

2018

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Recommended Citation

Stoneburner, Samuel J.; Truhlar, Donald G.; and Gagliardi, Laura, "MC-PDFT Can Calculate Singlet-Triplet Splittings of Organic Diradicals." (2018). *Educator Scholarship*. 5.
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MC-PDFT Can Calculate Singlet-Triplet Splittings of Organic Diradicals

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Abstract. The singlet-triplet splittings of a set of diradical organic molecules are calculated using multiconfiguration pair-density functional theory (MC-PDFT) and the results are compared with those obtained by Kohn-Sham density functional theory (KS-DFT) and complete active space second-order perturbation theory (CASPT2) calculations. We found that MC-PDFT, even with small and systematically defined active spaces, is competitive in accuracy with CASPT2, and it yields results with greater accuracy and precision than Kohn-Sham DFT with the same parent functional. MC-PDFT also avoids the challenges associated with spin contamination in KS-DFT. It is also shown that MC-PDFT is much less computationally expensive than CASPT2 when applied to larger active spaces, and this illustrates the promise of this method for larger diradical organic systems.

Our objective here is to validate multiconfiguration pair-density functional theory (MC-PDFT) for predicting the energy splitting between singlet and triplet states of organic diradical molecules. Diradicals have two unpaired electrons, usually in degenerate or nearly degenerate molecular orbitals. For the present study we define the singlet–triplet splitting (ΔE_{ST}) as the vertical transition energy between the lowest-energy triplet state and the lowest-energy singlet state (positive if the triplet is lower in energy, negative if the singlet state is lower in energy). Calculating ΔE_{ST} can be challenging, since the lowest singlet state is inherently multiconfigurational due to the near-degeneracy of the singly occupied molecular orbitals (SOMOs).¹ Inherently multiconfigurational systems usually require careful balancing of dynamic and static correlation energy, and in wave function theory this typically requires either expensive post-self-consistent-field (SCF) dynamic correlation calculations to be added to a multi-configuration self-consistent-field (MCSCF) reference function or even more expensive high excitations (for example, quadruples) to be added to a single-configuration SCF reference function.

If one wishes to use a theory with a single-configuration SCF wave function, such as Kohn-Sham (KS) density functional theory (DFT), it is important to understand that open-shell determinants are generally not spin eigenfunctions. As a result, the expectation value of the S^2 operator (where S is total electron spin) is not equal to the correct value (i.e., $S(S+1)$) for a given spin multiplicity;^{2,3} this is commonly called “spin contamination.” In spin-unrestricted KS-DFT, the expectation value of S^2 is calculated from the determinant,³ and nonzero amounts of spin contamination are always present.² (A review of spin in open-shell KS-DFT calculations is beyond the scope of this work; interested readers may consult the detailed discussion in Ref. 3.) In order to obtain accurate singlet and triplet energies in KS-DFT, one uses broken-spin-symmetry functions⁴ in which the SCF determinants are mixtures of singlet and triplet states. For diradicals, spin contamination is much greater than for simple radicals (e.g., the spin contamination is much greater for very stretched H_2 , which is a diradical, than for Li atom, which is a simple radical). There have been numerous efforts to “decontaminate” broken-spin-symmetry results,^{5,6,7,8,9,10} and they have met with some success,⁴ but the methods are not completely satisfactory.^{11,12,13}

Broken spin-symmetry is not required when the SCF function is a properly symmetrized MCSCF wave function, such as a complete active space self-consistent field (CASSCF)¹⁴ or a restricted active space self-consistent field (RASSCF)¹⁵ wave function. A CASSCF wave function partitions the molecular orbitals into three categories: inactive, active, and secondary. Active orbitals are permitted to take any occupation, while inactive and secondary orbitals are kept doubly occupied and unoccupied, respectively. Static correlation, i.e., correlation arising from inherently multiconfigurational character, is accounted for by doing full configuration

interaction (CI) within the active space. However, dynamic correlation (due to fully representing the Coulomb hole at short electron-electron distances or correlating subsystem multipole moments for separated subsystems) is not fully accounted for in CASSCF, and this necessitates a post-SCF calculation such as second-order perturbation theory (CASPT2)^{16,17}. Similar remarks apply to RASSCF and RASPT2,¹⁸ with the difference being that some less important excitations are left out in the MCSCF step. While CASPT2 and RASPT2 methods provide good accuracy for many problems, they rapidly become unaffordably expensive as active-space size increases. Multiconfiguration pair-density functional theory (MC-PDFT)¹⁹ was created to combine the benefits of multiconfigurational self-consistent field calculations, such as CASSCF or RASSCF, for representing the character and spin symmetry of inherently multiconfigurational states with the speed and cost advantages of density functional theory (DFT) for calculating the dynamic correlation energy. MC-PDFT employs an on-top density functional (which is a functional of the total electron density and the on-top pair density, which is the probability that two electrons are found at a given point); the kinetic energy and classical electrostatic energy are taken from the MCSCF results, while the electron exchange and additional correlation energy (where the latter includes the difference between the accurate kinetic energy and the MCSCF kinetic energy) are provided by the on-top functional. Because the electron density and on-top densities are taken from the MCSCF wave function, which is a spin eigenfunction, there is no spin contamination.

MC-PDFT has already been shown to be competitive in accuracy with the more expensive CASPT2 method for a variety of cases, including electronic excitation energies of organic molecules and transition-metal bond dissociation energies.^{20,21,22,23} Additionally, systematic choices for the active space in the preceding MCSCF calculation have been explored with the correlated participating orbital (CPO) scheme.²⁴ CPO has been successfully used in conjunction with MC-PDFT for both transition metal bond dissociation energies²⁵ and simple divalent diradicals.²⁶ In a recent paper²⁷ we described the application of the CPO scheme to anti-aromatic diradical systems to design active spaces for CASSCF/CASPT2 and RASSCF/RASPT2 calculations. Due to the wide variances in other published ΔE_{ST} values, new reference calculations were performed using doubly electron-attached (DEA) equation-of-motion (EOM) coupled-cluster (CC) calculations. The CASPT2 and RASPT2 results compared well with the DEA-EOM-CC reference results for most of the active spaces considered. CASPT2 and RASPT2 had mean unsigned errors (MUEs) of less than 1 kcal/mol, while the multireference coupled-cluster results of Saito et al. had MUEs of over 3 kcal/mol. We now show that similarly accurate results can be obtained using MC-PDFT, but at a much lower cost.

Computational details. The seven systems considered in this work are shown in Figure 1, namely square cyclobutadiene (**1**), cyclopentadienyl cation (**2**), aminocyclobutadiene (**3**), formylcyclobutadiene (**4**), 1-amino-2-formylcyclobutadiene (**5**), 1,2

basis(methylene)cyclobutadiene (**6**), and 1,3-basis(methylene)cyclobutadiene (**7**). These systems were chosen in our previous paper²⁷ for the sake of comparison to the multireference coupled-cluster work of Saito et al.⁴ To be consistent with the benchmark results to which we compare, geometries were taken from Saito et al.⁴ (Their geometries correspond to the triplet for systems **1** to **5**, but for the other two systems it is not stated in their work whether the geometries are for the singlet or the triplet.) The singlet-triplet energy gap, ΔE_{ST} , was calculated as the difference between the lowest singlet state and the lowest triplet state:

$$\Delta E_{ST} = E_{\text{singlet}} - E_{\text{triplet}} \quad (1)$$

where a positive/negative sign indicates the triplet/singlet is lower.

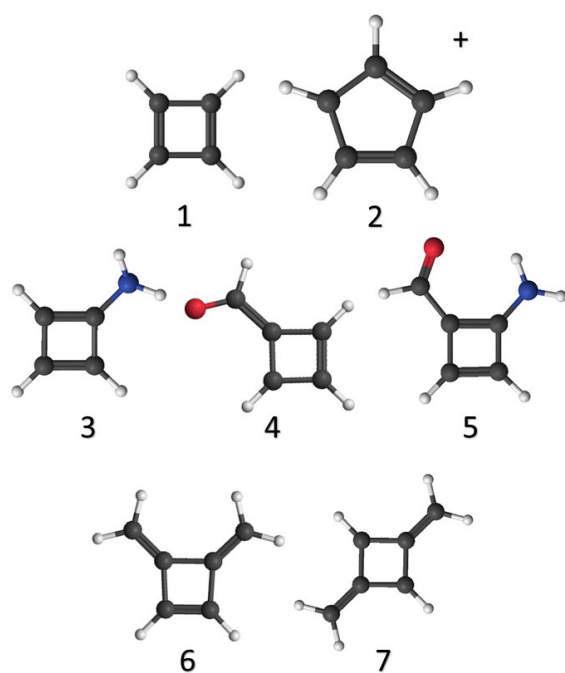


Figure 1: Diradical systems under investigation. **1**: C_4H_4 , **2**: $C_5H_5^+$, **3**: $C_4H_3NH_2$, **4**: C_4H_3CHO , **5**: $C_4H_2NH_2CHO$, **6**: $C_4H_2-1,2-(CH_2)_2$, **7**: $C_4H_2-1,3-(CH_2)_2$.²⁷

MC-PDFT calculations were performed using the maug-cc-pVTZ²⁸ and ANO-RCC-VTZP²⁹ basis sets with Cholesky decomposition³⁰ using *Molcas* 8.2.³¹ For MC-PDFT, several on-top functionals were used: translated¹⁹ and fully translated²² versions of LSDA,³² BLYP,^{33,34} PBE,³⁵ and revPBE,³⁶ labeled as tLSDA, tBLYP, tPBE, and trevPBE for the translated and ftLSDA, ftBLYP, ftPBE, and ftBLYP for the fully translated functionals.

We used the CPO active spaces developed in our previous work.²⁷ The full descriptions of these spaces can be found there, but we briefly summarize them here. In a CPO scheme, one first selects a set of primary orbitals, and then one adds a correlating orbital to each primary

orbital that is not already correlated. The four levels of the CPO scheme employed here and their corresponding choices of primary orbitals are as follows:

- nominal CPO (nCPO): The primary orbitals are the frontier orbitals, which in all cases except **5** are the two singly occupied molecular orbitals (SOMOs). For system **5**, one of the frontier orbitals is doubly occupied and the other is unoccupied, so the frontier orbitals are the highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO) instead of SOMOs.
- π CPO: The primary orbitals include all π orbitals of all atoms involved in the frontier orbitals.
- moderate CPO (mCPO): The primary orbitals include all p orbitals of all atoms involved in the frontier orbitals.
- extended CPO (eCPO): The primary orbitals include all p and s orbitals of all atoms involved in the frontier orbitals.

We used both CASSCF and RASSCF with the above active spaces. While in CASSCF, all active orbitals are in a single active space, in RASSCF, there are three subspaces: RAS1 contains doubly occupied orbitals, with limited excitations into RAS2 and RAS3 permitted. RAS3 contains unoccupied orbitals, with limited excitations from RAS1 and RAS2 permitted. RAS2 orbitals can have any occupancy, i.e., they are treated with full CI. We employed the same space subdivisions as in our previous work:²⁷

- Valence- π RASSCF: All valence π orbitals are in RAS2. All remaining doubly occupied active orbitals are in RAS1, and all remaining unoccupied active orbitals are in RAS3.
- Limited- π RASSCF: Similar to valence- π , except that only the highest two occupied (singly or doubly) π orbitals are in RAS2. Any additional occupied π orbitals are in RAS1, and their correlating orbitals are in RAS3.

In both kinds of RASSCF, up to 2 electrons are permitted to be excited from RAS1, and up to 2 electrons are permitted to be excited into RAS3.

As discussed in our previous work,²⁷ CI-only calculations (i.e., CI without SCF) were used in three cases where CASSCF or RASSCF was not possible. For systems **6** and **7** with limited- π RASSCF- π CPO, the RASSCF calculations did not converge, so CI-only calculations were performed using orbitals from the valence- π RASSCF- π CPO active space. The CASSCF-mCPO calculation for system **2** was prohibitively expensive, so CI-only calculations were performed using orbitals from the valence- π RASSCF-mCPO active space.

*Gaussian 09*³⁷ with the maug-cc-pVTZ basis set was used for KS-DFT calculations using the PBE and PBE0³⁸ exchange-correlation functionals. All KS-DFT calculations were spin-unrestricted. Two methods were used to calculate ΔE_{ST} from KS-DFT energies: The first

method, called the variational method, uses Eq. 1 with the variationally lowest-energy solution, and the second method, called the weighted-average broken-symmetry (WABS) method, uses the Yamaguchi formula^{4,39,40,41} for the singlet energy, which results in

$$\Delta E_{ST} = \frac{-2S_{\text{triplet}}(E_{\text{triplet}} - E_{\text{singlet}})}{\langle S^2 \rangle_{\text{triplet}} - \langle S^2 \rangle_{\text{singlet}}} \quad (2)$$

where $\langle S^2 \rangle$ is the expectation value of the square of the total electron spin (calculated from the electron density) and S_{triplet} is calculated by

$$S_{\text{triplet}}(S_{\text{triplet}} + 1) = \langle S^2 \rangle_{\text{triplet}} \quad (3)$$

Note that a similar equation was used in a previous paper,²⁶ but here we insert a negative sign to conform to the convention used here that ΔE_{ST} is negative when the singlet is lower in energy than the triplet.

Results. In all cases, the MUEs of nCPO calculations are much larger than all the others. As shown in our previous work,²⁷ nCPO-based active spaces are insufficient. While most of the multiconfigurational character is due to variable occupancy of the two frontier orbitals, the second-highest occupied π orbital and second-lowest unoccupied π orbital also lead to significant multiconfigurational character, which necessitates at least a π CPO active space. We also note that functionals based on the simple LSDA approximation perform worse than the functionals based on generalized gradient approximation (GGA) functionals,⁴² that is, based on BLYP, PBE, and revPBE. Therefore nCPO results, tLSDA results, and ftLSDA results are relegated to the supplementary material and are not discussed further here. Mean unsigned errors (averaged over the seven molecules) for the other three active spaces with the other six functionals are in Table I for the maug-cc-pVTZ basis set. Results with the ANO-RCC-VTZP basis set are similar and are presented in the supplementary material.

Table I shows that the fully translated functionals perform noticeably better than their translated counterparts. The functional yielding the smallest MUEs is ftPBE. None of the MUEs for ftPBE exceed 2.2 kcal/mol, and they vary by only 0.6 kcal/mol, thus demonstrating both accuracy and precision. The other fully translated functionals that we employed, ftrevPBE and ftBLYP, are also quite good, but the MUEs of ftrevPBE span a larger range than those of ftPBE, and MUEs of ftBLYP are slightly higher than those for ftPBE. For brevity, molecule-by-molecule results will be discussed only for ftPBE, but molecule-by-molecule results for the other functionals are presented in the supplementary material.

Table I: MC-PDFT mean unsigned errors (MUEs,^a kcal/mol) for various translated functionals, active spaces, and active space subdivisions with the maug-cc-pVTZ basis set.

Functional	Active space	CASSCF	RASSCF	
			Valence- π	Limited- π
tPBE	eCPO	<i>b</i>	3.3	2.9
	mCPO	2.8	1.7	1.6
	π CPO	3.4	3.4	3.4
ftPBE	eCPO	<i>b</i>	1.9	1.7
	mCPO	2.2	1.8	1.7
	π CPO	2.0	2.0	2.0
trevPBE	eCPO	<i>b</i>	3.3	3.1
	mCPO	2.8	1.9	1.8
	π CPO	3.5	3.5	3.5
ftrevPBE	eCPO	<i>b</i>	1.5	1.4
	mCPO	2.6	2.2	2.0
	π CPO	1.8	1.8	1.8
tBLYP	eCPO	<i>b</i>	3.7	3.2
	mCPO	3.1	1.9	1.8
	π CPO	3.4	3.4	3.4
ftBLYP	eCPO	<i>b</i>	2.3	2.1
	mCPO	2.6	2.2	2.0
	π CPO	2.0	2.0	2.0

^aThe MUEs exclude unavailable data, which are cases that we were unable to complete due to computer time or memory requirements. MUEs are in reference to the DEA-EOM-CC reference values published previously.²⁷ ^bUnavailable.

Table II: Singlet-triplet gaps (ΔE_{ST} , kcal/mol) by ftPBE, CASPT2/RASPT2, KS-DFT, and benchmark calculations^a

System		CAS ftPBE	CAS- PT2 ²⁷	Val- π RAS- ftPBE	Val- π RAS- PT2 ²⁷	Lim- π RAS- ftPBE	Lim- π RAS- PT2 ²⁷	PBE	PBE0	Bench- mark ²⁷
1 C ₄ H ₄	e	<i>b</i>	<i>b</i>	-3.6	-3.8	-3.6	-3.8			-4.2
	m	-5.5 ^c	-4.3 ^c	-4.4	-4.0	-4.4	-4.0	var.	-1.8	-4.8
	π	-2.5	-4.4	-2.5	-4.4	-2.5	-4.4	WABS	-3.6	-10.3
2 C ₅ H ₅ ⁺	e	<i>b</i>	<i>b</i>	11.3	14.5	11.3	14.5			13.9
	m	10.6	13.5	10.6	13.7	10.6	13.7	var.	5.0	4.5
	π	14.8	14.9	14.8	15.0	14.8	15.0	WABS	10.2	9.3
3 C ₄ H ₃ NH ₂	e	<i>b</i>	<i>b</i>	-2.1	-2.2	-2.1	-2.2			-2.7
	m	-3.3	-2.7	-3.7	-2.8	-3.7	-2.8	var.	-0.8	-3.4
	π	-0.7	-2.5	-0.7	-2.5	-0.7	-2.5	WABS	-1.6	-7.1
4 C ₄ H ₃ CHO	e	<i>b</i>	<i>b</i>	-2.5	-3.5	-2.5	-3.5			-3.6
	m	-3.8	-4.0	-6.2	-4.0	-6.2	-4.0	var.	-1.4	-4.1
	π	-2.1	-3.9	-2.1	-3.6	-2.1	-3.6	WABS	-2.9	-8.8
5 C ₄ H ₂ NH ₂ CHO	e	<i>b</i>	<i>b</i>	-10.0	-7.2	-10.0	-7.2			-5.7
	m	-11.4	-6.3	-9.8	-6.3	-9.8	-6.3	var.	-8.7	-4.9
	π	-10.5	-6.7	-10.5	-7.4	-10.5	-7.4	WABS	-9.1	-5.1
6 C ₄ H ₂ -1,2- (CH ₂) ₂	e	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	-78.9	-75.9			-77.7
	m	<i>b</i>	<i>b</i>	-77.0	-75.1	-77.1	-77.0	var.	-74.3	-73.5
	π	-77.6	-75.5	-77.6	-75.3	-77.6 ^c	-75.4 ^c	WABS	-74.1	-73.1
7 C ₄ H ₂ -1,3- (CH ₂) ₂	e	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	17.3	18.7			18.5
	m	<i>b</i>	<i>b</i>	17.5	18.8	18.4	18.4	var.	7.4	12.2
	π	15.4	18.6	15.4	18.4	15.4 ^c	19.0 ^c	WABS	13.9	22.2
MUE ^d	e	<i>b</i>	<i>b</i>	1.9	0.6	1.7	0.7			
	m	2.2	0.3	1.8	0.6	1.7	0.3	var.	4.7	3.2
	π	2.0	0.7	2.0	0.8	2.0	0.9	WABS	2.5	4.2

^aVal- π denotes Valence- π ; Lim- π denoted Limited- π ; e, m, and π denote eCPO, mCPO, and π CPO. ^bNot available. ^cCI optimization only. ^dMean unsigned errors excluding absent data.

Table III: Expectation values of the square of the total electron spin $\langle S^2 \rangle$ from ftPBE^a and PBE.^b

System	$2S+1$	$\langle S^2 \rangle$		
		Pure	ftPBE ^a (MC-PDFT)	PBE (KS-DFT)
1: C ₄ H ₄	1	0.00	0.00	1.03
	3	2.00	2.00	2.00
2: C ₅ H ₅ ⁺	1	0.00	0.00	1.02
	3	2.00	2.00	2.00
3: C ₄ H ₃ NH ₂	1	0.00	0.00	1.03
	3	2.00	2.00	2.00
4: C ₄ H ₃ CHO	1	0.00	0.00	1.03
	3	2.00	2.00	2.01
5: C ₄ H ₂ NH ₂ CHO	1	0.00	0.00	0.08
	3	2.00	2.00	2.00
6: C ₄ H ₂ -1,2-(CH ₂) ₂	1	0.00	0.00	0.00
	3	2.00	2.00	2.01
7: C ₄ H ₂ -1,3-(CH ₂) ₂	1	0.00	0.00	0.95
	3	2.00	2.00	2.03

^aMC-PDFT $\langle S^2 \rangle$ values are pure by construction. ^bPBE0 results are similar to PBE ones and are presented in the supplementary material.

Calculated singlet-triplet gaps (ΔE_{ST}) for individual molecules are presented in Table II. CASPT2 and RASPT2 singlet-triplet splittings from our previous work²⁷ are included for comparison, along with KS-DFT ΔE_{ST} results based on the parental functionals. Expectation values of S^2 for PBE and ftPBE are presented in Table III. As discussed in the introduction, MC-PDFT spin states are pure by construction because the electron density and on-top density are taken from an MCSCF wave function that is a spin eigenfunction. In the KS-DFT calculations, the calculated S^2 expectation values for the singlet states of **1**, **2**, **3**, **4**, and **7** are approximately halfway between the values corresponding to the pure singlet and the pure triplet; this reflects the spin contamination that is known⁴ to be a common problem in KS-DFT for intermediate spin states.

The MUEs for KS-DFT using the variational method are noticeably larger than those of PT2 or ftPBE. While WABS is generally expected to perform better than the variational method,²⁶ here it is inconsistent: The MUEs for KS-DFT using the WABS method are better than for the variational method with PBE, but are worse than those with PBE0. The differences are much less dramatic for systems **5** and **6**, which have less spin contamination in the singlet states. In all cases, the MUEs of KS-DFT are greater than the MUEs of ftPBE, which does not require or use any broken-spin-symmetry treatment. The maximum errors using the variational method for KS-DFT are 11.0 kcal/mol for PBE (system **7**) and 9.4 kcal/mol for PBE0 (system **2**). The maximum errors for KS-DFT are smaller with the WABS method, with 4.6 and 6.1 kcal/mol for PBE and PBE0, respectively, but they are still quite large. The highest error for ftPBE is 5.8 kcal/mol (Table II: CASSCF, mCPO, system **5**), but for other than for system **5**, ftPBE's error never exceeds 3.2 kcal/mol, which is not far above PT2's maximum error of 2.6 kcal/mol. Thus, ftPBE is shown to have significantly greater reliability than the Kohn-Sham methods for the cases studied, while also entirely avoiding all complications arising from spin contamination or broken spin symmetry. Additionally, ftPBE performs competitively with CASPT2 and RASPT2. With one exception (Table II: CASSCF, mCPO), ftPBE MUEs are within 1.4 kcal/mol of the MUEs of CASPT2 and RASPT2.

In comparing MC-PDFT to CASPT2 and RASPT2, computational costs should also be considered. Timings for all active spaces are presented in the supplementary material. For the largest active space, which is eCPO with limited- π RASPT2 for triplet **6**, the post-SCF perturbation theory calculations required several days to complete on a single processor, while the post-SCF ftPBE step required less than a half hour on a single processor, with a savings of a factor of 410. Note that the post-SCF steps of CASPT2, RASPT2, and MC-PDFT are all preceded by MCSCF calculations, which take considerable time for large active spaces. The total time (SCF plus post-SCF) for the longest calculation was 217 hours for RASPT2, but only 13

hours for MC-PDFT, a savings of a factor of 17. MC-PDFT also has the advantage of requiring far less memory, as discussed in previous work.²⁶

Conclusions. Our calculations of singlet-triplet splittings for several organic diradical systems demonstrate that MC-PDFT is effective for these systems. When compared to benchmark calculations from our previous paper,²⁷ the ftPBE on-top functional shows better precision and accuracy than PBE, the KS-DFT parent functional, and it eliminates the complexities of spin contamination and broken-spin-symmetry in KS-DFT. The accuracy of ftPBE is competitive with CASPT2 and RASPT2, but at a much lower computational cost. As active spaces become very large, CASPT2 and RASPT2 take much more time than the preceding CASSCF and RASSCF calculations. In contrast, MC-PDFT time requirements are small in proportion to the CASSCF and RASSCF requirements, and this shows that MC-PDFT can be used for much larger active spaces than CASPT2 or RASPT2. The quality of results using the small π CPO active space scheme is particularly encouraging, as this suggests MC-PDFT could be used on similar, but larger, systems requiring much larger active spaces which would be unaffordable with CASPT2 or RASPT2.

Supplementary Material. See supplementary material for hardware information, sample input files, ANO-RCC-VTZP results, nCPO results, tLSDA and ftLSDA results, PBE0 spin expectation values, and all absolute energies, active space sizes, numbers of CSFs, and timings for all functionals and active spaces.

Acknowledgments. This work was supported in part by AFOSR grant FA9550-16-1-0134.

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