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Journal

The Journal of Chemical Physics, 158(22)

ISSN

0021-9606

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Publication Date

2023-06-14

DOI

10.1063/5.0146975

Peer reviewed

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Studying excited-state-specific perturbation theory on the Thiel set

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ABSTRACT

We explore the performance of a recently introduced N^5-scaling excited-state-specific second order perturbation theory (ESMP2) on the singlet excitations of the Thiel benchmarking set. We find that, without regularization, ESMP2 is quite sensitive to π system size, performing well in molecules with small π systems but poorly in those with larger π systems. With regularization, ESMP2 is far less sensitive to π system size and shows a higher overall accuracy on the Thiel set than CC2, equation of motion-coupled cluster with singles and doubles, CC3, and a wide variety of time-dependent density functional approaches. Unsurprisingly, even regularized ESMP2 is less accurate than multi-reference perturbation theory on this test set, which can, in part, be explained by the set's inclusion of some doubly excited states but none of the strong charge transfer states that often pose challenges for state-averaging. Beyond energetics, we find that the ESMP2 doubles norm offers a relatively low-cost way to test for doubly excited character without the need to define an active space.

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I. INTRODUCTION

Quantum chemistry approaches to modeling singly excited states have been highly successful, but it remains true that the methods that are most reliably accurate are also highly computationally intensive. As in ground state theory, coupled cluster (CC) methods that go beyond doubles but stop short of a full treatment of triples are often used as reliable benchmarks.[1–10] However, with a cost that scales as N^7 with the system size N, these methods are quite limited in the size of molecule that they can treat. Density functional theory (DFT) [and, in particular, time-dependent DFT (TD-DFT)] is much more affordable, with costs ranging from N^3 to N^5 depending on the functional, with N^4 being typical for many hybrid functionals. By choosing a functional that is known to work well for the chemistry in question, TD-DFT can offer impressive accuracy, especially for its computational price, but it would be an overstatement to claim that it is as reliable as CC methods that include some triples effects. Lower cost CC options for excited states, especially in the linear response (LR) and equation of motion (EOM) formalisms, are also widely used, but without triples effects, these methods are more

varied in their reliability. Examples include EOM-CC with singles and doubles (EOM-CCSD),[11] which has an N^6 cost but tends to overestimate excitation energies, and CC2,[12,13] which has an N^5 cost and typically displays lower average errors than EOM-CCSD. These methods are both widely used and have been quite successful, but nonetheless, there is room for improvement, as they can produce surprisingly large errors in some cases that are not obviously ill-suited to their assumptions, as in the $2^1A'$ state of formamide. Adding partial triples contributions—as in CC3,[13–15] equation of motion coupled cluster with singles, doubles, and perturbative triples [EOM-CCSD(T)],[16,17] δ-completely renormalized (CR)-EOM(2,3)D,[6] and many related methods—can certainly improve matters but brings us back to N^7 scaling. In this study, we will use a large test set to investigate to what degree it may be helpful to move away from the linear response paradigm and instead build traditional correlation methods upon a mean field reference, starting, for now, with second order perturbation theory.

Like ground state second order Møller–Plesset perturbation theory (MP2),[18] the recently introduced excited-state-specific Møller–Plesset theory (ESMP2)[19–21] seeks to provide a second order

Rayleigh–Schrödinger correction atop a mean field starting point. In the ground state, MP2 perturbs around Hartree–Fock theory, while in ESMP2, the starting point is provided by excited state mean field (ESMF) theory,[19,20] which refines the configuration interaction singles (CIS) picture[22] through excited-state-specific orbital relaxations to create a method that shares much in common with ground state mean field theory.[23] The early studies of ESMP2 have shown promising accuracy, which has become more relevant, thanks to a refinement of the theory[21] that brings its cost scaling down to N^5. This is asymptotically comparable to MP2, although it should be noted that ESMP2's cost is an iterative N^5 due to its zeroth order Hamiltonian not being diagonal. With a relatively low scaling and early promise in initial tests, we now seek to deepen our understanding of the strengths and weaknesses of ESMP2 by exploring its performance on a widely used excited state benchmark.

The Thiel set[24] offers theoretical best estimates (TBEs) for over one hundred singlet excited states (and also many triplet states) spread over 28 molecules, which include nucleobases, carbonyls, aromatic rings, heterocyclic rings, small polyenes, and other small unsaturated hydrocarbons. In the original work, both complete active space second-order perturbation theory (CASPT2)[25,26] and the LR or EOM coupled cluster methods CC2, EOM-CCSD, and CC3 were compared across these molecules. Since then, a large number of other research groups have used the Thiel set to make further comparisons between methods.[27–43] Both the quality of the initial test set and its broad subsequent use make the Thiel set especially attractive for helping to put ESMP2 in context and for understanding its strengths and weaknesses. We note that for consistency with this significant body of previous work, we have employed the original test set's TBEs in our analysis below, although we acknowledge that in some cases, such as the nucleobases,[44,45] more recent studies may offer even more reliable best estimates.

Thiel *et al.* organized their test set into four groups of molecules. In one group, they placed aldehydes, ketones, and amides, in which, with the exception of benzoquinone, ESMP2 shows a highly competitive performance even without regularization. Another group contains unsaturated aliphatic hydrocarbons, some of whose excited states have large amounts of doubly excited character and so do not satisfy the assumptions of ESMP2's singly excited zeroth order reference state. Although ESMP2 cannot treat doubly excited character accurately, it does prove to be a relatively cost-effective way to offer warning that such character is present. Thiel's third group consists of aromatic rings and heterocycles, in which ESMP2's sensitivity to π system size and the practical efficacy of regularization become especially apparent. In our discussion below, we reorganize these two groups into three—conjugated polyenes, heterocycles, and other rings—as the polyenes are particularly illuminating for ESMP2. The fourth and final Thiel group contains the nucleobases cytosine, thymine, uracil, and adenine. As in other cases, ESMP2 struggles with their π system sizes but improves substantially with regularization.

II. THEORY

A. Zeroth order reference

The zeroth order reference state for ESMP2 is the ESMF wave function, which in its simplest form is an orbital-relaxed linear combination of single excitations that can be written as follows:

$$|\Phi_0\rangle = e^{\hat{X}}\left(\sum_{ia} c_{ia}|_i^a\rangle + \sum_{\bar{i}\bar{a}} c_{\bar{i}\bar{a}}|_{\bar{i}}^{\bar{a}}\rangle\right). \quad (1)$$

In this work, the indices i, j, k represent occupied alpha orbitals, a, b, c represent virtual alpha orbitals, and $\bar{i}$ and $\bar{a}$ likewise represent beta orbitals. Note that it is possible to formulate ESMF so as to also include the closed-shell Aufbau configuration,[19] but we have not yet implemented the corresponding ESMP2 terms in our N^5-scaling ESMP2 code, and so the ESMF reference used in this work is as shown in Eq. (1). Here, $\hat{X}$ is an anti-Hermitian one-body operator that, when exponentiated, produces a unitary orbital rotation that moves the linear combination of single excitations from the HF to the ESMF orbital basis. To find each ESMF state, we employ either the recently introduced generalized variational principle (GVP)[20] or, where possible, the more efficient ESMF self-consistent field (SCF) approach.[23] The latter is not as robust as the GVP, and so we fall back to using the GVP in cases where the SCF approach proves unstable.

B. ESMP2

ESMP2 builds a second-order Rayleigh–Schrödinger perturbation theory atop ESMF in a way that parallels MP2's construction atop HF theory. As ESMF already contains singly excited components, the initial formulation[19] of ESMP2 included all doubly excited and triply excited determinants in its first order interacting space. This choice comes from the basic logic that if MP2 can stop at doubles when expanding around its Aufbau reference, ESMP2 should stop at triples. This approach led to promising accuracy in initial tests, but due to the large number of triples, it came with an N^7 cost scaling. More recently, an N^5 reformulation of ESMP2 has been introduced[21] that includes only the most important subset of triples by first converting the ESMF wave function into a "transition orbital pair" basis that shares much in common with the concept of a natural transition orbital basis.[46] For the present study, we employ the N^5 theory and refer to the reader to its original publication[21] for most of its details, but let us very briefly explain the added level shift as it has not been discussed previously.

The zeroth order Hamiltonian for ESMP2 is

$$\hat{H}_0 = \hat{R}(\hat{F} - \hat{H})\hat{R} + \hat{P}\hat{H}\hat{P} + \hat{Q}(\hat{F} + \varepsilon)\hat{Q}, \quad (2)$$

where $\hat{R}$ projects onto the ESMF state, $\hat{P}$ projects onto the subspace containing the Aufbau and all singly excited configurations, and $\hat{Q} = 1 - \hat{P}$. $\hat{H}$ is the full Hamiltonian, whereas $\hat{F}$ is the Fock operator formed from the ESMF one-body density matrix. Note that, in part, this choice of $\hat{H}_0$ is employed so as to ensure size intensivity.[21] In previous ESMP2 work, the level shift ε has not been used, and all results reported as "ESMP2" below use $\varepsilon = 0$. By instead setting a positive value for ε, we can widen the zeroth order energy spacing that separates the singles from the doubles and triples, which as discussed above may help mitigate perturbative failures in larger π systems. Due to the structure of $\hat{H}_0$, the only modification that ε makes to ESMP2's working equations is to shift the zeroth order Hamiltonian matrix's diagonal in the amplitude equations, and so adopting a nonzero ε involves a trivial algorithmic change. As the ESMP2 excitation energy is

$$\Delta E = E_{\mathrm{ESMP2}} - E_{\mathrm{MP2}}, \quad (3)$$

we also add ε to the denominators in the standard MP2 energy expression so as to maintain a balanced treatment between the ground and excited state. Of course, the value chosen for ε will matter, and after some preliminary testing revealed that shifts below $0.2\ E_h$ made very little difference, we ran the full test set with the substantially larger shift value of $0.5\ E_h$ to find out what would happen with a much more aggressive shift. Interestingly, this resulted in substantially better excitation energies, and so we have not attempted to optimize ε any further in this study. We show examples of individual states' shift sensitivities in the supplementary material. All results presented below that are labeled "ε-ESMP2" employed $\varepsilon = 0.5\ E_h$.

C. Amplitude diagnostics

Although they are not a perfect guide,[47] amplitude diagnostics, such as the T_1 diagnostic,[48] have long been used to help predict whether ground states are indeed weakly correlated enough for single-reference methods to be reliable. Might similar diagnostics offer useful information for ESMP2? Unlike linear response excited state methods, such as EOM-CCSD, in which doubly excited configurations must account for both orbital relaxation and correlation effects, ESMP2 is built on a reference in which mean-field orbital relaxations are already accounted for by the MO basis. Thus, its doubles amplitudes are more closely related to ground state singles amplitudes: both are singly excited relative to their reference state and both are only expected to be present in large amounts if the reference wave function is a poor approximation for the state. Certainly, we would not expect ESMP2 to be accurate for a state in which any doubly excited configurations have large weights, as this would be a violation of the assumption that we are perturbing around the singly excited ESMF reference. Thus, both from their similarity to the ground state singles at the heart of the T_1 diagnostic and from the perturbative argument that they should not be large, we expect that the ESMP2 doubles should be able to offer useful information about the reliability of ESMP2, and possibly other theories too, for a given excited state.

What functions of the doubles would make for good diagnostics? In many studies involving linear-response coupled cluster theory, the percentage of the wave function that is described by single excitations is used as a gauge.[13] While we could adopt a similar method for ESMP2, except using the percentage of the first order wave function coming from the doubles instead, we choose not to as the resulting diagnostic is not size consistent. Instead, we make use of the fact that in ESMP2, any excitation that is localized to some molecule or molecular region (as most excitations in chemistry are) will see the triples percentage of its wave function grow indefinitely with system size as additional far-away molecules are added, as the size intensivity of the theory guarantees that those far-away molecules will simplify to MP2 descriptions, thus adding additional triples (MP2 doubles on top of the ESMF single excitation) components for every far-away molecule that is added.[21] Therefore, the ESMP2 doubles percent will drop to zero in the large system limit, in the same way that the RHF determinant's percentage of the MP2 wave function goes to zero in the large system limit. This effect implies that the meaning of the %T_1 and %T_2 measures will vary with system size in ESMP2, even when one is simply adding far-away molecules that do not interact with the original system. This is clearly undesirable.

In contrast, the norm of the doubles amplitudes (when working in intermediate normalization) is unaffected by the addition of far-away molecules, as the size intensivity of ESMP2 guarantees that so long as the excitation is still on the original molecule, the new molecules add only triples in the form of the far-away molecules' MP2 doubles acting atop the ESMF singles. Furthermore, like many other diagnostics, $|T_2|$ is invariant to occupied–occupied and virtual–virtual rotations. Thus, $|T_2|$ offers ESMP2 a size-consistent, orbital-invariant measure of the quality of ESMF's assumption of a purely singly excited state. It should therefore allow us to flag cases, like states with large doubly excited components, for which ESMF and ESMP2 are not appropriate.

III. COMPUTATIONAL DETAILS

Following the general considerations described by Schreiber *et al.*,[24] we have employed the same ground state MP2/6-31G* geometries and TZVP basis set[49] in all calculations. Our ESMP2 code does not currently make use of point group symmetry, so calculations were run in C1 and manual checks were performed to ensure that states' symmetry labels are correct. In part to ensure that the same states were being used when comparing to existing results and, in part, for convenience, we employed the largest singles components from EOM-CCSD calculations as the guess singles in ESMF. We employed PySCF[50] for most EOM-CCSD calculations, while QChem[51] and Molpro[52] were used for the 2^1E_{2g} benzene state and the 2^1A_u and 1^1B_{2g} states of tetrazine. We also verified state characters by direct comparisons of the converged ESMF and EOM-CCSD wave functions, including visual inspection of the most relevant orbitals for each state using Molden v2.0.[53] We further verified state character and, in particular, the nature of doubly excited states using Schreiber *et al.* active spaces[24] and Molpro's implementation of state-averaged complete active space self-consistent field (CASSCF). Detailed information on these various comparisons can be found in the supplementary material. Note that in some of our comparisons below, we have excluded states not found by ESMF or that are flagged by ESMP2 as having large amounts of doubly excited character, as these either cannot be compared or are not appropriate for treatment by any of the single-reference methods. We have verified that crunching the numbers with these states included makes little difference, as discussed in Sec. IV and as seen in the additional tables in the supplementary material.

IV. RESULTS
A. Overview

Table I shows our results on the 103 singlet states that have CC results and TBEs in the Thiel benchmark,[24] with the ESMP2 and CC methods' accuracies summarized in Fig. 1 and Table II. Orbital-optimized ESMF stationary points were successfully located for 100 of these 103 states, which, while not perfect, represents the clearest evidence to date that ESMF energy stationary points can be expected to exist for the vast majority of low-lying singlet excited states in single-reference molecules. Six of the states showed especially large ESMP2 doubles norms with $|T_2| > 0.5$, and five of these six likewise had CC3 T_1 percentages below 80, indicating that ESMP2's $|T_2|$ can indeed help predict states with challenging amounts of doubly excited character. As seen in Fig. 2, ESMP2's $|T_2|$ also shows the

TABLE I. Singlet excitation energies in eV. TBEs and results for CASPT2, CC2, EOM-CCSD, and CC3 are from the original Thiel benchmark,[24] except for CC3 results on cytosine, thymine, uracil, and adenine, which are from Kánnár and Szalay.[45] CASPT2 "a" refers to Roos's results, while CASPT2 "b" refers to Thiel's results. States where no ESMF solution was found are highlighted in gray, those with known Rydberg character are in blue, and those in which ESMP2's $|T_2|$ was above 0.5 are in red.

Molecule	π size	State	TBE	CASPT2 a	CASPT2 b	CC2	CCSD	CC3 (%T_1)	ESMP2	ε-ESMP2	ESMP2 $|T_2|$
formaldehyde	2	1^1A_2	3.88	3.91	3.98	4.09	3.97	3.95 (91.2)	3.96	3.81	0.17
		1^1B_1	9.10	9.09	9.14	9.35	9.26	9.18 (90.9)	9.12	8.98	0.17
		2^1A_1	9.30	9.77	9.31	10.34	10.54	10.45 (91.3)	9.78	9.90	0.25
acetone	2	1^1A_2	4.40	4.18	4.42	4.52	4.43	4.40 (90.8)	4.39	4.28	0.18
		1^1B_1	9.10	9.10	9.27	9.29	9.26	9.17 (91.5)	9.22	9.16	0.19
		2^1A_1	9.40	9.16	9.31	9.74	9.87	9.65 (90.1)	9.08	9.28	0.25
benzoquinone	8	1^1A_u	2.80	2.50	2.80	2.92	3.19	2.85 (83.0)	1.77	2.61	0.40
		1^1B_{1g}	2.78	2.50	2.78	2.81	3.07	2.75 (84.1)	1.69	2.52	0.40
		1^1B_{3g}	4.25	4.19	4.25	4.69	4.93	4.59 (87.9)	3.67	4.12	0.32
		1^1B_{1u}	5.29	5.15	5.29	5.59	5.89	5.62 (88.4)	4.70	5.31	0.34
		1^1B_{3u}	5.60	5.15	5.60	5.69	6.55	5.82 (75.2)	4.88	6.14	0.40
		2^1B_{3g}	6.98	6.34	6.98	7.36	7.62	7.27 (88.8)	6.03	7.01	0.40
formamide	3	$1^1A''$	5.63	5.61	5.63	5.76	5.66	5.65 (90.7)	5.62	5.47	0.17
		$2^1A'$	7.44	7.41	7.44	8.15	8.52	8.27 (87.9)	7.42	7.52	0.20
acetamide	3	$1^1A''$	5.80	5.54	5.80	5.77	5.71	5.69 (90.6)	5.66	5.53	0.18
		$2^1A'$	7.27	7.21	7.27	7.66	7.85	7.67 (89.1)	6.88	7.30	0.27
propanamide	3	$1^1A''$	5.72	5.48	5.72	5.78	5.74	5.72 (90.6)	5.69	5.56	0.18
		$2^1A'$	7.20	7.28	7.20	7.56	7.80	7.62 (89.2)	6.83	7.26	0.28
ethene	2	1^1B_{1u}	7.80	7.98	8.62	8.40	8.51	8.37 (96.9)	8.05	8.04	0.16
butadiene	4	1^1B_u	6.18	6.23	6.47	6.49	6.72	6.58 (93.7)	6.02	6.18	0.23
		2^1A_g	6.55	6.27	6.83	7.63	7.42	6.77 (72.8)	4.31	6.98	0.77
hexatriene	6	1^1B_u	5.10	5.01	5.31	5.41	5.72	5.58 (92.6)	4.92	5.14	0.26
		2^1A_g	5.09	5.20	5.42	6.67	6.61	5.72 (65.8)	2.37	5.81	1.00
octatetraene	8	2^1A_g	4.47	4.38	4.64	5.87	5.99	4.97 (62.9)	1.19	4.99	1.15
		1^1B_u	4.66	4.42	4.70	4.72	5.07	4.94 (91.9)	4.16	4.43	0.28
cyclopropene	2	1^1B_1	6.76	6.36	6.76	6.96	6.96	6.90 (93.0)	6.56	6.61	0.20
		1^1B_2	7.06	7.45	7.06	7.17	7.24	7.10 (95.5)	6.75	6.85	0.20
cyclopentadiene	4	1^1B_2	5.55	5.27	5.51	5.69	5.87	5.73 (94.3)	5.23	5.36	0.23
		2^1A_1	6.31	6.31	6.31	7.05	7.05	6.61 (79.3)	4.83	6.60	0.60
norbornadiene	2	1^1A_2	5.34	5.28	5.34	5.57	5.80	5.64 (93.4)	5.09	5.31	0.25
		1^1B_2	6.11	6.20	6.11	6.37	6.69	6.49 (91.1)	5.79	6.31	0.28
benzene	6	1^1B_{2u}	5.08	4.84	5.05	5.27	5.19	5.07 (85.8)	4.03	4.98	0.42
		1^1B_{1u}	6.54	6.30	6.45	6.68	6.74	6.68 (93.6)	6.07	6.24	0.27
		1^1E_{1u}	7.13	7.03	7.07	7.44	7.65	7.45 (92.2)	6.48	7.11	0.31
		2^1E_{2g}	8.41	7.90	8.21	9.03	9.21	8.43 (65.6)	7.60	9.37	0.60
naphthalene	10	1^1B_{3u}	4.24	4.03	4.24	4.45	4.41	4.27 (85.2)	3.22	4.13	0.42
		1^1B_{2u}	4.77	4.56	4.77	4.96	5.21	5.03 (90.6)	4.33	4.73	0.33
		2^1A_g	5.90	5.39	5.90	6.22	6.23	5.98 (82.2)	5.06	6.11	0.42
		1^1B_{1g}	6.00	5.53	6.00	6.21	6.53	6.07 (79.6)	5.96	6.37	0.31
		2^1B_{3u}	6.07	5.54	6.07	6.25	6.55	6.33 (90.7)	5.33	5.99	0.33
		2^1B_{1g}	6.48	5.87	6.48	6.82	6.97	6.79 (91.3)	4.96	6.30	0.49
		2^1B_{2u}	6.33	5.93	6.33	6.57	6.77	6.57 (90.5)	5.42	6.22	0.36
		3^1A_g	6.71	6.04	6.71	7.34	7.77	6.90 (70.0)	N/A	N/A	N/A
furan	5	1^1B_2	6.32	6.04	6.43	6.43	6.80	6.60 (92.6)	6.18	6.32	0.24
		2^1A_1	6.57	6.16	6.52	6.87	6.89	6.62 (84.9)	5.04	6.50	0.51
		3^1A_1	8.13	7.66	8.22	8.83	8.83	8.53 (90.7)	7.87	8.38	0.28

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TABLE I. (*Continued*.)

|												
pyrrole	5	2^1A_1	6.37	5.92	6.31	6.61	6.61	6.40 (86.0)	5.30	6.41	0.45
		1^1B_2	6.57	6.00	6.33	6.83	6.87	6.71 (91.6)	6.25	6.45	0.25
		3^1A_1	7.91	7.46	8.17	8.44	8.44	8.17 (90.2)	7.50	8.04	0.29
imidazole	5	$1^1A''$	6.81	6.52	6.81	6.86	7.01	6.82 (87.6)	6.80	6.72	0.19
		$2^1A'$	6.19	6.72	6.19	6.73	6.80	6.58 (87.2)	5.65	6.49	0.43
		$3^1A'$	6.93	7.15	6.93	7.28	7.27	7.10 (89.8)	7.01	7.36	0.27
pyridine	6	1^1B_2	4.85	4.84	5.02	5.32	5.27	5.15 (85.9)	4.52	5.19	0.36
		1^1B_1	4.59	4.91	5.14	5.12	5.25	5.05 (88.1)	4.93	4.98	0.24
		2^1A_2	5.11	5.17	5.47	5.39	5.73	5.50 (87.7)	5.25	5.50	0.26
		2^1A_1	6.26	6.42	6.39	6.88	6.94	6.85 (92.8)	6.22	6.45	0.29
		3^1A_1	7.18	7.23	7.46	7.72	7.94	7.70 (91.5)	6.55	7.29	0.33
		2^1B_2	7.27	7.48	7.29	7.61	7.81	7.59 (89.7)	6.54	7.25	0.34
pyrazine	6	1^1B_{3u}	3.95	3.63	4.12	4.26	4.42	4.24 (89.9)	3.34	4.00	0.34
		1^1A_u	4.81	4.52	4.70	4.95	5.29	5.05 (88.4)	3.84	4.81	0.36
		1^1B_{2u}	4.64	4.75	4.85	5.13	5.14	5.02 (86.2)	4.25	4.86	0.34
		1^1B_{2g}	5.56	5.17	5.68	5.92	6.02	5.74 (85.0)	4.92	5.65	0.37
		1^1B_{1g}	6.60	6.13	6.41	6.70	7.13	6.75 (85.8)	5.42	6.69	0.41
		1^1B_{1u}	6.58	6.70	6.89	7.10	7.18	7.07 (93.3)	6.48	6.66	0.28
		2^1B_{1u}	7.72	7.57	7.79	8.13	8.34	8.06 (90.9)	6.91	7.62	0.32
		2^1B_{2u}	7.60	7.70	7.65	8.07	8.29	8.05 (89.7)	6.99	7.76	0.35
pyrimidine	6	1^1B_1	4.55	3.81	4.44	4.49	4.70	4.50 (88.4)	3.65	4.24	0.32
		1^1A_2	4.91	4.12	4.81	4.84	5.12	4.93 (88.2)	4.18	4.83	0.33
		1^1B_2	5.44	4.93	5.24	5.51	5.49	5.36 (85.7)	4.96	5.55	0.34
		2^1A_1	6.95	6.72	6.64	7.12	7.17	7.06 (92.2)	6.36	7.25	0.38
pyridazine	6	1^1B_1	3.78	3.48	3.78	3.90	4.11	3.92 (89.0)	3.26	3.67	0.30
		1^1A_2	4.32	3.66	4.32	4.40	4.76	4.49 (86.6)	3.66	4.25	0.31
		2^1A_1	5.18	4.86	5.18	5.37	5.35	5.22 (85.2)	4.28	5.16	0.40
		2^1A_2	5.77	5.09	5.77	5.81	6.00	5.74 (86.6)	4.82	5.53	0.35
triazine	6	$1^1A_1''$	4.60	3.90	4.60	4.70	4.96	4.78 (88.0)	3.23	4.44	0.37
		$1^1A_2''$	4.66	4.08	4.68	4.80	4.98	4.76 (88.0)	3.65	4.48	0.39
		$1^1E''$	4.71	4.36	4.71	4.77	5.01	4.81 (88.1)	3.49	4.48	0.37
		$1^1A_2'$	5.79	5.33	5.79	5.82	5.84	5.71 (85.1)	4.34	5.48	0.44
tetrazine	6	1^1B_{3u}	2.24	1.96	2.24	2.47	2.71	2.53 (89.6)	1.36	2.12	0.36
		1^1A_u	3.48	3.06	3.48	3.67	4.07	3.79 (87.5)	2.48	3.55	0.37
		1^1B_{1g}	4.73	4.51	4.73	5.10	5.32	4.97 (82.5)	4.06	4.94	0.41
		1^1B_{2u}	4.91	4.89	4.91	5.20	5.27	5.12 (84.6)	3.98	4.86	0.40
		2^1A_u	5.47	5.28	5.47	5.50	5.70	5.46 (87.4)	3.61	4.75	0.41
		1^1B_{2g}	5.18	5.05	5.18	5.53	5.70	5.34 (80.7)	4.25	5.28	0.43
cytosine	8	$2^1A'$	4.66	4.39	4.68	4.80	4.98	4.72 (86)	N/A	N/A	N/A
		$1^1A''$	4.87	5.00	5.12	5.13	5.45	5.16 (86)	4.47	5.06	0.32
		$2^1A''$	5.26	6.53	5.54	5.01	5.99	5.52 (83)	5.83	5.80	0.21
		$3^1A'$	5.62	5.36	5.54	5.71	5.95	5.61 (85)	4.78	5.56	0.37
thymine	8	$1^1A''$	4.82	4.39	4.94	4.94	5.14	4.98 (87)	4.91	4.90	0.23
		$2^1A'$	5.20	4.88	5.06	5.39	5.60	5.34 (89)	4.84	5.29	0.29
		$3^1A'$	6.27	5.88	6.15	6.46	6.78	6.34 (83)	4.56	5.94	0.50
		$2^1A''$	6.16	5.91	6.38	6.33	6.57	6.45 (89)	6.55	6.44	0.19
		$4^1A'$	6.53	6.10	6.52	6.80	7.05	6.71 (88)	4.91	6.45	0.48
uracil	8	$1^1A''$	4.80	4.54	4.90	4.91	5.11	4.90 (86)	4.82	4.83	0.23
		$2^1A'$	5.35	5.00	5.23	5.52	5.70	5.44 (88)	4.80	5.36	0.32
		$3^1A'$	6.26	5.82	6.15	6.43	6.76	6.29 (83)	N/A	N/A	N/A
		$3^1A''$	6.56	6.37	6.97	6.26	6.50	6.77 (91)	5.63	6.93	0.42
		$2^1A''$	6.10	6.00	6.27	6.73	7.68	6.32 (88)	6.49	6.39	0.19
		$4^1A'$	6.70	6.46	6.75	6.96	7.19	6.87 (88)	5.14	6.40	0.43
adenine	10	$2^1A'$	5.25	5.13	5.20	5.28	5.37	5.18 (86)	4.41	5.36	0.41
		$3^1A'$	5.25	5.20	5.30	5.42	5.61	5.39 (89)	4.90	5.37	0.32
		$1^1A''$	5.12	6.15	5.21	5.27	5.58	5.34 (88)	4.87	5.44	0.32
		$2^1A''$	5.75	6.86	5.97	5.91	6.19	5.96 (88)	5.12	5.84	0.34

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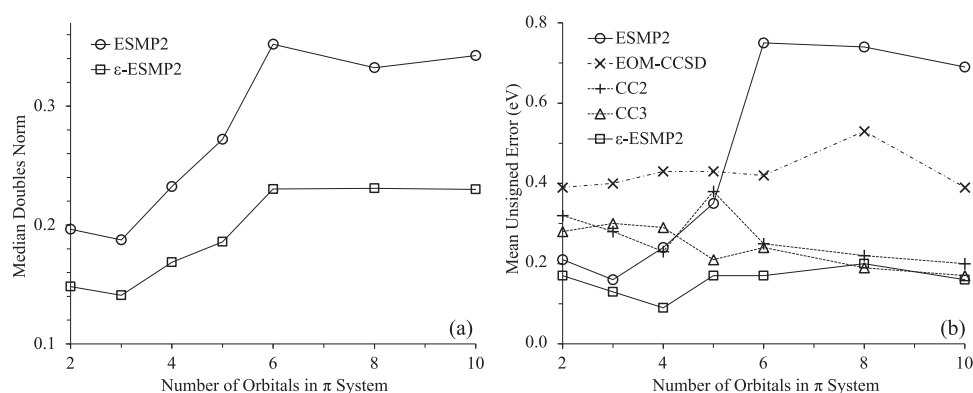
FIG. 1. (a) Median $|T_2|$ doubles norms and (b) MUEs for excitation energies by π system size. States identified by ESMP2 to have strongly doubly excited character and states not found by ESMF (red and gray rows in Table I) are excluded.

TABLE II. Mean unsigned errors and standard deviations for singlet excitation energies in eV. States without ESMF solutions and states identified by ESMP2 to have large doubly excited components (gray and red rows in Table I) are excluded.

	SA-CASPT2	MS-CASPT2	CC2	EOM-CCSD	CC3	ESMP2	ε-ESMP2
Ketones and amides	0.20 ± 0.18	0.02 ± 0.05	0.29 ± 0.26	0.45 ± 0.38	0.26 ± 0.31	0.39 ± 0.37	0.17 ± 0.16
Conjugated polyenes	0.14 ± 0.09	0.34 ± 0.34	0.32 ± 0.22	0.57 ± 0.13	0.43 ± 0.12	0.27 ± 0.16	0.13 ± 0.13
Conjugated rings	0.32 ± 0.17	0.01 ± 0.03	0.22 ± 0.07	0.36 ± 0.16	0.18 ± 0.12	0.60 ± 0.40	0.15 ± 0.10
Heterocycle	0.34 ± 0.21	0.10 ± 0.13	0.28 ± 0.19	0.43 ± 0.19	0.23 ± 0.16	0.68 ± 0.42	0.17 ± 0.14
Nucleobases	0.41 ± 0.37	0.15 ± 0.10	0.21 ± 0.13	0.47 ± 0.33	0.17 ± 0.08	0.68 ± 0.52	0.19 ± 0.15
All	0.31 ± 0.24	0.09 ± 0.13	0.26 ± 0.18	0.43 ± 0.26	0.23 ± 0.19	0.60 ± 0.43	0.17 ± 0.14

expected correlations with both ESMP2 excitation energy errors and the CC3 T_1 percentage across a wider range of $|T_2|$ values. With regard to excluding states from some comparisons, we note that the exclusion of the three missing ESMF states from the statistics, for example, in Table II, changes the overall mean unsigned error (MUE) by 0.01 eV or less for CC2, EOM-CCSD, and CC3. Excluding the states with $|T_2| > 0.5$ improves the overall MUEs of CC2, EOM-CCSD, CC3, and ε-ESMP2 by just 0.04, 0.03, 0.0, and 0.02 eV, respectively, and so does not affect the ordering of their overall accuracy. As there were only three states out of about 100 that ESMF did not find, we do not expect their absence from the ESMP2 statistics to alter any of the broad conclusions drawn from this study. The supplementary material has additional tables in which fewer states are excluded.

As seen in Fig. 1, unregularized ESMP2's accuracy for excitation energies in singly excited states depends strongly on the size of a molecule's π system, while ε-ESMP2 is insensitive to π system size and highly accurate. The degradation of ESMP2's accuracy with increasing π system size closely follows the rise of its $|T_2|$ doubles norm, indicating that the poor accuracy in molecules with larger π systems is indeed related to a perturbative failure born of small zeroth order energy spacings between the reference and the lowest-lying doubles. With its level shift suppressing the spurious growth of large doubles contributions, ε-ESMP2 is significantly more reliable, displaying an accuracy that is as good or better than the other single-reference methods at all π system sizes. Among the methods compared, only the multi-reference CASPT2 approach using Thiel's active spaces offers better overall accuracy on this test set than
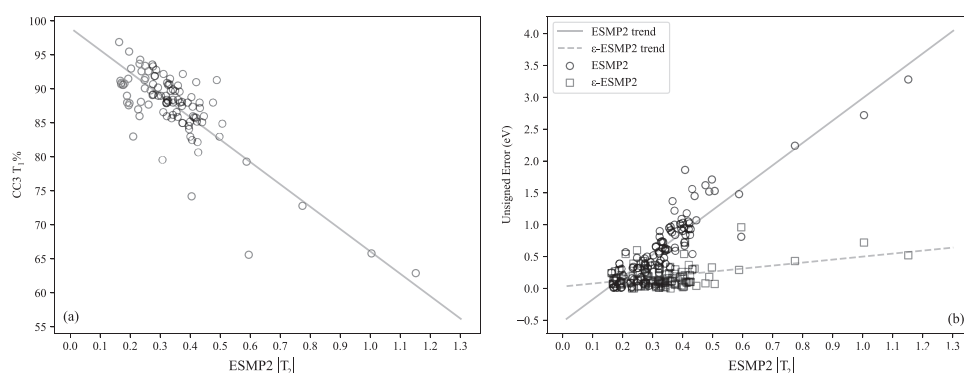
FIG. 2. (a) CC3 T_1 percentages and (b) ESMP2 and ε-ESMP2 unsigned excitation energy errors plotted against the ESMP2 doubles norm $|T_2|$ for all states. The lines are linear fits to the points.

TABLE III. Mean unsigned errors and standard deviations for singlet excitation energies in eV. States without ESMF solutions and states identified by ESMP2 to have large doubly excited components (gray and red rows in Table I) are excluded.

π system size	SA-CASPT2	MS-CASPT2	CC2	EOM-CCSD	CC3	ESMP2	ε-ESMP2
2	0.19 ± 0.17	0.11 ± 0.24	0.32 ± 0.27	0.39 ± 0.36	0.28 ± 0.34	0.21 ± 0.14	0.17 ± 0.16
3	0.12 ± 0.11	0.00 ± 0.00	0.28 ± 0.26	0.40 ± 0.43	0.30 ± 0.32	0.16 ± 0.18	0.13 ± 0.09
4	0.17 ± 0.16	0.17 ± 0.18	0.23 ± 0.12	0.43 ± 0.16	0.29 ± 0.16	0.24 ± 0.12	0.09 ± 0.13
5	0.41 ± 0.13	0.10 ± 0.10	0.38 ± 0.20	0.43 ± 0.18	0.21 ± 0.15	0.35 ± 0.34	0.17 ± 0.14
6	0.31 ± 0.22	0.11 ± 0.13	0.25 ± 0.17	0.42 ± 0.20	0.24 ± 0.17	0.75 ± 0.39	0.17 ± 0.14
8	0.34 ± 0.26	0.11 ± 0.11	0.22 ± 0.14	0.53 ± 0.31	0.19 ± 0.10	0.74 ± 0.47	0.20 ± 0.16
10	0.48 ± 0.34	0.04 ± 0.07	0.20 ± 0.08	0.39 ± 0.13	0.17 ± 0.10	0.69 ± 0.41	0.16 ± 0.10
5 or less	0.24 ± 0.18	0.09 ± 0.17	0.32 ± 0.23	0.41 ± 0.31	0.26 ± 0.27	0.24 ± 0.23	0.16 ± 0.13
6 or more	0.34 ± 0.26	0.10 ± 0.10	0.24 ± 0.15	0.45 ± 0.23	0.21 ± 0.14	0.74 ± 0.41	0.18 ± 0.14

ε-ESMP2. With an N^5 scaling and no need to choose an active space, these results suggest that ε-ESMP2 has much to offer in modeling singly excited states, while ESMP2 can act as a relatively affordable detector of doubly excited character. This information is summarized by the averages presented in Table III.

B. Amplitude diagnostics

As seen in Fig. 2, the ESMP2 $|T_2|$ values tend to increase as the CC3 %T_1 values decrease, in line with expectation. With one exception, the most worrying CC3 %T_1 values (those significantly below 80%) all correspond to ESMP2 $|T_2|$ values above 0.5. The exception is the 1^1B_{3u} state of benzoquinone, which has a CC3 %T_1 of 75.2% but an ESMP2 doubles norm of just 0.4. Interestingly, both CC2 and CC3 are reasonably accurate for this state despite the low %T_1 value, although EOM-CCSD and ε-ESMP2 are not. This exception makes it tempting to recommend that states with $|T_2| > 0.4$ be considered "hard" for ε-ESMP2, but Fig. 2 also makes clear that there are many states with doubles norms this large that ε-ESMP2 is quite accurate for and a couple with lower doubles norms where ε-ESMP2 struggles. Hence, we see 0.5 as a better rough threshold for when to firmly set ε-ESMP2 and other single-reference methods aside and reach for multi-reference approaches. For ESMP2, large energy errors clearly start much earlier, and it would be difficult to recommend relying on it for any state where $|T_2| > 0.3$.

C. Comparison to TD-DFT

Shortly after the introduction of the Thiel benchmark set, a follow up study evaluated the performance of TD-DFT and DFT/MRCI on the same molecules and states.[54] In Table IV, we compare the results of that study to ESMP2 and ε-ESMP2. Due to its sensitivity to π system size, ESMP2 without regularization is clearly less accurate than typical TD-DFT approaches, which, having a very different mathematical structure, do not suffer the same issue of small denominators as the lowest doubly excited configurations come down in energy. Indeed, TD-DFT under the usual adiabatic approximation leads to a formalism in which doubles do not participate in excited states at all.[22] ε-ESMP2, on the other hand, proves to be more accurate on the Thiel set singlet states than any of the TD-DFT functionals originally tested by Thiel, and this favorable comparison holds even when considering more recent benchmarking[27] of a much wider range of functionals, where MUEs were seen to range from just above 0.2 eV to more than 0.5 eV. Even when the states with large $|T_2|$ are included (see tables in the supplementary material), ε-ESMP2 shows a MUE of 0.19 eV, although it is far from obvious that such states should be used in comparing these methods as TD-DFT cannot treat their doubly excited parts at all. Table IV also shows that ε-ESMP2's accuracy is largely consistent across different types of molecules, whereas the density functionals tested by Thiel have accuracies that vary more widely, with the nucleobases proving the most difficult.

Another difference between TD-DFT and ESMP2 is the latter's ability to offer diagnostic information about the presence of doubly excited character. Although TD-DFT at N^4 is less expensive than ESMP2, it offers no information on such character, whereas ESMP2 can do so at N^5 cost. This is substantially lower than the N^7 cost of CC3, and the original Thiel set study makes clear that lower-level CC methods, such as EOM-CCSD, are much less effective at predicting

TABLE IV. Mean unsigned errors and standard deviations for singlet excitation energies in eV. States without ESMF solutions and states identified by ESMP2 to have large doubly excited components (gray and red rows in Table I) are excluded.

	BP86	B3LYP	BHLYP	DFT/MRCI	ESMP2	ε-ESMP2
Ketones and amides	0.55 ± 0.35	0.29 ± 0.19	0.35 ± 0.44	0.34 ± 0.21	0.39 ± 0.37	0.17 ± 0.16
Conjugated polyenes	0.52 ± 0.32	0.40 ± 0.22	0.22 ± 0.11	0.22 ± 0.13	0.27 ± 0.16	0.13 ± 0.13
Conjugated rings	0.51 ± 0.34	0.36 ± 0.19	0.29 ± 0.22	0.16 ± 0.13	0.60 ± 0.40	0.15 ± 0.10
Heterocycles	0.44 ± 0.29	0.21 ± 0.18	0.49 ± 0.26	0.17 ± 0.12	0.68 ± 0.42	0.17 ± 0.14
Nucleobases	0.83 ± 0.30	0.50 ± 1.20	0.57 ± 0.29	0.15 ± 0.12	0.68 ± 0.52	0.19 ± 0.15
All	0.54 ± 0.34	0.31 ± 0.54	0.44 ± 0.31	0.20 ± 0.16	0.60 ± 0.43	0.17 ± 0.14

doubly excited character.[24] Thus, when checking for doubly excited character when trying to assess the trustworthiness of TD-DFT for a particular excited state, ESMP2 may offer a relatively affordable approach.

D. Group 1: Aldehydes, ketones, and amides

These molecules have many uses as functional groups in biological and photocatalytic settings,[55–58] making them interesting both from a formal and a practical perspective. Thiel's CASPT2 approach (CASPT2 b) is especially accurate in this set of molecules with a MUE of just 0.02 eV. ε-ESMP2 is the next most accurate, followed by Roos's CASPT2, CC3, and CC2, with EOM-CCSD and ESMP2 being the least accurate. Previous TD-DFT work shows that TD-DFT methods with hybrid functionals usually give results comparable to EOM-CCSD in these molecules.[54,59,60] ε-ESMP2 proves to be more accurate than B3LYP in these molecules, which, in turn, is interestingly significantly more accurate than DFT/MRCI, which has more difficulty with this set of molecules than with any other.

1. Formaldehyde and acetone

For formaldehyde and acetone, three states were studied: 1^1A_2 of $n \rightarrow \pi^*$ character, 1^1B_1 of $\sigma \rightarrow \pi^*$ character, and 2^1A_1 of $\pi \rightarrow \pi^*$ character. It should be noted that the 2^1A_1 states of these molecules are known to have considerable Rydberg character, which cannot be described properly in the TZVP basis set as it lacks diffuse functions. We have chosen not to exclude these states from our analysis because many other states in the Thiel set also have some Rydberg character to varying degrees, making it difficult to draw a clear line between what to include and what not to. Of course, all the methods we are comparing with each other use the same TZVP basis and so are faced with this same issue.

These two molecules are particularly interesting for ESMP2, as they are the only cases in this benchmark where ESMP2 did as well as ε-ESMP2. Both methods produced errors with a relatively small magnitude of 0.1 eV for the non-Rydberg states. Interestingly, the addition of the level shift actually increased errors for the 1^1B_1 state in formaldehyde and the 1^1A_2 state in acetone, although ε-ESMP2 remains quite accurate. Another interesting and potentially noteworthy observation we made was that ESMP2 showed larger doubles norms for the Rydberg states and a much larger maximum individual amplitude value, raising the question of whether it would have any value in flagging Rydberg character. We do not have enough data in this study to say anything conclusive on this front, but it may be interesting to study further.

2. p-benzoquinone

For benzoquinone, three $n \rightarrow \pi^*$ states—1^1A_u, 1^1B_{1g}, and 1^1B_{3u}—and three $\pi \rightarrow \pi^*$ states—1^1B_{3g}, 1^1B_{1u}, and 2^1B_{3g}—were studied. Within this group of molecules, benzoquinone showed by far the largest amount of doubly excited character, as seen in both the CC3 %T_1 and the ESMP2 $|T_2|$ values. Unsurprisingly, unregularized ESMP2 performed quite poorly in benzoquinone, with ε-ESMP2 performing much better and more comparably to CC2 and CC3. ε-ESMP2's largest error in this molecule was 0.54 eV for the 1^1B_{3u} state, which has the most significant doubly excited character. This reminds us that although ε-ESMP2 can improve significantly over

ESMP2 when such character is present, it is no substitute for multi-reference methods in cases where the doubly excited component is large enough.

3. Formamide, acetamide, and propanamide

For each of these molecules, the $1^1A''$ $n \rightarrow \pi^*$ state and the $2^1A'$ $\pi \rightarrow \pi^*$ state were studied. In the $2^1A'$ state of propanamide and especially acetamide, the excitation within the converged ESMF wave function contained fewer components than in EOM-CCSD, placing a higher fraction of the overall weight on the dominant HOMO $\rightarrow$ LUMO+2 component. We see this as a good reminder that both orbital relaxation and the degree to which correlation effects are captured can affect the degree of predicted mixing between excitation components.

ESMP2 was quite accurate for the $1^1A''$ excitation energies, with ε-ESMP2 less so, while ε-ESMP2 was much more accurate than ESMP2 for the $2^1A'$ states. Although none of these states has a particularly high degree of doubly excited character, the ESMP2 doubles norms do correctly predict the relative accuracy for the unregularized theory between these two states. A final noteworthy point is the unusually high errors made by CC2, EOM-CCSD, and CC3 in the $2^1A'$ state of formamide. It is not obvious what is driving this error, especially considering ESMP2's accuracy and the small effect of introducing regularization.

E. Group 2: Conjugated polyenes

The four unsaturated polyene molecules in this group—ethene, butadiene, hexatriene, and octatetraene—provided a great deal of insight into how ESMP2 performs in the presence of doubly excited character, as the 2^1A_g states of butadiene, hexatriene, and octatetraene all have large doubly excited components,[61] which can, for example, be seen in their CC3 %T_1 values. The ESMP2 doubles norm correctly flags all three of these doubly excited 2^1A_g states as likely to be problematic for ESMP2 and other single-reference methods. Although far superior to the other methods in the doubly excited state, Thiel's CASPT2 results (CASPT2 b) are not especially competitive for the 1^1B_2 states. Even more surprising is the degree of difficulty that CC3 has with the 1^1B_2 states, as they are dominated by singly excited components. Excited-state-specific DFT in the form of restricted open-shell Kohn–Sham (ROKS) has also shown difficulty in these states,[59] with accuracy appearing to decrease as the basis set is enlarged. In the TD-DFT benchmark presented by Wiberg et al.,[60] it was shown that the ethene and butadiene singly excited states were modeled best by functionals with higher amounts of Hartree Fock exchange. Indeed, in Thiel's TD-DFT benchmark,[54] BHLYP significantly outperformed B3LYP and BP86 in the 1^1B_2 states, although we find that ε-ESMP2 does better still.

1. Ethene

The only state studied for ethene was the 1^1B_{1u} state as the other low lying excited states for the molecule are strongly Rydberg in character and cannot be accurately described using the TZVP basis set used here.[62,63] The 1^1B_{1u} state also contains significant valence-Rydberg mixing; however, it is still mostly described as a valence excited state. The Thiel best estimate value of 7.80 eV is based on a mixture experimental data and high-level ab initio results, though it was noted in this paper that defined the best estimates that the

vertical excitation of the 1^1B_{1u} state could not be assigned precisely based on experimental data.[24]

In this state, ESMP2 and ε-ESMP2 performed similarly with errors of 0.25 and 0.24 eV, respectively, which makes sense given how strongly dominated this state is by single excitations. The CC methods EOM-CCSD, CC2, and CC3 all perform relatively poorly for this state with errors around 0.6–0.7 eV, and Thiel's CASPT2 shows an unusually large error of 0.82 eV. Roos's CASPT2 error is much smaller at 0.18 eV, and Schreiber *et al.* reported an almost exact result with a greatly expanded (8, 20) active space,[24] a useful reminder of how important the choice of active space can be.

2. Butadiene, hexatriene, and octatetraene

For these three molecules, two states were studied each: the single-excitation-dominated 1^1B_u state and the substantially doubly excited 2^1A_g state. As expected, ESMP2 performs considerably better for the 1^1B_u states (errors of 0.5 eV or below) than for the 2^1A_g (errors between 2 and 3 eV). Its redeeming quality in the latter states is its ability to signal its own failure through unusually large doubles norms of 0.77, 1.0, and 1.15, clearly warning the user to get their hands on a multi-reference method instead. To put how extreme these norms are in context, remember that the weight of the zeroth order reference in intermediate normalization is 1, meaning that this perturbation theory's perturbation is coming out as big or bigger than the zeroth order piece. Such a grossly nonsensical result is a clear sign of failure, which if heeded can help guide a user in selecting a more appropriate method. As for the 1^1B_u state, because our summary tables exclude states flagged as strongly doubly excited by ESMP2, the entry in Table II offers at a glance the performance on this less challenging, singly excited state. ε-ESMP2 is considerably more accurate for this state than the CC methods, rivaled only by CASPT2 approaches with well-chosen active spaces.

F. Group 3: Conjugated rings

With their larger π systems, this group of molecules proved especially difficult for unregularized ESMP2, whose overall accuracy in this group was worse than the other wave function methods. ε-ESMP2, on the other hand, outperformed the CC methods and was, in turn, outperformed by Thiel's CASPT2. Although Thiel's selection of CASPT2 to be the TBE in cyclopropene, norbornadiene, and naphthalene no doubt gives it a statistical advantage, we certainly expect it to be more accurate than ε-ESMP2 in these molecules. As in the polyenes, ROKS has shown a tendency for its accuracy to decrease with increasing basis set size in a number of these conjugated rings, both with and without the use of range separation.[59] DFT/MRCI, on the other hand, performs quite well in these molecules, as does CC3.

1. Cyclopropene

For cyclopropene, two states were studied, the $1^1B_1 \sigma \rightarrow \pi^*$ state and the $1^1B_2 \pi \rightarrow \pi^*$ state. The Thiel best estimate for these states comes directly from a multi-state (MS)-CASPT2/TZVP calculation as it gives a more accurate description for the valence-Rydberg mixing in the 1^1B_2 state even though these values are slightly higher than experiment.[24,64] Neither of these states shows any reason for great concern for ESMP2, and it offers reasonable accuracy that is slightly

improved in both cases by regularization. Unsurprisingly, CC2 and especially CC3 work well in these states.

2. Cyclopentadiene

We look at two $\pi \rightarrow \pi^*$ excitations in cyclopentadiene—the 1^1B_2 and 2^1A_1 states. While both are valence excited states without significant Rydberg mixing,[65] the former state is dominated by a single excitation, while the latter is a superposition of components that includes doubly excited pieces. Thiel calculates a 5.55 eV excitation energy from EOM-CCSDT evaluated with an "exhaustive" basis set as the TBE for the 1^1B_2 state, which is a bit above the carefully estimated 5.43(5) eV experimental value.[66] For the 2^1A_1 state, Thiel uses CASPT2 for the TBE. ESMP2 successfully predicts its own failure in the 2^1A_1 state, while ε-ESMP2 is similar in accuracy to CC3. As expected, ESMP2 does better for the 1^1B_2 state and in that case is further improved by ε-ESMP2, which errors low by about the same amount that CC3 errors high.

3. Norbornadiene

Norbornadiene can be seen as the third and most structurally complicated member of a series begun by *cis*-butadiene and cyclopentadiene.[67] For calculations on the excited states of norbornadiene, one must consider that while it is formally not conjugated, there is indirect conjugation of the double bonds, allowing for through-space and through-bond interactions—thus, interactions between π and σ orbitals are more important.[67] Two $\pi \rightarrow \pi^*$ excitations are examined in this benchmark—an experimentally forbidden 1^1A_2 state and a 1^1B_2 excited state that can mix strongly with nearby Rydberg states.[67] CASSCF studies,[67] CC3, and ESMP2 all indicate that both states are dominated by single excitations. Thiel selects CASPT2/TZVP for both TBEs, 5.34 and 6.11 eV, which lie a little above the reported experimental values of 5.25 and 5.95 eV.[68]

ESMP2 produces excitation energy errors of 0.25 and 0.32 eV for the 1^1A_2 and 1^1B_2 states, respectively, making it more accurate than EOM-CCSD and on par with CC2 and CC3. ε-ESMP2 is the most accurate non-active-space method for these states but is not as accurate as CASPT2.

4. Benzene

For benzene, we looked at the 1^1B_{1u}, 1^1B_{2u}, 1^1E_{1u}, and $2^1E_{2g} \pi \rightarrow \pi^*$ excitations. The first three of these excitations are dominated by equally weighted superpositions of excitations out of the degenerate π system HOMOs, while the largest component of the 2^1E_{2g} state is a single excitation out of the lowest energy π orbital. Thiel adopts the CC3/ANO1 results of Christiansen *et al.* as best estimates for the states.[69]

Benzene is a good example of a molecule where the EOM-CCSD can overestimate the degree of singly excited character compared to CC3. This issue is particularly stark in the 2^1E_{2g} state, where EOM-CCSD and CC3 disagree in their % T1 measures by 19%. Similarly, the inclusion of triples drops CC3's excitation energy in this state by 0.6 eV compared to CC2. As pointed out by Christiansen *et al.*,[69] not all of these states show a uniform convergence order between CCS, CC2, EOM-CCSD, and CC3, with EOM-CCSD's excitation energy in the 1^1B_{2u} state lying below that of CC2, which is atypical among Thiel set states. These authors go on to use benzene to support an argument that EOM-CCSD is

not a reliable guide to doubly excited character. With such considerable changes when going from the inclusion of doubles to the inclusion of triples, we have some doubts about the accuracy of the CC3 results as a best estimate for the significantly doubly excited 2^1E_{2g} state and might instead have adopted CASPT2 values.

As in many other cases, ESMP2's doubles norms tell a similar story about doubly excited character as the CC3 % T1 and, in particular, signal clearly that ESMP2 is not appropriate for use in the 2^1E_{2g} state. ESMP2's excitation energy accuracy is poor in all of benzene's states, as is common for systems with six or more orbitals in their π system, but, with the exception of the 2^1E_{2g} state, ε-ESMP2 makes a large improvement to the point that it is competitive with CC2 and CC3. In 2^1E_{2g}, where ESMP2 signals its own failure, it is difficult not to look to CASPT2 as the preferred method among those tested, all things considered.

5. Naphthalene

We looked at the 1^1B_{3u}, 1^1B_{2u}, 2^1A_g, 1^1B_{1g}, 2^1B_{3u}, 2^1B_{1g}, 2^1B_{2u}, and 3^1A_g states of naphthalene, all of which are $\pi \rightarrow \pi^*$ transitions. The TBEs for these states were taken directly from the MS-CASPT2/TZVP results, as this molecule's size limits other options. Based on the T1% values from CC3, it is likely that many of these states involve significant amounts of doubly excited character. The 3^1A_g state had a particularly low T1% of 70% and is the first state we come to for which the ESMF stationary point could not be found.

For the other states, ESMP2 displayed a range of accuracies. It showed a particularly small error of 0.04 eV for the 1^1B_{1g} state, which, despite a relatively low CC3 T1%, was also treated accurately by CC3 and CC2. In fact, this is one of the rare states in which regularization made the excitation energy prediction worse, with ε-ESMP2 giving an error of 0.37 eV. ESMP2's errors in the other naphthalene states were much larger, with some states showing significantly larger doubles norms as well, although not as large as in the doubly excited polyene states. In these other states, regularization makes a large improvement, making ε-ESMP2 competitive with CC2 and CC3.

G. Group 4: Heterocycles

The molecules in this group are furan, pyrrole, imidazole, pyridine, pyrazine, pyrimidine, pyridazine, triazine, and tetrazine. A common theme in these molecules is that almost all of the states studied here have at least moderate contributions from double excitations, at least as measured by the CC3 T1%. As one might therefore expect, ESMP2's predictions were fairly inaccurate in this group. Regularization via ε-ESMP2 dramatically reduces these errors to the point that it is more accurate than CC2, EOM-CCSD, and CC3. As in many other cases, only CASPT2 with Thiel's active spaces did better. It should, however, be noted that the CASPT2 b error is somewhat artificially small in this group, as it was used as the TBE for imidazole, pyridazine, triazine, and tetrazine.[24] Among DFT approaches, DFT/MRCI and TD-DFT/B3LYP perform particularly well in the heterocycles,[54] while ROKS performs well for some cases but shows difficult basis set dependence in others.[59] Further analysis of TD-DFT in some of these molecules can be found in a study by Caricato et al.[70]

1. Pyrrole and furan

We consider the following $\pi \rightarrow \pi^*$ excitations in pyrrole and furan: the 1^1B_2, 2^1A_1, and 3^1A_1 states. We analyze these two molecules together as their spectra are similar. Pyrrole's 2^1A_1 state and furan's 1^1B_2 and 2^1A_1 states are valence excited states, while the remaining states are considered to have Rydberg character.[65] For both molecules, Thiel's TBEs are based on CC3 calculations with basis set corrections.[71,72]

The ESMP2 predictions were mixed in terms of accuracy. Both molecules had two states, the 3^1A_1 and 1^1B_2 states, that produces errors lower than 0.5 eV and then a 2^1A_1 state with an error of 1.53 eV in furan and 1.07 eV in pyrrole. This is not surprising, given the large ESMP2 doubles norms in these states and the relatively low CC3 T_1 percentages of 85% and 86% As in many other molecules, regularization makes a big difference, and ε-ESMP2 reduces the errors in the 2^1A_1 states to below 0.05 eV while also lowering errors in most other states as well.

2. Imidazole

Imidazole is a case where experimental comparison is particularly challenging, as the UV-Vis spectrum has only been taken in ethanol and aqueous solutions.[73–80] Furthermore, there is disagreement about whether imidazole and imidazolium (the protonated form) have overlapping broad bands or each form separate strong peaks.[73] In any case, Thiel selected their CASPT2 results as the TBE for three singlet vertical excitations: the $1^1A'' n \rightarrow \pi^*$ state at 6.81 eV and two $\pi \rightarrow \pi^*$ excitations of A' symmetry at 6.19 and 6.93 eV, respectively. CASSCF and CASPT2 calculations have shown that these states are not Rydberg in nature.[73]

Interestingly, there is some disagreement between different CASSCF approaches and also ESMF about the nature of these three states. If we consider the six-electron, five-orbital π system in imidazole, we would not expect the lowest-energy and nodeless 1a'' π orbital to participate strongly in low-lying excitations. Instead, the occupied 2a'' and 3a'' π orbitals, which both have an additional nodal plane, can form up to four singlet excitations into the unoccupied 4a'' and 5a'' π^* orbitals. Thiel's work on MS-CASPT2 and CC3 shows the $2^1A'$ state as being dominated by the 3a'' $\rightarrow$ 4a'' excitation, while the $3^1A'$ state involves a positive superposition of the 2a'' $\rightarrow$ 4a'' and 3a'' $\rightarrow$ 5a'' excitations.[44] However, Roos found the states of A' symmetry to both have significant contributions from each of the 3a'' $\rightarrow$ 4a'', 2a'' $\rightarrow$ 4a'', and 3a'' $\rightarrow$ 5a'' excitations.[73] In our ESMF results, the A' states are essentially the plus and minus combinations of the 3a'' $\rightarrow$ 4a'' and 3a'' $\rightarrow$ 5a'' transitions, with very little contribution from 2a'' $\rightarrow$ 4a''. Taken together, these results show that imidazole is a case where the exact mixing of the components within excited states is quite sensitive to the amount of correlation and orbital relaxation in play.

In terms of energetics, ESMP2's excitation energies have an overall accuracy similar to that of CC3. Regularization only improves the accuracy in one of the three states, making this an unusual molecule in that regard and raising the question of how accurately ESMF has captured the zeroth order representation, especially in light of the disagreement between it and multiple versions of CASSCF in the A' states. It seems possible that this is a case where the primary singly excited components are close enough in energy that how they mix is substantially affected by correlation effects from

doubly excited determinants, which is an effect that is simply beyond the reach of ESMF.

3. Pyridine

We studied the 1^1B_1 and $2^1A_2 n \rightarrow \pi^*$ excitations and four $\pi \rightarrow \pi^*$ states: 1^1B_2, 2^1A_1, 3^1A_1, and 2^1B_2. The best estimates for these states comes from Wan *et al.* symmetry adapted cluster (SAC)-CI calculations,[81] which are close to experimental gas-phase excitation values. Using ESMP2 to predict the excitation energies for these states led to a mixture of errors. 2^1A_1 and 2^1A_2 had the smallest errors of 0.04 and 0.14 eV, respectively. 1^1B_2 and 1^1B_1 had errors of 0.33 and 0.34 eV, and the largest errors were from the 3^1A_1 and 2^1B_2 states with 0.63 and 0.73 eV, respectively. None of these states show especially large doubles norms, at least not compared, for example, to those seen in the polyenes. Although ESMF and EOM-CCSD both agree that the excited states of A_1 symmetry are superpositions of two main components, ESMF predicts much more equal superpositions than EOM-CCSD. Compared to other methods, ESMP2 is overall slightly more accurate than the coupled cluster methods, although the accuracy of both varies significantly from state to state. The overall accuracy of ε-ESMP2 is better, but this comes from improvements in some states partially counteracted by detriments in others.

4. Pyrazine

For pyrazine, four $n \rightarrow \pi^*$ states—1^1B_{3u}, 1^1A_u, 1^1B_{2g}, and 1^1B_{1g}—and four $\pi \rightarrow \pi^*$ states—1^1B_{2u}, 1^1B_{1u}, 2^1B_{1u}, and 2^1B_{2u}—were studied. Thiel selected EOM-CCSD($\widetilde{T}$) calculations for the TBEs,[24] compared to which ESMP2 produced a wide variety of errors, ranging from 0.10 eV in the 1^1B_{1u} state to 1.18 eV in the 1^1B_{1g} state. ε-ESMP2 shows significant improvements, with errors of less than 0.25 eV in all states. The CC methods do better than ESMP2 but worse than ε-ESMP2. The same is true of CASPT2, although its accuracy is much closer to that of ε-ESMP2.

5. Pyrimidine

Four excited states were studied for pyrimidine, two $n \rightarrow \pi^*$ states—1^1B_1 and 1^1A_2—and two $\pi \rightarrow \pi^*$ states—1^1B_2 and 2^1A_1. The Thiel best estimates for the excited states of pyrimidine were based on coupled cluster results with non-iterative triples and basis set corrections. Generally, these values error a few tenths of an electron volt high compared to experimental values. Based on the work presented in benchmarking studies by Loos *et al.*[82] and Schreiber *et al.*,[24] most *ab initio* methods error high for these states compared to experiment, not only the ones based on coupled cluster. An unusual feature in pyrimidine as compared to the other azabenzenes studied here is that EOM-CCSD does comparably to Thiel's CASPT2 and only slightly worse than CC2 and CC3. In the other azabenzenes, EOM-CCSD had noticeably higher errors when compared to CC2 and CC3. Without a level shift, ESMP2 is most similar in accuracy to Roos's CASPT2, with both methods producing large errors. ε-ESMP2 shows smaller errors, ranging from 0.08 to 0.31 eV, which is closer to but not as accurate as Thiel's CASPT2 and the CC methods.

6. Pyridazine

Three $n \rightarrow \pi^*$ states were studied in pyridazine: 1^1B_1, 1^1A_2, and 2^1A_2. While all of these states had ESMP2 errors above 0.5 eV, those

for the 2^1A_2 and 2^1A_1 states were particularly large at almost 1 eV. Pyridazine is thus another good example of ESMP2's difficulties in larger π systems, but it is also one of the most powerful examples of the practical efficacy of regularization, with all of ε-ESMP2's errors coming in at less than 0.25 eV. Comparing these results to other wave function methods, ESMP2 was easily the least accurate, while ε-ESMP2 performed similarly to CC2, was more accurate than EOM-CCSD, and was only slightly less accurate than CC3. The TBEs for this molecule were directly taken from Thiel's CASPT2 values, so it is difficult to make a fair comparison to that method.

7. s-triazine

In triazine, we studied three $n \rightarrow \pi^*$ states—$1^1A_1''$, $1^1A_2''$, and $1^1E''$—and one $\pi \rightarrow \pi^*$ state, $1^1A_2'$. Even compared to its performance on other azabenzenes, ESMP2 did poorly here with typical errors around 1 eV, making it by far the least accurate among the wave function methods. The CC3 T_1 values are all below 90% and the ESMP2 doubles norms are all above 0.35, suggesting that triazine is simply a particularly painful example of the difficulty unregularized ESMP2 has when an extended π system brings the lowest doubly excited configurations too close to the primary singly excited configurations. Again, ε-ESMP2 significantly mitigates this difficulty, reducing the worst error to 0.31 eV instead of 1.45 eV. ε-ESMP2 is still less accurate than CC2 and CC3 but is comparable to EOM-CCSD and noticeably better than Roos's CASPT2.

8. s-tetrazine

In this molecule, we look at four $n \rightarrow \pi^*$ excitations—1^1B_{3u}, 1^1B_{1g}, 1^1B_{2g}, and 2^1A_u—and two $\pi \rightarrow \pi^*$ excitations—1^1A_u and 1^1B_{2u}. Note that we have not studied the strongly doubly excited 1^1B_{3g} state, and indeed, the original Thiel benchmark does not even contain CC numbers for this state. As in a number of other heterocycles, Thiel's TBEs for tetrazine were taken directly from the CASPT2(b) results without basis set extrapolation. Against this TBE, CC2 and CC3 show errors mostly below about 0.3 eV, whereas EOM-CCSD errors are higher. As in triazine, all of tetrazine's CC3 %T_1 values for the states studied are between 80 and 90, again implying a difficult playing field for unregularized EMSP2, which duly makes errors on the order of 1 eV and shows doubles norms above 0.35. ESMP2 was especially bad for the 2^1A_u state, with an error of 1.86 eV, its worst error among the heterocycles. Introducing regularization via ε-ESMP2 makes a huge difference, reducing errors to less than 0.22 eV in all states except for 2^1A_u. The 2^1A_u state's error only falls to 0.72 eV, making it one of the worst for ε-ESMP2, especially considering that the ESMP2 doubles norm, although not small at 0.41, is not as large as in the difficult benzene or polyene states and so it is not as clear in this case that ESMP2 would be able to predict ε-ESMP2's failure. Outside of the 2^1A_u state, the accuracy of ε-ESMP2 is similar to the other wave function based methods.

H. Group 5: Nucleobases

This group of molecules includes cytosine, thymine, uracil, and adenine. Due to the size of these molecules, there were no CC3/TZVP calculations reported in the original Thiel benchmark,[24] and we have instead taken the CC3 data from a more recent study.[45] Thiel selected CC2/aug-cc-pVTZ results for the TBEs in all nucleobase states. We note that many of the nucleobase states were

difficult for ESMF to converge to, which was even true in some cases in which the state was dominated by a single singly excited component. In both of the cases where ESMF failed to converge to a stationary point (the $2^1A'$ state of cytosine and the $3^1A'$ state of uracil), we hypothesize that a loss of good orthogonality with lower states during the ESMF optimization was partially to blame. Still, it is not clear why this was such an issue in these cases, as at least a small loss of orthogonality is normal in ESMF due to its state-specific orbital relaxation, and the same difficulty was not present in most other states.

For the excited states in this group, ESMP2 had an MUE of 0.61 eV, making it the wave function method with the worst overall accuracy, as seen in Table II. ε-ESMP2, on the other hand, had a much smaller MUE of 0.19 eV, putting it on par with CC2 and ahead of EOM-CCSD. ε-ESMP2 was also more accurate in the nucleobases than the TD-DFT methods shown in Table IV while being a little less accurate than DFT/MRCI.

1. Cytosine

In cytosine, we studied two $\pi \to \pi^*$ states—$2^1A'$ and $3^1A'$—and two $n \to \pi^*$ states—$1^1A''$ and $2^1A''$. In the states ESMF successfully converged, ESMP2 with no level shift did fairly poorly with errors between 0.5 and 1 eV, which is similarly inaccurate to EOM-CCSD and worse than the other wave function methods. ESMP2 shows a notably peculiar result for the $2^1A''$ state in that it overestimates the excitation energy. In most other cases, ESMP2 tends to error low. This $2^1A''$ state remains an outlier even after introducing regularization, with the error barely changing. In contrast, regularization brings the errors for the other two below 0.2 eV.

2. Uracil

Five states were successfully studied in uracil: the $n \to \pi^*$ states with symmetry labels $1^1A''$, $2^1A''$, and $3^1A''$ and the $\pi \to \pi^*$ states with symmetry labels $2^1A'$ and $4^1A'$. ESMF failed to converge the $3^1A'$ state in uracil. Similar to the cytosine state, this state is dominated by a single singly excited component, so the reasons for this failure are not obvious. In the other states, ESMP2 does very well for the $1^1A''$ state with an error of just 0.02 eV, somewhat poorly for the $2^1A'$ and $2^1A''$ states with errors around 0.5 eV, and very poorly for the $3^1A''$ and $4^1A'$ states. Overall, ESMP2 performs comparably to EOM-CCSD but worse than the other wave function methods. Regularization reduces error for the $2^1A'$ state to just 0.01 eV, leaves the error in the $1^1A''$ state essentially unchanged, and brings the other states' errors to around 0.3 eV. This places the accuracy of ε-ESMP2 ahead of EOM-CCSD and CC2, but still behind that of Thiel's CASPT2.

3. Thymine

For thymine, we studied two $n \to \pi^*$ states, $1^1A''$ and $2^1A''$, and three $\pi \to \pi^*$ states, $2^1A'$, $3^1A'$, and $4^1A'$. ESMP2 does very well for $1^1A''$, achieves errors of around 0.5 eV for $2^1A'$ and $2^1A''$, and has errors of over 1.5 eV for $3^1A'$ and $4^1A'$. For both of the latter states, large doubles norms of 0.497 and 0.476, respectively, warn of the trouble. ε-ESMP2 has much lower errors for all states and makes particularly large improvements in the $3^1A''$ and $4^1A'$ states, with an overall accuracy in this molecule better than EOM-CCSD or Roos's CASPT2 but worse than CC2 and Thiel's CASPT2.

4. Adenine

For adenine, we studied two $\pi \to \pi^*$ states, $2^1A'$ and $3^1A'$, and two $n \to \pi^*$ states, $1^1A''$ and $2^1A''$. ESMP2 gives errors above 0.5 eV for $2^1A'$ and $2^1A''$ and errors of around 0.3 eV for the $3^1A'$ and $1^1A''$ states, with an overall accuracy comparable to EOM-CCSD but worse than the other wave function methods. ε-ESMP2's worst error was 0.32 eV for the $1^1A''$ state, with its other errors all around 0.1 eV, making it much more comparable to CC2, although not as accurate as Thiel's CASPT2.

V. CONCLUSION

We have applied ESMP2 and its regularized ε-ESMP2 cousin to the singlet excitations in the 28 molecules of the Thiel set, which has clarified multiple aspects of this excited-state-specific perturbation theory's behavior and performance. First, we found that the underlying ESMF possesses a well-defined excited-state-specific stationary point in 100 out of the 103 states tested, suggesting that such stationary points typically exist for singly excited singlet states in single-reference molecules. Second, we found that ESMP2 is highly sensitive to the size of a molecule's π system. For molecules with five or fewer orbitals in their π systems, unregularized ESMP2's mean unsigned error was 0.32 eV, while for molecules with six or more orbitals in their π system, it was 0.71 eV. Third, this sensitivity closely tracks the size of the ESMP2 doubles norm, which helps us understand the issue as a straightforward failure of perturbation theory brought about by doubly excited configurations that are too close in energy to the primary singles in the zeroth order reference. Fourth, although this sensitivity is bad news for accuracy, it allows the unregularized ESMP2 doubles norm to act as a reasonably effective predictor of doubly excited character. Finally, this sensitivity can be mitigated by repartitioning the zeroth order approximation via a level shift, resulting in the regularized ε-ESMP2 method that outperforms TD-DFT, CC2, EOM-CCSD, and even CC3 in overall accuracy on the singlet states in the Thiel set. While CASPT2 showed the highest overall accuracy, ε-ESMP2's unsigned error of just 0.17 eV on singly excited states was the lowest among methods that do not rely on an active space.

SUPPLEMENTARY MATERIAL

See the supplementary material for more detailed information of the electronic structure calculations presented in this article.

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recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

R.C. and J.A.R.S. contributed equally to this work.

Rachel Clune: Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Software (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **Jacqueline A. R. Shea**: Formal analysis (equal); Investigation (equal); Methodology (equal); Software (equal); Writing – original draft (supporting); Writing – review & editing (supporting). **Tarini S. Hardikar**: Investigation (supporting); Software (supporting); Writing – review & editing (supporting). **Harrison Tuckman**: Investigation (supporting); Software (supporting); Writing – review & editing (supporting). **Eric Neuscamman**: Conceptualization (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Project administration (equal); Resources (equal); Software (equal); Supervision (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

[1] I. R. Ariyarathna, C. R. Duan, and H. J. Kulik, "Understanding the chemical bonding of ground and excited states of HfO and HfB with correlated wavefunction theory and density functional approximations," J. Chem. Phys. **156**, 184113 (2022).

[2] N. Beizaei and S. P. A. Sauer, "Benchmarking correlated methods for static and dynamic polarizabilities: The T145 data set evaluated with RPA, RPA(D), HRPA, HRPA(D), SOPPA, SOPPA(CC2), SOPPA(CCSD), CC2, and CCSD," J. Phys. Chem. A **125**, 3785–3792 (2021).

[3] P. O. Dral, X. Wu, and W. Thiel, "Semiempirical quantum-chemical methods with orthogonalization and dispersion corrections," J. Chem. Theory Comput. **15**, 1743–1760 (2019).

[4] M. W. Jorgensen, R. Faber, A. Ligabue, and S. P. A. Sauer, "Benchmarking correlated methods for frequency-dependent polarizabilities: Aromatic molecules with the CC3, CCSD, CC2, SOPPA, SOPPA(CC2), and SOPPA(CCSD) methods," J. Chem. Theory Comput. **16**, 3006–3018 (2020).

[5] J. Pedersen and K. V. Mikkelsen, "A benchmark study of aromaticity indexes for benzene, pyridine and the diazines—I. Ground state aromaticity," RSC Adv. **12**, 2830–2842 (2022).

[6] P. Piecuch, J. A. Hansen, and A. O. Ajala, "Benchmarking the completely renormalised equation-of-motion coupled-cluster approaches for vertical excitation energies," Mol. Phys. **113**, 3085–3127 (2015).

[7] S. P. A. Sauer, H. F. Pitzner-Frydendahl, M. Buse, H. J. A. Jensen, and W. Thiel, "Performance of SOPPA-based methods in the calculation of vertical excitation energies and oscillator strengths," Mol. Phys. **113**, 2026–2045 (2015).

[8] J. Sharma and P. A. Champagne, "Benchmark of density functional theory methods for the study of organic polysulfides," J. Comput. Chem. **43**, 2131–2138 (2022).

[9] A. Tajti, B. Kozma, and P. G. Szalay, "Improved description of charge-transfer potential energy surfaces via spin-component-scaled CC2 and ADC(2) methods," J. Chem. Theory Comput. **17**, 439–449 (2021).

[10] D. Tuna, Y. Lu, A. Koslowski, and W. Thiel, "Semiempirical quantum-chemical orthogonalization-corrected methods: Benchmarks of electronically excited states," J. Chem. Theory Comput. **12**, 4400–4422 (2016).

[11] A. I. Krylov, "Equation-of-motion coupled-cluster methods for open-shell and electronically excited species: The Hitchhiker's guide to Fock space," Annu. Rev. Phys. Chem. **59**, 433–462 (2008).

[12] O. Christiansen, H. Koch, and P. Jørgensen, "The second-order approximate coupled cluster singles and doubles model CC2," Chem. Phys. Lett. **243**, 409–418 (1995).

[13] K. Sneskov and O. Christiansen, "Excited state coupled cluster methods," Wiley Interdisc. Rev.: Comput. Mol. Sci. **2**, 566–584 (2012).

[14] O. Christiansen, H. Koch, and P. Jørgensen, "Response functions in the CC3 iterative triple excitation model," J. Chem. Phys. **103**, 7429–7441 (1995).

[15] H. Koch, O. Christiansen, P. Jørgensen, A. M. Sanchez de Merás, and T. Helgaker, "The CC3 model: An iterative coupled cluster approach including connected triples," J. Chem. Phys. **106**, 1808–1818 (1997).

[16] T. J. Watson, V. F. Lotrich, P. G. Szalay, A. Perera, and R. J. Bartlett, "Benchmarking for perturbative triple-excitations in EE-EOM-CC methods," J. Phys. Chem. A **117**, 2569–2579 (2013).

[17] J. D. Watts and R. J. Bartlett, "Economical triple excitation equation-of-motion coupled-cluster methods for excitation-energies," Chem. Phys. Lett. **233**, 81–87 (1995).

[18] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* (Dover Publications, Mineola, NY, 1996).

[19] J. A. R. Shea and E. Neuscamman, "Communication: A mean field platform for excited state quantum chemistry," J. Chem. Phys. **149**, 081101 (2018).

[20] J. A. R. Shea, E. Gwin, and E. Neuscamman, "A generalized variational principle with applications to excited state mean field theory," J. Chem. Theory Comput. **16**, 1526–1540 (2020).

[21] R. Clune, J. A. R. Shea, and E. Neuscamman, "N^5-scaling excited-state-specific perturbation theory," J. Chem. Theory Comput. **16**, 6132–6141 (2020).

[22] A. Dreuw and M. Head-Gordon, "Single-reference ab initio methods for the calculations of excited states of large molecules," Chem. Rev. **105**, 4009 (2005).

[23] T. S. Hardikar and E. Neuscamman, "A self-consistent field formulation of excited state mean field theory," J. Chem. Phys. **153**, 164108 (2020).

[24] M. Schreiber, M. R. Silva-Junior, S. P. A. Sauer, and W. Thiel, "Benchmarks for electronically excited states: CASPT2, CC2, CCSD, and CC3," J. Chem. Phys. **128**, 134110 (2008).

[25] B. O. Roos, P. Linse, P. E. M. Siegbahn, and M. R. A. Blomberg, "A simple method for the evaluation of the second-order-perturbation energy from external double-excitations with a CASSCF reference wavefunction," Chem. Phys. **66**, 197–207 (1982).

[26] K. Andersson, P. Å. Malmqvist, and B. O. Roos, "Second-order perturbation theory with a complete active space self-consistent field reference function," J. Chem. Phys. **96**, 1218–1226 (1992).

[27] A. D. Laurent and D. Jacquemin, "TD-DFT benchmarks: A review," Int. J. Quantum Chem. **113**, 2019–2039 (2013).

[28] C. Bannwarth, J. K. Yu, E. G. Hohenstein, and T. J. Martínez, "Hole–hole Tamm–Dancoff-approximated density functional theory: A highly efficient electronic structure method incorporating dynamic and static correlation," J. Chem. Phys. **153**(2), 024110 (2020).

[29] S. Battaglia, L. Fransén, I. F. Galván, and R. Lindh, "Regularized CASPT2: An intruder-state-free approach," J. Chem. Theory Comput. **18**, 4814–4825 (2022).

[30] M. Feldt and A. Brown, "Assessment of local coupled cluster methods for excited states of BODIPY/Aza-BODIPY families," J. Comput. Chem. **42**, 144–155 (2021).

[31] S. Haldar, T. Mukhopadhyay, and A. K. Dutta, "A similarity transformed second-order approximate coupled cluster method for the excited states: Theory, implementation, and benchmark," J. Chem. Phys. **156**, 014110 (2022).

[32] M. Hodecker, S. M. Thielen, J. Liu, D. R. Rehn, and A. Dreuw, "Third-order unitary coupled cluster (UCC3) for excited electronic states: Efficient implementation and benchmarking," J. Chem. Theory Comput. **16**, 3654–3663 (2020).

[33] C. Holzer, "An improved seminumerical Coulomb and exchange algorithm for properties and excited states in modern density functional theory," J. Chem. Phys. **153**, 184115 (2020).

[34] M. Hubert, E. D. Hedegård, and H. J. A. Jensen, "Investigation of multiconfigurational short-range density functional theory for electronic excitations in organic molecules," J. Chem. Theory Comput. **12**, 2203–2213 (2016).

[35] E. M. Kempfer-Robertson, T. D. Pike, and L. M. Thompson, "Difference projection-after-variation double-hybrid density functional theory applied to the calculation of vertical excitation energies," J. Chem. Phys. **153**, 074103 (2020).

[36] C. Kollmar, K. Sivalingam, and F. Neese, "An alternative choice of the zeroth-order Hamiltonian in CASPT2 theory," J. Chem. Phys. **153**, 019901 (2020).

[37] G. Levi, A. V. Ivanov, and H. Jónsson, "Variational density functional calculations of excited states via direct optimization," J. Chem. Theory Comput. **16**, 6968–6982 (2020).

[38] C. A. McKeon, S. M. Hamed, F. Bruneval, and J. B. Neaton, "An optimally tuned range-separated hybrid starting point for *ab initio* GW plus Bethe–Salpeter equation calculations of molecules," J. Chem. Phys. **157**, 074103 (2022).

[39] S. P. Neville and M. S. Schuurman, "A perturbative approximation to DFT/MRCI: DFT/MRCI(2)," J. Chem. Phys. **157**, 164103 (2022).

[40] K. Pernal and O. V. Gritsenko, "Embracing local suppression and enhancement of dynamic correlation effects in a CASΠDFT method for efficient description of excited states," Faraday Discuss. **224**, 333–347 (2020).

[41] S. P. A. Sauer, M. Schreiber, M. R. Silva-Junior, and W. Thiel, "Benchmarks for electronically excited states: A comparison of noniterative and iterative triples corrections in linear response coupled cluster methods: CCSDR(3) versus CC3," J. Chem. Theory Comput. **5**, 555–564 (2009).

[42] Y. Song, Y. Guo, Y. Lei, N. Zhang, and W. Liu, "The static-dynamic-static family of methods for strongly correlated electrons: Methodology and benchmarking," Top. Curr. Chem. **379**, 43 (2021).

[43] P.-F. Loos, A. Scemama, and D. Jacquemin, "The quest for highly accurate excitation energies: A computational perspective," J. Phys. Chem. Lett. **11**, 2374–2383 (2020).

[44] D. Kánnár and P. G. Szalay, "Benchmarking coupled cluster methods on valence singlet excited states," J. Chem. Theory Comput. **10**, 3757–3765 (2014).

[45] D. Kánnár and P. G. Szalay, "Benchmarking coupled cluster methods on singlet excited states of nucleobases," J. Mol. Model. **20**, 2503 (2014).

[46] R. L. Martin, "Natural transition orbitals," J. Chem. Phys. **118**, 4775–4777 (2003).

[47] A. Karton, E. Rabinovich, J. M. L. Martin, and B. Ruscic, "W4 theory for computational thermochemistry: In pursuit of confident sub-kJ/mol predictions," J. Chem. Phys. **125**, 144108 (2006).

[48] T. J. Lee and P. R. Taylor, "A diagnostic for determining the quality of single-reference electron correlation methods," Int. J. Quantum Chem. **36**, 199–207 (1989).

[49] A. Schäfer, H. Horn, and R. Ahlrichs, "Fully optimized contracted Gaussian basis sets for atoms Li to Kr," J. Chem. Phys. **97**, 2571–2577 (1992).

[50] Q. Sun, T. C. Berkelbach, N. S. Blunt, G. H. Booth, S. Guo, Z. Li, J. Liu, J. D. McClain, E. R. Sayfutyarova, S. Sharma, S. Wouters, and G. K.-L. Chan, "PySCF: The Python-based simulations of chemistry framework," Wiley Interdiscip. Rev.: Comput. Mol. Sci. **8**, e1340 (2017).

[51] Y. Shao, Z. Gan, E. Epifanovsky, A. T. B. Gilbert, M. Wormit, J. Kussmann *et al.*, "Advances in molecular quantum chemistry contained in the Q-Chem 4 program package," Mol. Phys. **113**, 184–215 (2015).

[52] H.-J. Werner *et al.*, MOLPRO, version 2019.2, a package of *ab initio* programs, 2019, see https://www.molpro.net.

[53] G. Schaftenaar, E. Vlieg, and G. Vriend, "Molden 2.0: Quantum chemistry meets proteins," J. Comput.-Aided Mol. Des. **31**, 789–800 (2017).

[54] M. R. Silva-Junior, M. Schreiber, S. P. A. Sauer, and W. Thiel, "Benchmarks for electronically excited states: Time-dependent density functional theory and density functional theory based multireference configuration interaction," J. Chem. Phys. **129**, 104103 (2008).

[55] J. M. Barrera-Andrade, E. Rojas-Garcia, J. Garcia-Valdes, M. A. Valenzuela, and E. Albiter, "Incorporation of amide functional groups to graphene oxide during the photocatalytic degradation of free cyanide," Mater. Lett. **280**, 128538 (2020).

[56] D. D. Bume, C. R. Pitts, F. Ghorbani, S. A. Harry, J. N. Capilato, M. A. Siegler, and T. Lectka, "Ketones as directing groups in photocatalytic sp^3 C–H fluorination," Chem. Sci. **8**, 6918–6923 (2017).

[57] M. Deng, J. Wu, C. A. Reinhart-King, and C.-C. Chu, "Synthesis and characterization of biodegradable poly(ester amide)s with pendant amine functional groups and in vitro cellular response," Biomacromolecules **10**, 3037–3047 (2009).

[58] S. Gnaim, A. Scomparin, X. Li, P. S. Baran, C. Rader, R. Satchi-Fainaro, and D. Shabat, "Tagging the untaggable: A difluoroalkyl-sulfinate ketone-based reagent for direct C–H functionalization of bioactive heteroarenes," Bioconjugate Chem. **27**, 1965–1971 (2016).

[59] T. Kowalczyk, T. Tsuchimochi, P.-T. Chen, L. Top, and T. Van Voorhis, "Excitation energies and Stokes shifts from a restricted open-shell Kohn-Sham approach," J. Chem. Phys. **138**, 164101 (2013).

[60] K. B. Wiberg, A. E. de Oliveira, and G. Trucks, "A comparison of the electronic transition energies for ethene, isobutene, formaldehyde, and acetone calculated using RPA, TDDFT, and EOM-CCSD. Effect of basis sets," J. Phys. Chem. A **106**, 4192–4199 (2002).

[61] K. Nakayama, H. Nakano, and K. Hirao, "Theoretical study of the $\pi \rightarrow \pi^*$ excited states of linear polyenes: The energy gap between $1^1B_u^+$ and $2^1A_g^-$ states and their character," Int. J. Quantum Chem. **66**, 157–175 (1998).

[62] M. Krauss and S. R. Mielczarek, "Minima in generalized oscillator strengths: C_2H_4," J. Chem. Phys. **51**, 5241 (1969).

[63] R. Lindh and B. O. Roos, "A theoretical study of the diffuseness of the $V(^1B_{1u})$ state of planar ethylene," Int. J. Quantum Chem. **35**, 813–825 (1989).

[64] R. González-Luque, M. Merchán, and B. O. Roos, "Multiconfigurational perturbation theory (CASPT2) applied to the study of the low-lying singlet and triplet excited states of cyclopropene," Z. Phys. D: At., Mol. Clusters **36**, 311–316 (1996).

[65] L. Serrano-Andres, M. Merchán, I. Nebot-Gil, B. O. Roos, and M. Fülscher, "Theoretical study of the electronic spectra of cyclopentadiene, pyrrole, and furan," J. Am. Chem. Soc. **115**, 6184–6197 (1993).

[66] Y. J. Bomble, K. W. Sattelmeyer, J. F. Stanton, and J. Gauss, "On the vertical excitation energy of cyclopentadiene," J. Chem. Phys. **121**, 5236–5240 (2004).

[67] B. O. Roos, M. Merchan, R. McDiarmid, and X. Xing, "Theoretical and experimental determination of the electronic spectrum of norbornadiene," J. Am. Chem. Soc. **116**, 5927–5936 (1994).

[68] J. P. Doering and R. McDiarmid, "An electron impact investigation of the forbidden and allowed transitions of norbornadiene," J. Chem. Phys. **75**, 87–91 (1981).

[69] O. Christiansen, H. Koch, A. Halkier, P. Jörgensen, T. Helgaker, and A. Sánchez de Merás, "Large-scale calculations of excitation energies in coupled cluster theory: The singlet excited states of benzene," J. Chem. Phys. **105**, 6921–6939 (1996).

[70] M. Caricato, G. W. Trucks, M. J. Frisch, and K. B. Wiberg, "Electronic transition energies: A study of the performance of a large range of single reference density functional and wave function methods on valence and Rydberg states compared to experiment," J. Chem. Theory Comput. **6**, 370–383 (2010).

[71] O. Christiansen, J. Gauss, J. F. Stanton, and P. Jörgensen, "The electronic spectrum of pyrrole," J. Chem. Phys. **111**, 525–537 (1999).

[72] O. Christiansen and P. Jörgensen, "The electronic spectrum of furan," J. Am. Chem. Soc. **120**, 3423–3430 (1998).

[73] L. Serrano-Andrés, M. P. Fülscher, B. O. Roos, and M. Merchán, "Theoretical study of the electronic spectrum of imidazole," J. Phys. Chem. **100**, 6484–6491 (1996).

[74] Physical methods in heterocyclic chemistry," in *Index to Reviews, Symposia Volumes and Monographs in Organic Chemistry*, edited by N. Kharasch and W. Wolf (Pergamon, 1966), p. 195.

12 February 2024 17:51:37

[75] S. A. Asher and J. L. Murtaugh, "UV Raman excitation profiles of imidazole, imidazolium, and water," Appl. Spectrosc. **42**, 83–90 (1988).

[76] E. Bernarducci, P. K. Bharadwaj, K. Krogh-Jespersen, J. A. Potenza, and H. J. Schugar, "Electronic-structure of alkylated imidazoles and electronic-spectra of tetrakis(imidazole)copper(II) complexes. Molecular-structure of tetrakis(1,4,5-trimethylimidazole)copper(II) diperchlroate," J. Am. Chem. Soc. **105**, 3860–3866 (1983).

[77] D. S. Caswell and T. G. Spiro, "Ultraviolet resonance Raman-spectroscopy of imidazole, histidine, and Cu(imidazole)42+: Implications for protein studies," J. Am. Chem. Soc. **108**, 6470–6477 (1986).

[78] T. G. Fawcett, E. E. Bernarducci, K. Krogh-Jespersen, and H. J. Schugar, "Charge-transfer absorption of Cu(II)-imidazole and Cu(II)-imidazole chromophores," J. Am. Chem. Soc. **102**, 2598–2604 (1980).

[79] M. Gelus and J.-M. Bonnier, "UV spectrophotometry of some heterocycles," J. Chim. Phys. Phys.-Chim. Biol. **64**, 1602 (1967).

[80] P. E. Grebow and T. M. Hooker, "Conformation of histidine model peptides. II. Spectroscopic properties of imidazole chromophore," Biopolymers **14**, 871–881 (1975).

[81] J. Wan, M. Hada, M. Ehara, and H. Nakatsuji, "Electronic excitation and ionization spectra of azabenzenes: Pyridine revisited by the symmetry-adapted cluster configuration interaction method," J. Chem. Phys. **114**, 5117–5123 (2001).

[82] P.-F. Loos, F. Lipparini, M. Boggio-Pasqua, A. Scemama, and D. Jacquemin, "A mountaineering strategy to excited states: Highly accurate energies and benchmarks for medium sized molecules," J. Chem. Theory Comput. **16**, 1711–1741 (2020).

12 February 2024 17:51:37