Capturing multireference excited states by constrained-density-functional theory

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Capturing Multireference Excited States by Constrained DFT

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Abstract

The computation of excited electronic states with commonly employed (approximate) methods is challenging, typically yielding states of lower quality than the corresponding ground state for a higher computational cost. In this work, we present a mean field method that extends the previously proposed eXcited Constrained DFT (XCDFT) from single Slater determinants to ensemble 1-RDMs for computing low-lying excited states. The method still retains an associated computational complexity comparable to a semilocal DFT calculation while at the same time is capable of approaching states with multireference character. We benchmark the quality of this method on well-established test sets, finding good descriptions of the electronic structure of multireference states and maintaining an overall accuracy for the predicted excitation energies comparable to semilocal TDDFT.

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I. INTRODUCTION

Models of molecules and materials typically require the knowledge of excited electronic states and must be able to approach complex dynamical regimes. For example, in energy sciences and photochemistry, often the dynamics involve interaction with external electromagnetic fields or require to characterize states that are very close in energy. Thus, the task at hand is formulating a computationally efficient model of electronic excited states capable of handling the many difficult cases that, unfortunately, routinely arise.

Density Functional Theory (DFT) has been the workhorse of electronic structure theory for the computation of excited electronic states and their dynamics *via* its time-dependent extension (TDDFT). Unfortunately, TDDFT has some notable shortcomings when it is implemented in the adiabatic and the semilocal density approximations. Conical intersections, charge transfer states and Rydberg states are among those cases where practical implementations of TDDFT struggle to provide a physical model. More recently, multiconfigurational DFT methods, such as ensemble DFT [1–5], constrained DFT [6–8], block-localized DFT [9, 10], DFT/MRCI [11], and even flavors of ground state DFT [12] have been proposed as innovative protocols for extracting excitation energies in a computationally efficient way while still making use of density functionals in their formulation.

Constrained DFT [13] is particularly interesting because it does not need an active space and, instead, targets directly the excited states with the wanted character [14]. Traditionally it has been employed for generating charge and spin-localized states (diabatic states). However, recent works including our own have borrowed the general constrained DFT idea and proposed methods for computing valence excited states [6, 7, 15–17].

In this work, we continue the development of the eXcited Constrained DFT (XCDFT) method[7]. In XCDFT, a variational procedure produces excited states energies and densities of similar quality to the ground states ones for a similarly comparable computational cost. In essence, XCDFT exploits the machinery of ground state Kohn-Sham DFT for the generation of excited states [18–20]. Inspired by density functional perturbation theory [21], XCDFT does not require the use of unoccupied bands (virtuals) as it resolves the space of virtuals by projection. The Fock operator is then augmented by a nonlocal and orbital dependent constraining potential exerting a force on the electrons, leading to a selfconsistent solution for the targeted excited state. XCDFT is similar in spirit to ΔSCF without the inconvenience of incurring in variational collapses. In our previous publication [7], we carried out a careful comparison of XCDFT against ΔSCF, and linear-response semilocal TDDFT and found that its accuracy compares to them (about 0.5 to 1.0 eV deviation from benchmark values for the chosen test set).

Unfortunately and similar to ΔSCF, due to the fact that XCDFT makes use of a single Slater determinant, when approaching degenerate excited states it fails to produce correct electronic structures. This is problematic because degenerate electronic excited states are ubiquitous.

In this work, we take inspiration from ensemble DFT methods and propose the use of ensemble one-body reduced density matrices (1-RDMs) for describing the electronic structure of excited states. We dub the resulting method τXCDFT. This allows us to partially occupy excited state's Kohn-Sham orbitals and reach an accurate depiction of a multireference excited state at merely the expense of needing to compute a larger number of occupied orbitals.

The paper is organized as follows: we first describe the theory and implementation of τXCDFT and clearly show the involved approximations. After a short description of the computational details, needed for the reproducibility of the results, we apply τXCDFT on the same test set considered previously [7], as well as additional complex large molecules, such as anthracene, tetracene and fullerene. These are included because the description of their excited states' electronic structure may require more than single excitations from the reference determinant. Due to the variational nature of τXCDFT, the orbitals are relaxed to infinite order making up for the relaxation effects that are captured by multiple excitations in those wavefunction-based methods exploiting a reference determinant.

II. THEORY AND BACKGROUND

The starting point of an XCDFT calculation is a reference ground state (gs) obtained from a regular KS calculation. From that, a projection operator $\hat{P}_o^g$ over the occupied space of gs, $\{|i_g\rangle\}$, is constructed. Namely,

$$\hat{P}_o^g = \sum_{i_g=1}^{\mathrm{occ}} |i_g\rangle\langle i_g|. \tag{1}$$

The electronic excitations are obtained by applying a nonlocal potential, $\hat{W}_c$, whose action is to "fish out" a custom number of electrons (i.e., N_c, which we take to be $N_c = 1$ throughout this work) into the virtual space of the reference gs. In the basis of the atomic orbitals (customarily indicated by Greek letters, ν and μ), such potential is written as:

$$\left(\hat{W}_c\right)_{\mu\nu} = \langle\mu|\hat{1} - \hat{P}_o^g|\nu\rangle, \tag{2}$$

which then is used to define the constraint that only N_c electrons should be excited to the virtual space of the reference gs,

$$N_c = \sum_{j=1}^{\mathrm{occ}} \langle j_e|\hat{1} - \hat{P}_o^g|j_e\rangle \equiv \mathrm{Tr}\left[\hat{W}_c\hat{\gamma}_e\right] = N_e - \sum_{i_g, j_e=1}^{\mathrm{occ}} \langle j_e|i_g\rangle\langle i_g|j_e\rangle. \tag{3}$$

Where $\hat{\gamma}_e$ is the 1-RDM of the excited state, N_e is the total number of electrons, N_c the number of excited electrons (which is typically taken to be $N_c = 1$), and $|j_e\rangle$ are the excited state occupied orbitals which are selfconsistently determined by the following KS-like equation,

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r}) + V_c\hat{W}_c\right]|j_e\rangle = \varepsilon_{j_e}|j_e\rangle, \tag{4}$$

where $v_s(\mathbf{r})$ is the Kohn-Sham potential, ε_{j_e} are the orbital energies and V_c is an appropriate Lagrange multiplier that ensures the constraint Eq. (3) is satisfied. In other words,

$$\frac{\delta E[\hat{\gamma}_e]}{\delta N_c} = -V_c, \tag{5}$$

where $E[\hat{\gamma}_e]$ is the total energy functional [7, 22]. In this context, V_c equals the value of the excitation energy (i.e., the work needed to excite one electron) and needs to be determined selfconsistently.

XCDFT yields excitation energies in semiquantitative agreement with TDDFT and benchmark calculations, however, we noticed [7] that whenever it is required to go beyond a single Slater determinant, spurious contributions from more than singly excited configuration state functions arise degrading the excited state's electronic structure. One particularly deteriorating factor is the resulting significant overlap with the gs KS wavefunction. As this problem only arises when multreference excited states are considered, we turned to the several studies carried out to understand and deal with static correlation in Kohn-Sham

DFT[23–25]. It is known that when near degeneracies arise (typical case of a multireference system), an ensemble of noninteracting electrons provides a more convenient reference than typical single Slater determinants[24, 26]. Thus, in this work, we allow XCDFT excited states to probe ensemble 1-RDMs as follows:

$$\hat{\gamma}_e = \sum_{j_e} |j_e\rangle f_{j_e} \langle j_e|, \tag{6}$$

with f_{j_e} are the occupation numbers which are determined by the Fermi-Dirac distribution function,

$$f_{j_e} \equiv f(\epsilon_{j_e} - \mu) = \left[1 + \exp(\beta(\varepsilon_{j_e} - \mu))\right]^{-1}, \tag{7}$$

with $\beta = \frac{1}{k_B \tau}$ (a parameter of the method), μ can be thought of as a chemical potential. Smearing the orbital occupations is a well-known strategy that has been used in mean-field calculations[27] of both finite and periodic systems when degeneracies appear.

Thus, Eq. (3) is modified to

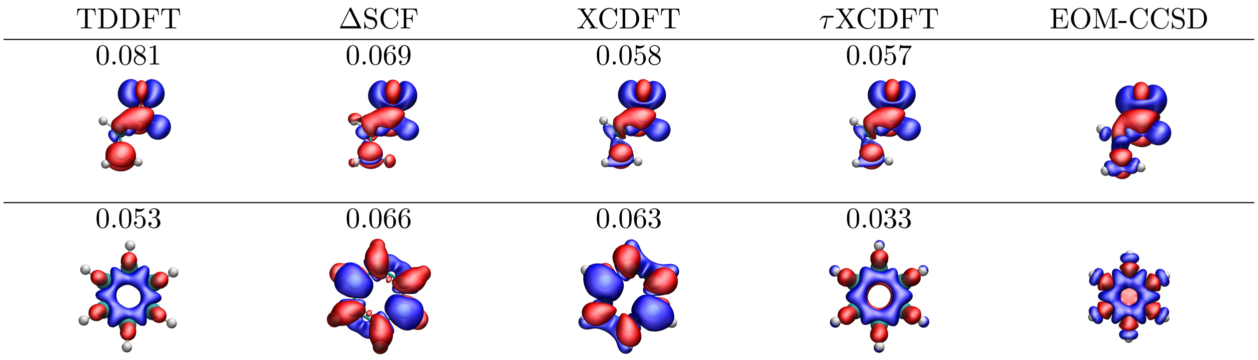
$$N_c = \mathrm{Tr}\left[\hat{W}_c \hat{\gamma}_e\right] = N_e - \sum_{i_g}^{occ} \sum_{j_e}^{\infty} \langle i_g | j_e \rangle f_{j_e} \langle j_e | i_g \rangle. \tag{8}$$

We dub the resulting method τXCDFT.

III. COMPUTATIONAL DETAILS

All XCDFT and τXCDFT excited state calculations are performed with a development version of the Amsterdam Density Functional (ADF) 2019 program[28]. To assess the performance of τXCDFT, we consider the lowest excited state for a set of fifteen molecules [7] with the addition of the anthracene, tetracene and fullerene. As described above (see theory section) we rely on the approximation that smearing provided by the Fermi–Dirac distribution function is sufficient to account for the fractional occupations resulting from the multireference character of certain excited states. This smearing can be achieved by employing a Fermi–Dirac distribution with $\tau = 500$ K which is consistently applied to all systems considered. The chemical potential, μ, is obtained by imposing the number of electrons be equal to N_e through finding the root by bisection of the function $f(\mu) = N(\mu) - N_e$. After

FIG. 1: Comparison of the computed differential densities for Acrolein (top) and benzene (bottom). We show all DFT functionals used against EOM-CCSD. The standard deviation, σ, of each density difference against EOM-CCSD densities (calculated using Gaussian [34]) are shown.



some testing, the numerical convergence of this root-finding algorithm could not be achieved for τ values much lower than 500 K. Therefore, $\tau = 500$ K is a choice that avoids unwanted occupations of high-lying virtual orbitals while delivering a stable algorithm. The GGA functional PBE[29], and the metaGGA functionals M06L[30], SCAN[31] and revTPSS[32] are employed across the entire study along with the TZP basis set. We report XCDFT and τXCDFT excitation energies by using the value of the corresponding V_c Lagrange multiplier. In addition, the differential densities obtained with XCDFT are compared against the ones obtained from TDDFT, calculated with ORCA [33].

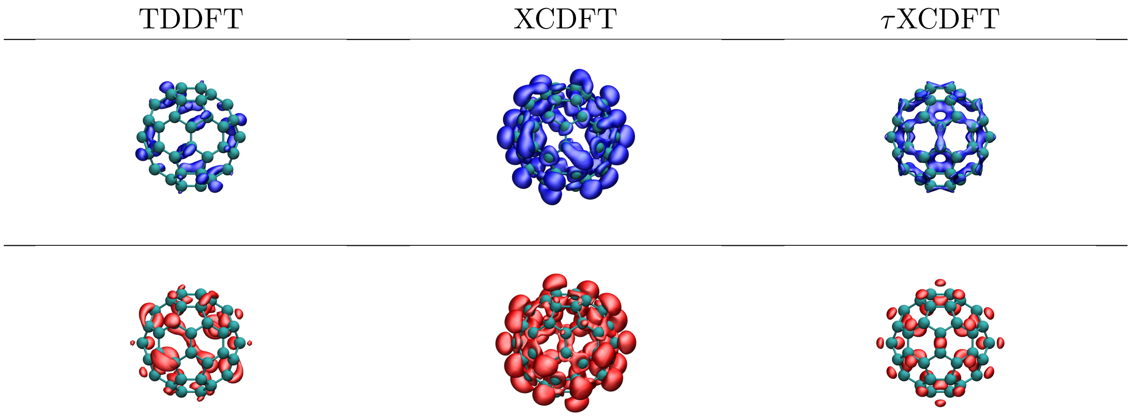
IV. RESULTS AND DISCUSSION

A. Quality of the electron density

We carried out an analysis of the electronic densities by comparing the differential densities (i.e., the density difference between the excited state and ground state densities, $\Delta(\mathbf{r}) = \rho_e(\mathbf{r}) - \rho_g(\mathbf{r})$) obtained form τXCDFT, XCDFT, TDDFT and EOM-CCSD. In Figure 1, $\Delta(\mathbf{r})$ is displayed for acrolein and benzene.

EOM-CCSD is accurate for these systems, as both single and double excitations are accounted for in the method. In Figure 1, we can see that the τXCDFT densities are improved with respect to the other methods. In our previous work [7], we showed that XCDFT densi-

FIG. 2: Fullerene density differences divided by contribution $\Delta(\mathbf{r}) > 0$ in blue (top), and $\Delta(\mathbf{r}) < 0$ in red (bottom). All isosurfaces are plotted with the same cutoff.



ties (especially benzene) are as inaccurate as the ones computed with ΔSCF and the results of Figure 2 confirm this observation also for other molecules featuring exact degeneracy (such as fullerene). We notice that τXCDFT is able to capture more accurately the electron density of the excited states compared to the original XCDFT. TDDFT is overall in good agreement with the benchmark, however, it lacks some small features. For example, the negative equatorial component in the EOM-CCSD density of benzene is partially present in τXCDFT but absent in TDDFT (as we could verify by inflating the isosurfaces and double checking the cube files). Such nodal structure in the differential densities are commonly found in the literature and are expected when substantial orbital relaxation occurs. Accounting for orbital relaxation in linear-response TDDFT has been a matter of intense study. For example Tom Ziegler's work on constricted varitaional TDDFT[15–17, 35] aimed at capturing orbital relaxation *via* a variational energy minimization wrt orbital rotations.

For acrolein, there are no degeneracies and thus τXCDFT and XCDFT deliver the same result which compares well against EOM-CCSD.

The orbital relaxation is also seen in fullerene (see Figure 2), where the τXCDFT differential density follows the TDDFT one but is more delocalized indicating relaxation. Unfortunately, due to the large computational expense involved, we do not have an EOM-CCSD calculation available to further confirm our findings.

From the above analysis, it is clear that the restriction in XCDFT and ΔSCF to a single Slater determinant is detrimental to the quality of the electronic structure of multireference excited states. In particular, focussing on the benzene molecule, we notice that in order to satisfy the criterion of excitation of a single electron, XCDFT's excited state orbitals are mixed (e and g superscripts indicate excited and ground state, respectively):

$$\phi^e_H(\mathbf{r}) = \frac{1}{\sqrt{2}}\left[\phi^g_H + \phi^g_{L+1}\right], \tag{9}$$

$$\phi^e_{H-1}(\mathbf{r}) = \frac{1}{\sqrt{2}}\left[\phi^g_{H-1} + \phi^g_{L}\right]. \tag{10}$$

As a result, the excited state wavefunction can be represented by the following superposition of configuration state functions built from the reference ground state and associated excited Slater determinants. Namely,

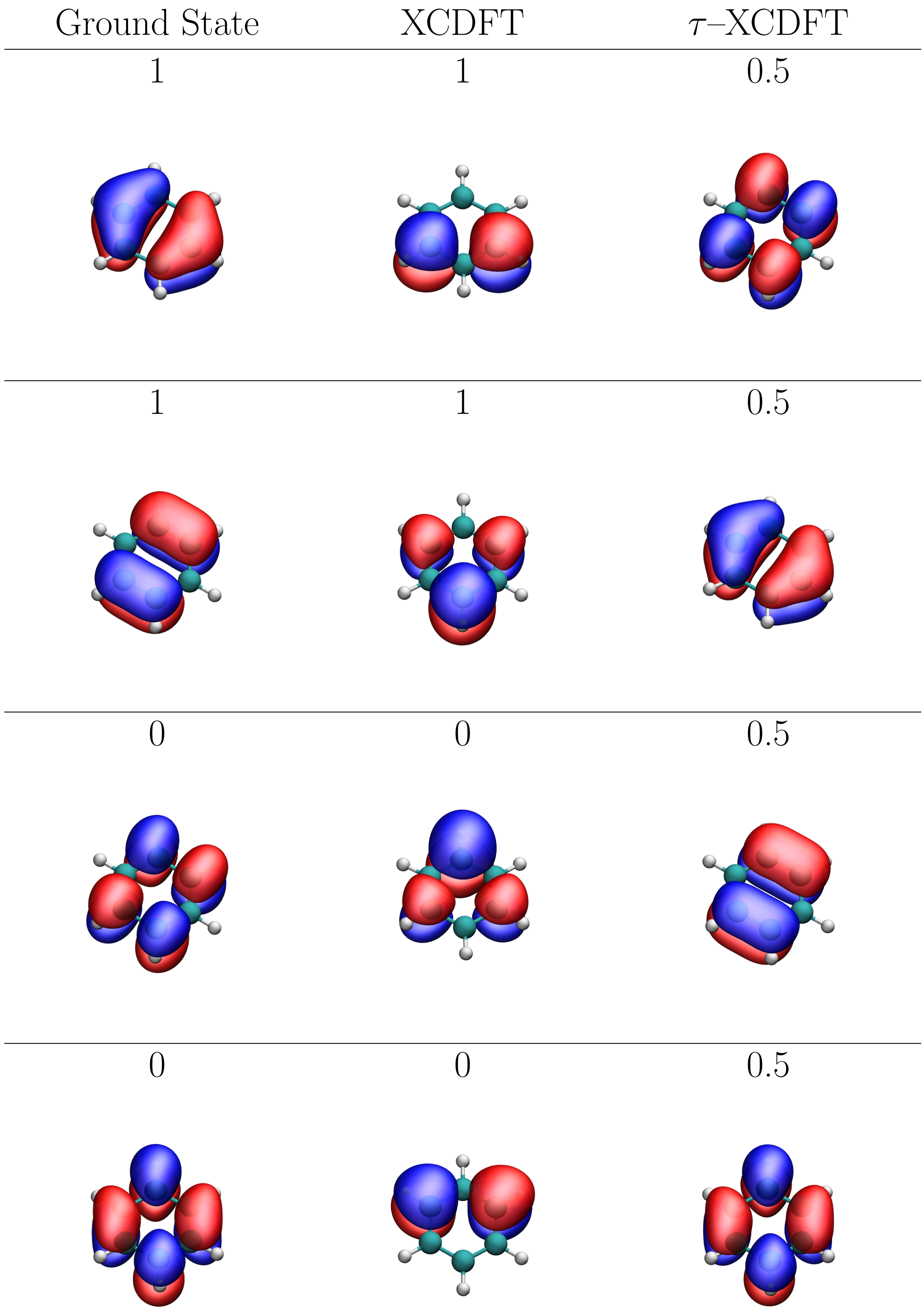
$$\Psi_e = \frac{1}{2}\Psi_g + \frac{1}{2}\Psi^L_{H-1} + \frac{1}{2}\Psi^{L+1}_H + \frac{1}{2}\Psi^{L,L+1}_{H-1,H}. \tag{11}$$

The above, clearly indicates that the XCDFT excited state wavefunction, Ψ_e, has strong overlap with the ground state wavefunction, Ψ_g, and an equally strong double excitation character arising from the $\Psi^{L,L+1}_{H-1,H}$ term.

In our trial calculations (not reported), we have noticed that the above described issue is shared among aromatic chromophores, casting serious doubts about the physicality of ΔSCF excited states which are frequently used as initial conditions for nonadiabatic dynamics simulations.

In Figure 3, we plot the frontier occupied and virtual orbitals of the ground, XCDFT and τXCDFT excited states. The figure indicates that the τXCDFT orbitals largely resemble the ground state orbitals with some small deviations due to orbital relaxation effects (typically accounted for in wavefunction methods by high order excitation contributions). Instead, the XCDFT orbitals are very different from the ground state ones indicating that in XCDFT, in order to satisfy the imposed constraint in Eq. (3), the frontier orbitals have mixed and rotated dramatically exposing an unphysical character. Thus, we can conclude this analysis by stating that for multireference excited states, τXCDFT orbitals indicate a degree of relaxation compared to the ground state orbitals while still retaining the overall character resulting in differential densities in agreement with EOM-CCSD calculations. A similar analysis can be carried out for Fullerene, although it is not reported.

FIG. 3: Comparison of the frontier molecular orbitals of benzene obtained with τXCDFT and XCDFT against the corresponding ground state orbitals. The occupation numbers of these orbitals are shown.



B. Quality of the excitation energies

We summarize in Table I the excitation energies computed with τXCDFT along with available benchmark data [36–41]. The performance of τXCDFT improves against XCDFT as the character of the states involved are now corrected. We find that for multireference excited states (pyrrole, benzene, and fullerene) the energies are slightly closer to the benchmark. In addition, in Figure S2 of the supplementary information, we show the electronic entropy computed for every excited state. By "electronic entropy" we refer to the electronic Gibbs entropy which in this context can also be called Shannon entropy, $S = -\sum_i p_i \ln(p_i) + (1 - p_i)\ln(1 - p_i)$. Entropy in this context has no thermodynamical meaning, rather it has an information theory meaning. I.e., it describes distributions (in this case distributions of occupation numbers) that are not infinitely narrow, but instead have a finite width. As expected, benzene and fullerene are those systems with the highest multireference character. In our previous work (Ref. 7 and an erratum to appear, see also supplementary materials Table S2), we used a different descriptor for detecting multireference character. Specifically, we used the eigenvalues of the difference between the excited state and the ground state 1-RDMs which led us to label as "mixed" additional molecules to the ones mentioned here such as naphthalene, pentcene and adenine. These molecules still display a multireference excited state in the context of the preset work, however, most likely the multireference character is captured already at the level of the orbital relaxation with no need to involve fractional orbital occupations. This explains why the entropy for these 3 systems is negligible, while the descriptor previously used flags them as multireference.

In principle τXCDFT should lead to higher accuracy excitation energies than XCDFT for mixed excited states. In practice, however, both XCDFT and ΔSCF take advantage of error cancellation [7]. As we have seen in our previous work, while for HOMO-LUMO excitations ΔSCF performs well [42], in the presence of a degenerate excited state, single-reference methods will result in HOMO-LUMO mixing (and mixing of lower/higher-lying orbitals depending on the system, see Eq. (9–11)). This generates an excited state Slater determinant that is a mix of ground, single excitations and double excitations. The single excitations are associated with an accurate energy, the double excitation are associated with a much higher energy, and the ground state contribution effectively hedge the double excitations. In our tests, τXCDFT never generates occupied-virtual mixed orbitals and

TABLE I: τXCDFT excitation energy values (in eV) for all exchange-correlation functionals considered. In bold font the excitation energies of systems with excited states of mixed character as seen in Figure S2.

System	PBE	M06–L	SCAN	revTPSS	Benchmark
Ethylene	6.06	6.14	5.90	6.08	7.80
Tetrafluoroethylene	6.23	6.59	6.42	6.35	7.08
Isoprene	4.99	4.53	4.35	5.32	5.74
1,3-Butadiene	4.56	4.51	4.35	4.56	6.18
Formaldehyde	3.95	3.48	2.86	3.48	3.88
Propanamide	5.76	5.51	5.11	5.79	5.72
Acrolein	3.89	3.28	2.68	3.42	3.75
Pyrrole	**5.46**	**5.73**	**5.52**	**5.57**	6.37
Thiophene	5.28	5.30	5.03	5.13	5.64
Benzaldehyde	3.75	3.31	2.67	3.49	3.34
Adenine	4.55	4.68	4.46	4.66	5.25
Cytosine	4.31	4.87	4.67	4.61	4.66
Benzene	**5.19**	**5.47**	**5.37**	**5.36**	5.08
Naphthalene	4.01	3.94	3.77	3.97	4.24
Anthracene	3.12	3.04	2.89	3.06	3.55
Tetracene	2.14	2.03	1.90	2.06	2.95
Pentacene	1.96	1.87	1.73	1.88	2.30
Fullerene	**1.59**	**1.73**	**1.69**	**1.65**	1.75

delivers higher quality electronic structures.

In Table II, we show the mean unsigned error (MUE) for the excitation energies computed with τXCDFT, XCDFT, ΔSCF, and TDDFT. The MUE shows that τXCDFT and XCDFT are comparable to TDDFT and significantly better than ΔSCF. We see that among all metaGGA functionals, revTPSS is the better performing. In an effort to explain some of the trends, in Figure 4 we report a histogram of a measure of spin contamination τXCDFT and XCDFT collecting all exchange-correlation functionanls considered (i.e., overlap between the α and β orbitals). The histograms show that overall the spin contamination is well handled by XCDFT and τXCDFT. However, we notice that in τXCDFT the spin contamination is less prevalent, and we also note that the systems with high contamination (above 0.5) correspond to benzene and fullerene (i.e., where there are strong degeneracies among the

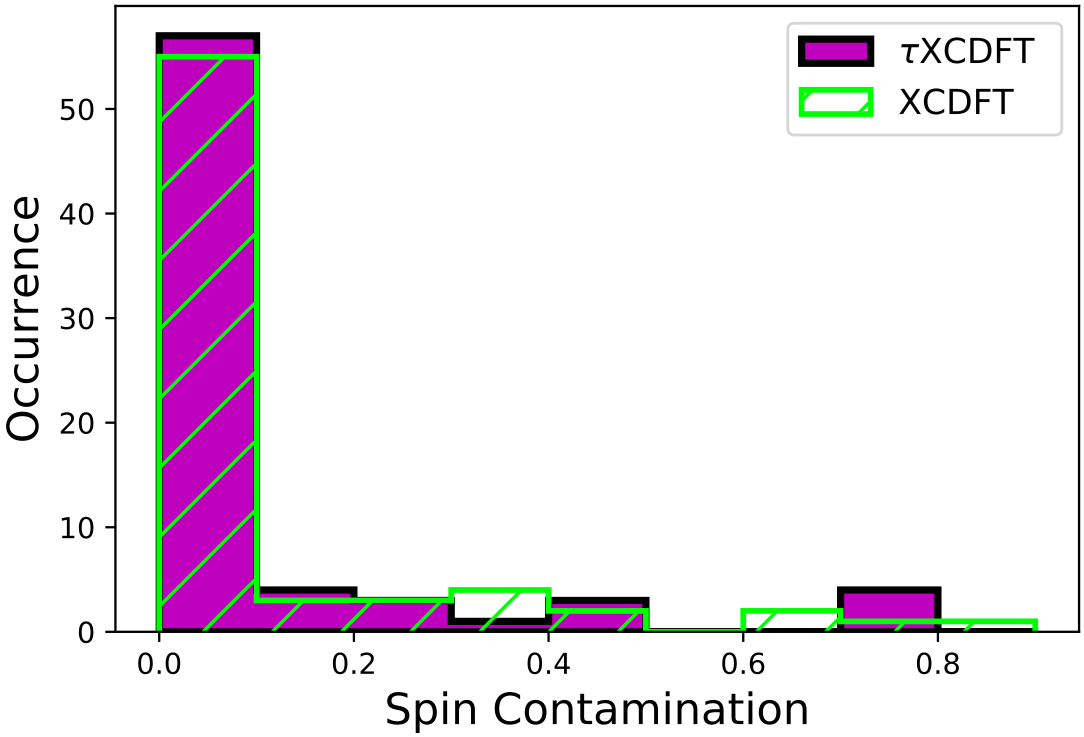


FIG. 4: Histogram of the spin contamination for all XCDFT and τXCDFT excited states collecting all exchange-correlation functionals.

frontier orbitals) computed with the SCAN functional.

TABLE II: Mean unsigned error (MUE) against benchmark values across the entire set of all excitation energies computed for all exchange-correlation functionals and methods considered.

Method	PBE	M06–L	SCAN	revTPSS
XCDFT	0.677	0.447	0.378	0.503
τXCDFT	0.566	0.591	0.816	0.557
ΔSCF	1.320	0.790	1.660	1.420
TDDFT	0.390	0.620	0.513	0.375

For sake of a complete presentation, we carry out an analysis of the sensitivity of the results with the chosen Fermi-Dirac smearing. We report our finding in Figure S1 and Table S1 of the supplementary information. Generally, τXCDFT energies improve if the KS gap is much smaller than the true gap of the interacting system. This points to a negative aspect of using unnecessarily broad smearing parameters ($\tau > 500$), i.e., the Fermi-Dirac distribution may populate high-lying virtual orbitals, which is not desired.

V. CONCLUSIONS

In conclusion, we developed, implemented in the ADF program, and benchmarked a mean field method for the computation of low-lying electronic excited states, τXCDFT. This method is capable of accounting for degenerate energy levels often present in excited states, such as aromatic chromophores. We show that quality low-lying excited states are found by using ensemble 1-RDMs. We also show that when considering multireference excited states, mean field methods that employ a single Slater determinant (such as ΔSCF and XCDFT) completely fail in predicting the electronic structure. τXCDFT, instead reproduces the electronic density of these excited states, avoids incorrect rotation among the frontier orbitals and correctly features effects of orbital relaxation.

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