	0.17	0.17	0.23	0.19	0.18	0.20	0.20
	RMS	0.29	0.25	0.24	0.23	0.23	0.29	0.25	0.24	0.24	0.24
	Δ_{err}	1.46	1.38	1.40	1.41	1.37	1.60	1.53	1.54	1.38	1.36
DSD-PBEP86	MD	−0.10	−0.09	0.01	0.02	0.06	−0.02	−0.01	0.02	−0.01	0.01
	MAD	0.17	0.16	0.15	0.15	0.16	0.18	0.16	0.16	0.17	0.17
	RMS	0.23	0.23	0.21	0.21	0.22	0.25	0.25	0.24	0.23	0.23
	Δ_{err}	1.39	1.40	1.35	1.36	1.35	1.52	1.53	1.48	1.35	1.33
PBE0-2	MD	0.05	0.14	0.05	0.09	0.17	0.13	0.21	0.06	0.05	0.11
	MAD	0.13	0.19	0.13	0.16	0.22	0.17	0.23	0.14	0.13	0.15
	RMS	0.20	0.25	0.20	0.22	0.28	0.25	0.30	0.24	0.21	0.23
	Δ_{err}	1.20	1.15	1.19	1.33	1.25	1.36	1.21	1.33	1.32	1.22
PBE0-DH ^a	MD	−0.02	0.01	−0.03	0.02	0.02	0.04	0.07	−0.02	−0.01	−0.01
	MAD	0.15	0.15	0.15	0.14	0.14	0.16	0.16	0.15	0.13	0.13
	RMS	0.21	0.21	0.20	0.21	0.21	0.24	0.23	0.21	0.20	0.20
	Δ_{err}	1.28	1.25	1.27	1.53	1.53	1.44	1.40	1.42	1.47	1.47

^a variant D is identical to E.

In most cases, the MADs are between 0.5 and 0.9 eV larger in comparison to the fit set. The main reason for that are the somewhat challenging cases of high-lying Rydberg states in small molecules, for which the largest deviations are observed. This is also the reason why TD-PBE0-2(A) is among the best functionals for this test set because of its high amount of Fock exchange. It is also exceptional because together with the TD approach, the fitted variants lower the performance slightly. Additionally, TD-PBE0-2(E) is the only SOS variant with a notable decrease in performance with respect to the related variant D.

Separate analyses of Rydberg and valence states reveal that TD-B2PLYP(A), TD-B2GPPLYP(A), TD-DSD-BLYP(A), and TD-DSD-PBEP86(A) show larger deviations for Rydberg excita-

tions. For this excitation class, their MADs are 0.10 to 0.25 eV higher than for valence states only. For PBE0-2 and PBE0-DH, the differences in the MADs are not significant. This relation changes with the SCS variants for which all DHDFAs have very similar MADs for both classes of excited states. It should be noted that this is achieved by reducing the deviations for the Rydberg states solely, whereas the performance for the valence states is very similar for SCS and non-SCS variants. This indicates that SCS can lead to a more balanced description of different types of excitations.

Overall, the general trends for SCS variants found in the previous test set also persist for this test set and the results are satisfying.

5.3 Results for the 0–0 excitation energy benchmark set

We conclude our cross-validation studies by testing the broader applicability of the TD(A)-DHDFAs with SCS or SOS. For this purpose, the methods were applied to the 0–0 excitation energy benchmark set by Hättig and co-workers.¹⁰⁸ The geometries were taken from the literature. Here, the TD(A)-DHDFAs were tested on both (TD-)B3LYP optimized geometries and SCS-CC2 geometries. The zero-point vibrational energy corrections for each geometry had been calculated for one level of theory and then applied to all tested methods in the original study. Here, we did the same and took those corrections from Ref. 108. Reference values for this test set are experimental 0–0 excitation energies from supersonic jet measurements. The data for all DHDFAs with the TD approach and their variants A–E are compiled in Tab. 7. The TDA results can be found in the SI in Tabs. S37-S61. In general, the TDA versions follow similar trends as discussed below, but show somewhat larger deviations overall. Upon inspection of Tab. 7, it becomes apparent that the previously discussed findings cannot be entirely confirmed for this test set. In general, the fitted variants show larger MADs with respect to experimental reference values than variants A and B do with the exception of PBE0-DH on B3LYP geometries. Typical values are 0.1 to 0.3 eV for non-fitted variants and 0.2 to 0.4 eV for the fitted ones. On the other hand, standard deviations and deviation

Table 7: Overview of results for the 0–0 excitation energy benchmark set for methods A–E (see main text) of the different double hybrid density functional approximations. The aug-cc-pVTZ basis set was used. Shown are the statistical key values: mean deviation (MD), mean absolute deviation (MAD), standard deviation (σ), and the deviation span (Δ_{err}). All values are in eV.

	B3LYP geometries					SCS-CC2 geometries				
	A	B	C	D	E	A	B	C	D	E
TD-B2PLYP ^a										
MD	0.01	0.03	0.24	0.21	0.21	−0.01	0.00	0.21	0.19	0.19
MAD	0.11	0.08	0.25	0.23	0.23	0.10	0.07	0.23	0.20	0.20
σ	0.16	0.13	0.14	0.13	0.13	0.14	0.10	0.13	0.10	0.10
Δ_{err}	1.18	1.13	1.26	1.18	1.18	0.76	0.68	0.86	0.71	0.71
TD-B2GPPLYP										
MD	0.21	0.22	0.21	0.40	0.40	0.07	0.04	0.17	0.13	0.09
MAD	0.24	0.25	0.23	0.41	0.41	0.10	0.08	0.19	0.14	0.10
σ	0.17	0.17	0.14	0.15	0.15	0.12	0.10	0.11	0.10	0.09
Δ_{err}	1.25	1.20	1.22	1.24	1.24	0.76	0.69	0.79	0.73	0.66
TD-DSD-BLYP										
MD	0.05	0.02	0.21	0.16	0.14	0.02	−0.03	0.16	0.11	0.08
MAD	0.10	0.09	0.22	0.17	0.15	0.06	0.07	0.18	0.12	0.09
σ	0.14	0.14	0.14	0.14	0.14	0.10	0.10	0.10	0.10	0.10
Δ_{err}	1.16	1.08	1.20	1.11	1.08	0.72	0.66	0.76	0.67	0.65
TD-DSD-PBEP86										
MD	0.03	−0.04	0.17	0.14	0.14	−0.02	−0.10	0.12	0.09	0.09
MAD	0.08	0.12	0.18	0.16	0.16	0.06	0.12	0.14	0.10	0.10
σ	0.14	0.15	0.14	0.14	0.15	0.10	0.11	0.10	0.09	0.11
Δ_{err}	1.12	1.05	1.16	1.11	1.10	0.70	0.63	0.73	0.66	0.66
TD-PBE0-2										
MD	0.19	0.16	0.17	0.21	0.10	0.15	0.11	0.13	0.17	0.03
MAD	0.21	0.19	0.20	0.23	0.15	0.17	0.14	0.16	0.18	0.12
σ	0.15	0.17	0.15	0.16	0.20	0.12	0.12	0.12	0.13	0.16
Δ_{err}	1.21	1.14	1.20	1.21	1.12	0.81	0.72	0.81	0.84	0.66
TD-PBE0-DH ^a										
MD	0.25	0.24	0.19	0.19	0.19	0.25	0.24	0.18	0.17	0.17
MAD	0.28	0.27	0.22	0.21	0.21	0.28	0.27	0.22	0.19	0.19
σ	0.20	0.19	0.18	0.14	0.14	0.19	0.18	0.16	0.12	0.12
Δ_{err}	1.29	1.28	1.26	1.17	1.17	1.02	0.96	0.92	0.74	0.74

^a variant D is identical to E.

spans are nearly constant or even lower. This, along with the fact that MDs are nearly identical to MADs, indicates a systematic blue-shift with respect to the experimental 0–0 excitation energies, but no general deterioration of the results.

That being said, when applied to the more reliable SCS-CC2 geometries, the picture changes somewhat. All statistical key values improve and the performance of the non-fitted and fitted variants become very similar. Again, the standard deviations are comparable for all variants,

but the MDs are again blue-shifted. Consequently, the best method is TD-DSD-PBEP86(A), which includes SCS, however, with parameters optimized for ground-state properties. TD-DSD-PBEP86(A) applied to SCS-CC2 geometries has an MD of -0.02 eV and a standard deviation of 0.10 eV. This has to be compared with SCS-CC2 itself, for which an MD of 0.02 eV and a standard deviation of 0.05 is found with the present setup (literature:¹⁰⁸ MD = 0.01 eV, $\sigma = 0.05$ eV).

0–0 excitation energies are calculated as energy differences between the total energy of the electronic ground state in its optimal structure and the sum of total ground-state energy for the excited-state geometry and its vertical excitation energy to the relevant excited state, including zero-point energy corrections for both states. As the present DHDFAs were tuned for excitation energies only, it could have been that they fail to compute the energy change on the ground-state energy surface due to the geometry distortion. This was checked by comparing these energies to corresponding SCS-CC2 energies. The MD for this comparison is practically constant across variants A to E and no significant outlier was observed. This can be understood from the fact that even if the fitted variants performed bad for ground state energies, the current problem benefits highly from error compensation due to the relatively small change in geometry. Conversely, the found error compensation for ground state energies also means that the results do not improve in general for the fitted variants when only vertical excitation energies are compared against the corresponding SCS-CC2 results.

Overall, DHDFAs show a satisfying performance for 0–0 excitation energies, for which they have not been assessed before. Especially the fact that they do benefit from the more reliable SCS-CC2 geometries indicate that they could be an efficient compromise between less well performing standard DFAs and the more costly (SCS-)CC2 approach to optimize ground- and excited-state geometries, pending the development of an efficient gradient in the near future.

6 Overall discussion and conclusion

Ten years since publication of the initial linear-response time-dependent formulation of DHD-FAs,²¹ we have revived this area and, for the first time, introduced and assessed SCS and SOS variants of DHDFAs for the computation of electronic excitation energies. Different flavors, ranging from standard SCS parameters to fully fitted parameter sets, were tested on three standard benchmark sets that cover small to medium-sized chromophores (up to 78 atoms) and different excitation types. For the popular Gordon set, we also presented new reference values with the linear-response CC3 approach. Based on our extensive data sets, several conclusions can be drawn.

First of all, the data confirm the good accuracy and broad applicability of DHDFAs for electronic excitation energies. In general, they show the same high accuracy as in previous benchmarks. When comparing TD and TDA, the TD approach is more accurate when DHDFAs without SCS are applied. However, when the fitted variants are used, the accuracy for TD and TDA variants are comparable. Application of the TD-optimized parameters in TDA computations was initially tested, but found unsatisfactory. Therefore, only parameter sets separately trained for TD or TDA should be used.

In general, introduction of SCS and SOS causes a systematic blue-shift, which is more pronounced for TDA-SCS/-SOS variants. This is contrary to observations for the related CIS(D) wave-function approach for which red-shifts can occur. Sometimes, the blue-shifts eliminate extreme outliers, so that deviation spans are reduced by up to 0.5 eV. While assessing the effect of SCS and SOS, it has to be taken into account that already the original approaches belong to the best TD-DFT methods and that improving them further, poses a particular challenge, as similarly demonstrated for the related ground-state DHDFAs in thermochemistry.⁵⁹ Also, it should be kept in mind that even much more sophisticated methods such as CASPT2 and CC3 might deviate more from each other than the DHDFAs do with respect to the reference values used in this study. Therefore, any significant improvement is difficult to demonstrate. Nevertheless, several benefits from an SCS/SOS treatment were found in

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2
3 this study, as outlined next.
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5 For vertical excitation energies in the Thiel and Gordon test sets, the blue-shift leads to
6 a more balanced description with respect to the CC3 reference values, with MDs usually
7 being closer to zero. Improvements in accuracy range from 0.05 to 0.14 eV for the re-fitted
8 variants of most DHDFAs compared to the non-fitted approaches (variant A), with the
9 exception of the DSD functionals, which already include SCS values adjusted for ground-
10 state thermodynamics. For the latter, any changes induced by the re-fit of the parameters
11 for excitation energies are marginal on an average absolute scale. SCS also leads to a more
12 balanced description of different types of excitations, with average (absolute) deviations in
13 the π - π^* , n - π^* and Rydberg subsets being more similar to one another. The best-performing
14 TD-based methods in our cross validation can have MADs as low as 0.14 eV and are, thus,
15 very close to the time- and resource-intensive CC3 approach.
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18 For 0-0 excitation energies, we note that DHDFAs show a much more consistent perfor-
19 mance when applied to reliable wave-function based reference structures, as opposed to
20 (TD-)B3LYP geometries. However, the final effect of SCS/SOS is much smaller compared
21 to the vertical-excitation sets. Nevertheless, one can state that the new TD-SCS-DHDFAs
22 show satisfying results and do not deteriorate the performance of their underlying non-scaled
23 DHDFAs.
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26 A very important finding is the fact that good-performing SOS variants can be obtained.
27 This is contrary to wave-function methods where SOS normally leads to inferior results
28 and one needs to make a trade-off between accuracy and efficiency. This is not the case
29 here. Almost identical performance is observed for variants E (in some cases the free fit
30 even resulted in an SOS variant). Very accurate SOS versions might open the route to
31 highly efficient methods for the optimization of excited-state geometries, particularly when
32 paired with efficient computing strategies, such as the Laplace transform. In this context,
33 it is promising that the 0-0 benchmark has shown that DHDFAs benefit from more reliable
34 SCS-CC2 geometries. This indicates that they should yield also more reliable excited-state
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geometries. This requires the derivation of an analytical gradient and work in that direction is currently being pursued in our groups.

For ground-state calculations, DHDFAs based on meta-generalized-gradient-approximation (meta-GGA) components were shown to be very accurate, for instance the spin-opposite scaled PWPB95⁵³ or spin-component scaled DSD-PBE(h)B95¹⁶ functionals. However, Bates and Furche pointed out how the gauge variance of the kinetic energy density makes the time-dependent application of meta-GGAs to excited states questionable.¹⁰⁹ We, therefore, excluded investigating TD(A) versions of those meta-GGA-based DHDFAs from the present work, but we will explore this idea in a future study.

While the TD-DH DFA idea in general constitutes an improvement over conventional TD-DFT, as conclusively shown in the literature,^{21,31–34,37} we can also recommend specific SCS- and SOS-based variants for further testing and subsequent applications. In most cases, it is best to use the fully fitted parameter sets in variants D and E, particularly when only excitation energies are required from a calculation. We observed little overall difference between variants D/E for PBE0-DH and B2(GP)PLYP. In addition, DSD-PBEP86(A) is also among the best performing functionals across all test sets. It already includes SCS parameters that were adjusted, however, to yield accurate thermochemical ground-state properties. We recommend usage of that approach when a functional is required that performs very well for both ground- and excited-state problems.

We hope we have achieved our aim to bring the TD(A)-DH DFA approach back to the method-user's attention. We would also like to encourage implementation of TD(A)-DHDFAs with and without SCS/SOS in standard software packages.

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Supporting Information Available

Information on how to calculate oscillator and rotational strengths with TD(A)-DHFAs; detailed results of all tested methods for the fit and the three cross-validation test sets; derivation of the new basis-set corrected CC3 reference values for the Gordon set; the optimized geometries for the fit and the Gordon sets.

This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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