Spin-flip pair-density functional theory: A practical approach to treat static and dynamical correlations in large molecules

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We present a practical approach to treat static and dynamical correlation accurately in large multi-configurational systems. The static correlation is accounted for using the spin-flip approach which is well known for capturing static correlation accurately at low-computational expense. Unlike previous approaches to add dynamical correlation to spin-flip models which use perturbation theory or coupled-cluster theory, we explore the ability to use the on-top pair-density functional theory approaches recently developed by Gagliardi and co-workers (JCTC, 10, 3669, 2014). External relaxations are carried out in the spin-flip calculations though a restricted active space framework for which a truncation scheme for the orbitals used in the external excitation is presented. The performance of the approach is demonstrated by computing energy gaps between ground and excited states for diradicals, triradicals and linear polyacene chains ranging from naphthalene to dodecacene. Accurate results are obtained using the new approach for these challenging open-shell molecular systems.

I. INTRODUCTION

An accurate computational description of large molecular systems with multi-configurational characters or strongly correlated systems still remains a challenge due to the lack of a general approach that delivers high accuracy while remaining computationally affordable.

The most widely used approach for treating multi-configurational systems is the complete active space self-consistent field (CASSCF) method in which the full configurational interaction (CI) is solved within a chosen active space with the orbitals and the CI coefficients optimized. The active space is typically selected with a prior knowledge of the important orbitals contributing to the target chemical problem or the electronic state (although recent advances are making it possible to algorithmically select active space orbitals). When supplied a well-defined active space, the method has been shown to reliably recover static correlation. However in doing so, the bulk of the dynamical correlation is absent, precluding any hope for quantitative predictions. A general strategy adopted to recover the dynamical correlation is to use the complete active space second-order perturbation theory (CASPT2) approach. As dynamical correlation is well-described by perturbation theory, CASPT2 provides significant accuracy improvements compared to CASSCF, albeit with increased computational cost and memory requirements. The CASSCF method itself is limited to 20 electrons in 20 orbital space with the current state-of-the-art computational resources. With a motivation to enable computation using larger active spaces, several approaches have been developed such as various flavors of selected configuration interaction (SCI) approaches, the density matrix renormalization group (DMRG), generalized active-space self-consistent field (GASSCF) method, the 2-RDM driven CASSCF (v2RDM-CASSCF) method or the full CI quantum Monte Carlo (FCIQMC) method. With these reduced cost methods, larger active spaces can be used which begin to account for dynamical correlation as well, but generally a large amount of dynamical correlation is still missing.

An alternative approach for treating multi-configurational systems is the spin-flip (SF) method. The SF method is a relatively simple approach which uses a well-defined single-determinant reference on which spin-flipping excitations are carried out to access electronic states starting from a high-spin configuration. The SF methods have been further extended to remain spin-pure, including external relaxations through a restricted active space framework (RAS-nSF). Recently, we have also proposed a redox SF approach that simultaneously accounts for both spin and spatial degeneracies which the SF approach alone cannot handle. The SF approaches have favorable computational scaling for practical applications to large multi-configurational systems. In addition to allowing traditionally single-reference methods to be applied to multi-reference problems, (e.g., coupled-cluster theory), spin-flip also reduces the dependence on user input, since the active-space is defined automatically once the reference spin state has been chosen. As a result, prior knowledge of the orbitals that are important for the target electronic state is not necessarily required. Here, the active space is simply chosen as the singly occupied orbitals. The external excitation space in RAS-nSF are simply the doubly occupied and the virtual orbitals although knowledge of the important contributing orbitals can be utilized as well. Another advantage of the SF approach is the treatment of the electronic states including the ground state on equal footing. However, because the RAS-nSF approach excludes all double excitations outside of the active space, it can only deliver qualitative accuracy due to the lack of dynamical correlation.

An appealing approach to recover dynamical correlations for practical applications to large molecular systems is the combination of multi-configurational wave-
function methods with a density functional theory (DFT) based method. Here, the idea is to use a qualitatively correct multi-configurational wavefunction to capture the static correlation and include a DFT-based description of the dynamical correlation. The idea was first introduced by Lie and Clementi where they demonstrated that the DFT results can be substantially improved by adding the correlation energy obtained from a multi-configurational wavefunction.\textsuperscript{48–62} However, the approach does not separate the static and dynamical correlation, thereby double counting the correlation energy. Several approaches have emerged in this line which attempts to overcome the deficiencies and improve over the previous work.\textsuperscript{48–62} Notable example include the approach by Colle and Solvetti,\textsuperscript{52,53} CAS-DFT by Savin and co-workers,\textsuperscript{54–60} modified CAS-DFT approaches by Grafenstein and Cremer,\textsuperscript{61,62} Yamaguchi and co-workers,\textsuperscript{63} and CAS-DFT using on-top pair density by Gusarov and co-workers.\textsuperscript{61,62} A nice review of the available approaches are provided in Ref. 63. The main challenge in combining multi-configurational wavefunction with a DFT-based description of the dynamical correlation is due to the double counting of electron correlation. The multi-configurational wavefunction generally includes some part of the dynamical correlation within the active space. The second complication is the “symmetry dilemma” in KS-DFT.\textsuperscript{65} The spin densities of the multi-configurational wavefunctions are not compatible with standard density functionals for low spin states.

Recently, a new approach has been proposed by Gagliardi and co-workers to include DFT-based correlation energy to a multi-configurational wavefunction which addresses both the double counting of correlation energy as well as the “symmetry dilemma” \textsuperscript{65-67} The method referred to as multi-configurational-pair density functional theory (MC-PDFT) only uses the multi-configurational wavefunction to compute the classical Coulomb and the kinetic energy while the rest of the exchange-correlation energy and correction to the kinetic energy is obtained from DFT using the on-top pair density functionals. The success of the method has been demonstrated in conjunction with CASSCF,\textsuperscript{61-63} GASSCF,\textsuperscript{63} DMRG\textsuperscript{64} and v2RDM-CASSCF.\textsuperscript{65}

In this work, we propose an alternate approach to combine MC-PDFT with the RAS-$n$SF approaches and our recently developed SF-IP/EA approach. The goal is to recover dynamical correlation energy in the SF approaches using MC-PDFT for practical applications to large multi-configurational systems at a considerably low computational cost. A brief description of the RAS-$n$SF approaches and the MC-PDFT method is provided in Section II A and II B. A practical scheme is also presented to further reduce the computational cost in the MC-PDFT calculation. Computational details are provided in Section III. The performance of the approach is demonstrated by computing energy gaps between spin states of challenging biradicals, triradicals and polyacenes ranging from naphthalene to dodecacene. The results are presented in Section IV A, IV B and IV C. Finally, a summary is provided in Section V.

II. METHODS

A. RAS-$n$SF and combined IP/EA approach

We give a short overview of the RAS-$n$SF and the combined IP/EA approaches. For further details of the methods, we refer the reader to Refs. 29, 72 and 71.

The spin-flip (SF) approach, proposed by Krylov, provides an efficient way to model a large number of multi-configurational problems using only a single reference determinant. The key idea in SF approach is that while the various $S_z$ multiplets of high spin states have identical electronic energies, states with maximum $S_z$ have a single determinant representation, while lower $S_z$ multiplets are highly multi-configurational. SF approach leverages this degeneracy, by optimizing the orbitals for the single configurational high spin ($S_z = S$) state, then uses spin-flipping excitations to access the target $S_z$ manifold of states. Because both high-spin and low-spin states appear in the target $S_z$ space, the high-spin states and low-spin states are treated on an equal footing.

As an example, the spin-degeneracy in the valence bonding orbitals $\left[\sigma^2 \pi^4\right]$ with the anti-bonding $\sigma^*$ and $\pi^*$ orbitals upon bond dissociation of N$_2$ molecule can be resolved using the SF approach. Using a high-spin heptet state $\left[\sigma^1 \pi^2 \pi^2 \pi^1\right]$ with $n_s = 3$ as the reference state, the ground singlet state can be accessed using a 3SF operator.

$$|\Psi\rangle = \sum_{i<j<k,a<b<c} \tilde{c}_{ijk} \tilde{a}_{abc} |\Psi_{\text{Reference}}\rangle \tag{1}$$

Systems with spin as well as spatial degeneracies can be treated using a combination of the spin-flip method and the electron addition (EA) or elimination (IP) method. Unlike in the SF approach, the combined SF-IP/EA approach works with the closest well-defined high spin state obtained either by oxidizing or reducing the the system. While only spatial degeneracies arise in the previous example, if the cationic system is considered instead (N$_2^+$) both spin and spatial degeneracy occur. In this case, the system is multi-configurational even in the high spin state as one of the degenerate bonding ($\sigma^2 \pi^3$) and anti-bonding ($\sigma^* \pi^*$) orbitals must be left unoccupied upon dissociation. The ambiguity is resolved by simultaneously using the 2SF-IP operator on the neutral N$_2$ molecule.

$$|\Psi\rangle = \sum_{ijkab} \tilde{c}_{ijk} \tilde{a}_{ab} |\Psi_{\text{Reference}}\rangle \tag{2}$$

The SF and IP/EA excitations are carried out only in the singly occupied orbital space to ensure spin-pure
TABLE I: Truncation schemes used for the RAS1 and RAS3 active space in the RAS(S) excitation in the natural orbital basis. The truncations are performed separately for the RAS1 and RAS3 space.

| Scheme | Abbreviation | Description |
|--------|--------------|-------------|
| I      | RAS-SS       | A state specific approach, truncate the active space for each state separately. Each state has different number of orbitals in the active space |
| II     | RAS-SA       | A state average (SA) approach, truncate based on an average density of the participating states. Each state has the same number of orbitals in the active space |
| III    | RAS-eff      | An effective SA approach, the active space is defined by the maximum of the number of orbitals in each state for a given threshold (separately for RAS1 and RAS3) |

state. External relaxation effects are taken into account using RAS(S) by allowing the full set of singles excitations defined by \( (h, p, h)p \). The approach without the external effects is denoted by CAS-nSF. Overall, the RAS-nSF and the combined IP/EA approaches provides qualitatively accurate descriptions of static correlation as demonstrated in earlier works with the only disadvantage being the neglect of dynamical correlations.

B. Multi-configurational pair-density functional theory

We shortly review the MC-PDFT approach which combines multi-configurational methods with DFT-based methods without incurring double counting of correlation energy and the symmetry dilemma in the context of KS-DFT. By using 1- and 2-RDMs from a multi-configurational calculation, the electronic energy in the MC-PDFT framework is given by

\[
E = \sum_{pq} \rho_{pq} D_{pq} + \frac{1}{2} \sum_{pqrs} g_{pqrs} D_{pq} D_{rs} + E_{ot} [\rho, \Pi] \tag{3}
\]

where \( \rho_{pq} \) and \( g_{pqrs} \) are the one- and two-electron integrals respectively, \( D_{pq} \) is the 1-RDM and \( E_{ot} \) is the on-top energy with \( \rho \) and \( \Pi \) being that total density and the on-top pair density respectively. The last two terms are the classical Coulomb term and an on-top density functional term which replaces the two-electron contribution in the usual electronic energy expression for many-electron systems. Here, the one-electron contribution containing the kinetic and electron-nuclear potential energy as well as the classical electrostatic contribution are directly taken from the multi-configurational wavefunction. The remainder exchange and the correlation contributions are folded into the on-top pair density functional.

The total density \( \rho \) and the on-top pair density, \( \Pi \) are defined in terms of 1-RDM and 2-RDM obtained from the multi-configurational calculations respectively as

\[
\rho(r) = \sum_{pq} \phi_p(r) \phi_q(r) D_{pq} \tag{4}
\]

\[
\Pi(r) = \sum_{pqrs} \phi_p(r) \phi_q(r) \phi_s(r) D_{pqrs} \tag{5}
\]

The on-top pair density functional used within the MC-PDFT formalism is simply obtained with “translated” existing exchange-correlation functionals employed in standard KS-DFT. The derivation of the “translated” and the corresponding “fully translated” functionals are provided in Ref. 73.

In the present RAS-nSF(-IP/EA)-PDFT strategies, the appropriate RDMs entering in Equation 3 are obtained from the RAS-nSF(-IP/EA) wavefunction presented in the previous section. Because the computation of the 2-RDM in the combined spaces of RAS1, RAS2, and RAS3 would prevent application to large systems, we propose the following truncation scheme which improves efficiency while producing only small affects on the final energies:

1. Perform RAS-nSF(-IP/EA) using the full space for the external RAS(S) excitations.

2. Diagonalize 1-RDMs of the RAS1 and RAS3 spaces separately to obtain natural orbitals for the RAS subspace. The RAS-nSF methods are invariant with respect to orbital rotations within a RAS subspace.

3. Define a threshold for the orbital occupation number to separately truncate the RAS1 and RAS3 active space for the RAS(S) excitation in the natural orbital basis. The truncation schemes are tabulated in Table I.

4. Using the truncated RAS1/RAS3 spaces repeat the RAS-nSF(-IP/EA) calculation to obtain the required one- and two-RDMs for the RAS-nSF(-IP/EA)-PDFT calculation.

III. COMPUTATIONAL DETAILS

In order to determine the accuracy of the RAS-nSF(-IP/EA)-PDFT approach presented in this work, we compare to existing accurate methods for the computation of the doublet-quartet gap of triradical and singlet-triplet...
FIG. 1: Schematic representations of the poly-radicals and polyacenes considered in this work.

gaps in aromatic biradicals and linear polyacenes and to experimental results wherever available. The structures of 1,3,5-trimethylenebenzene (TMB) and its negative ion (TMB−) were optimized with UB3LYP/cc-pVDZ. The structure of meta-xylylene was taken from Ref. 74, the ortho-, para- and meta-benzyne radicals from Ref. 75, 76 and the polyacenes from naphthalene to dodecacene from Ref. 69. A schematic representation of the poly-radicals and polyacenes considered in this work is provides in Figure 1.

The doublet state of neutral 1,3,5-trimethylenebenzene triradical was obtained by performing a single SF operation on the quartet reference state with $m_s = \frac{3}{2}$. The singlet and triplet state of its negative ion was obtained by performing 1SF-EA operation on the neutral high-spin quartet state obtained by oxidizing the target anionic state. For the benzyne radicals as well as the polyacenes, the singlet states are obtained by performing only a single SF operation on the triplet reference state as done in Refs. 75 and 33.

Augmented Dunning’s correlation consistent aug-cc-pVDZ basis set was employed for all the calculations. The RAS-nSF-PDFT and the RAS-nSF-IP/EAPDFT calculations were performed with tPBE, ftPBE, tBLYP and ftBLYP on-top density functional. Cholesky decomposition was used in all the two-electron integral calculations with a decomposition threshold of $10^{-6}$ a.u. Calculations were performed using OpenMolcas and the truncation scheme described in Section II B was computed using an in-house python plug-in code to OpenMolcas.

FIG. 2: Illustration of the operation of 1SF and 1SF-EA on the high spin reference state for (a) TMB, (b) TMB− and (c) MX. The orbitals shown corresponds to the non-bonding orbitals and the spin-flips are indicated by red in color.

IV. RESULTS AND DISCUSSION

A. All π-polyradicals

The 1,3,5-trimethylenebenzene (TMB) presents as a prototypical high-spin all-π triradical. The triradical system has an open-shell quartet ground state with the three unpaired electrons each occupying the nondisjoint π non-bonding orbitals (NBO). Here, the three NBOs are nearly degenerate and most of the low-lying states have heavily multiconfigurational wavefunctions. Accurate theoretical studies are available for the energy gap between the ground state and the energetically lowest doublet state. The doublet state is accessible with just a single spin-flip operation on the high spin quartet state ($m_s = \frac{3}{2}$), see the sketch in Figure 2(a).

The negative ion of TMB (TMB−) on the other hand cannot be described solely by the spin-flip approach. Four electrons occupy the nearly degenerate three NBOs and it is ambiguous to which of the three orbitals should be doubly occupied. The ground state is a triplet state and thus is basically a π-π-diradical. The ground state as well as the low-lying singlet states can be accessed using 1SF-EA operation on the quartet reference state obtained by oxidizing the anion. This is illustrated in Figure 2(b).
Another prototypical all $\pi$-diradical is the meta-xylene (MX) with two electrons distributed in two nearly degenerate NBOs. The singlet-triplet gap of MX has been intensively studied both theoretically as well as experimentally. The diradical has an open-shell triplet ground state. The low-lying singlet state can be accessed using a single SF operation on the triplet reference state ($m_s = 1$), see the illustration in Figure 2(c).

![Figure 3](image)

**FIG. 3:** Convergence of energy gap w.r.t. truncation of natural orbitals, doublet-quartet gap of TMB (top), singlet-triplet gap of TMB$^-$ (center) and MX (bottom). Natural orbitals with occupation number $<\text{threshold}$ or $>2.0$—threshold are truncated in the RAS-$n$SF(-IP/EA)-PDFT computation following the truncation schemes (in parenthesis), SS, SA, eff as outlined in Table II.

Figure 3 plots the convergence of the different truncation schemes described in the last part of Section II B. The natural orbitals computed from the 1-RDM of the RAS3 active space with occupation number smaller than a given threshold are truncated in the RAS(S) excitation scheme. The doubly occupied orbitals in the natural orbital basis constructed from the 1-RDM of the RAS1 space are truncated with occupation number larger than the difference of two and the given threshold. In the three truncation schemes namely, SS, SA, and eff, the distinction between the SS and the eff schemes vanishes at the convergence. The RAS(S)-nSF-PDFT converges with a threshold of 0.0001 for all the truncation schemes with the exception of SS truncation scheme in TMB$^-$. Here, the difference in the energy gap between spin states of TMB$^-$ obtained using the SS and eff truncation scheme is 0.13 kcal/mol at the tightest threshold considered which is well within the target accuracy of the presented approach. Furthermore, the SA truncation scheme is slightly slower to converge for TMB$^-$ and MX, with the largest difference at the minimum threshold considered being 0.24 kcal/mol. Hereafter, we will consider the eff truncation with a threshold of 0.0001 for the RAS3 orbitals and 1.9999 for the RAS1 orbitals.

The energy gap between spin-states of TMB, TMB$^-$ and MX computed using CAS-SF, CASSCF, RAS(S)-SF and the corresponding MC-PDFT method using the tPBE functional is provided in Table II. Literature values for the energy gaps from previous electronic structure calculations as well the experimental energy gap for MX are also reported in therein. For the TMB and TMB$^-$ radicals, experimental values were not available and so comparisons are made to the available literature values. First, we consider the vertical doublet-quartet (DQ) energy gap of TMB radical. The application of MC-PDFT on CAS-1SF which does not account for any external relaxation effect decreases the DQ energy gap by almost 15.0 kcal/mol. CAS-1SF-tPBE strongly underestimates the DQ energy gap as compared to the previously reported gaps from CASPT2 and DDCI methods. Contrary to this, CASSCF-tPBE increase the DQ energy gap computed with CASSCF (with CAS(2,2)) by 7.3 kcal/mol. Interestingly, the CASSCF-tPBE energy gap is very close to a previously reported CASSCF value with a larger active space (CAS(9,9)). On the other hand RAS(S)-1SF-tPBE reduces the DQ energy gap from the bare RAS(S)-1SF by almost 10 kcal/mol. Comparing to the available DDCI and CASPT2 literature, the inclusion of dynamical correlation in the MC-PDFT framework greatly improves the bare RAS(S)-1SF doublet-quartet energy gap.

Next, we consider the vertical singlet-triplet (ST) gap for the anion of TMB. Here, CAS-1SF as well as CAS-1SF-tPBE predicts a singlet ground state as opposed to the experimental evidences for a high spin triplet ground state for the anion. The ST gap of bare CASSCF with CAS(2,2) active space is increased by about 2.0 kcal/mol with the corresponding MC-PDFT method. In contrast to this, RAS(S)-1SF-tPBE decreases the ST gap computed using the bare RAS(S)-1SF by 1.7 kcal/mol. Here, the ST gap agrees well with an existing CASPT2 result available in literature based on CASSCF orbital with CAS(10,9).

For the MX diradical, the experimental ST energy gap is available and so comparisons can be made to the adiabatic ST energy gap from the various methods tabulated in Table II. The CAS-1SF-tPBE strongly underestimates the ST energy gap which collectively with the results obtained for the TMB and TMB$^-$ radicals suggest that the
one- and two-RDMs from the bare CAS-1SF without any external relaxation effect is not accurate to be used in the MC-PDFT equation. The CAS-1SF-tPBE equation even produces qualitatively wrong ordering of spin-states in the TMB radical. On the other hand, the CASSCF-tPBE based on CAS(2,2) active space underestimates the experimental ST gap of MX by 2.2 kcal/mol whereas the RAS(S)-1SF-tPBE underestimates the energy gap by almost 4 kcal/mol. In literature, the different wavefunction based methods tend to overestimate the ST gap of MX, see Table [11] LCCQMC based on a stochastic approach from Alavi et al. provides the ST gap of MX very close to experimental result[94]. The difficulty in achieving an ST gap using wavefunction-based approaches comparable to the experimental result have been demonstrated in earlier works[95,96]. An extensive study using different wavefunction methods and DFT methods for the ST gap of MX radical can be found in Ref. 93. The authors therein pointed out the importance of including dynamical correlation with high accuracy[93]. In our case, while the bare RAS(S)-1SF which also includes some dynamical correlation[91] overestimates the experimental ST gap by 4.3 kcal/mol, RAS(S)-1SF-tPBE underestimates the ST by 3.9 kcal/mol.

B. Benzyne radicals

The ortho-, meta- and para-benzyne isomers have been used as benchmarks for new theoretical approaches and at the same time challenging because of the strongly correlated biradical electron[74,91,92]. The benzyne isomers have a closed-shell singlet state with the diradical character correlating with the distance between the unpaired electrons. As a result, the energy gap between the ground singlet and the lowest excited triplet state decreases following the ortho-, meta- and para-sequence.

The adiabatic singlet-triplet-gaps of the benzene iso-
mers computed using bare CAS-1SF, CASSCF, RAS(S)-1SF and the corresponding MC-PDFT methods are presented in Table [11] along with the available experimental values and selected literature values for comparison. The RAS(S)-1SF and RAS(S)-1SF-PDFT ST energy gaps were computed using truncated natural orbitals outlined in Section [11]A A threshold of 0.0001 and 1.9999 was used for the virtual and doubly occupied space respectively following the results from Section [IV A] in the external RAS(S) excitation scheme. The different truncation schemes, namely, SS, SA and eff resulted in similar ST gaps and so only results from the eff truncation scheme is presented. The largest difference in the ST gaps between the different truncation schemes was only 0.22 kcal/mol. Also presented in Table [11] are the results from employing different on-top functionals, viz., tPBE, tBLYP and the fully translated variants. Overall the results obtained from using tPBE performs better than the other functionals and so we focus our discussion only to using the tPBE functional.

The CAS-1SF and the CASSCF methods are based on minimal active spaces, i.e., CAS-1SF does not account for any external relaxations while the CASSCF method is based on CAS(2,2) active space. This is reflected in the ST gaps obtained from CAS-1SF-tPBE as compared to the experimental results (ZPE included) for ortho- and meta-benzyne radicals. In spite of the small active space, CASSCF-tPBE on the other hand performs well for the ortho-benzyne radical, within 1.0 kcal/mol of the experimental value whereas the ST gap is overestimated by 3.4 kcal/mol for the meta-benzyne radical. Contrary to this, RAS(S)-1SF-tPBE underestimates the experimental ST gap by 3.2 kcal/mol for ortho-benzyne while it exactly matches the result for the meta-benzyne. Here, the ST gap of ortho-benzyne obtained from RAS(S)-1SF is within 0.1 kcal/mol of the experimental value. We note that the corresponding bare RAS(S)-1SF method ac-

|          | TMB | TMB | MX |
|----------|-----|-----|----|
| CAS-1SF  | 17.6| -1.9| 4.3|
| CAS-1SF-tPBE | 2.8 | -6.1| 1.7|
| CASSCF  | 8.3 | 2.9 | 2.1|
| CASSCF-tPBE | 15.6 | 5.0 | 7.7|
| RAS(S)-1SF | 19.6 | 5.5 | 14.2|
| RAS(S)-1SF-tPBE | 9.8 | 3.8 | 6.0|
| expt. - ZPE | — | — | 9.6|
| Literature | 15.7<sup>d</sup>, 3.5<sup>e</sup>, 11.7<sup>f</sup>, 11.2<sup>g</sup>, 13.6<sup>h</sup>, 11.3<sup>i</sup>, 11.8<sup>j</sup>, 9.5<sup>h</sup>|

<sup>a</sup>Optimized geometry with UB3LYP/cc-pVDZ
<sup>b</sup>Geometry from Ref. 74 UB3LYP/6-31G(d,p)
<sup>c</sup>CAS(3,3) for TMB, CAS(4,3) for TMB<sup>−</sup> and CAS(2,2) for MX
<sup>d</sup>CASSCF(9,9)/6-31G(d,p) from Ref. 85
<sup>e</sup>DDCI/6-31G(d) using localized orbitals and complete virtual orbitals (fully variational) from Ref. 51
<sup>f</sup>CASPT2/6-31G(d) with CASSCF orbitals from Ref. 83
<sup>g</sup>CASSCF(10,9)/ANO-L and CASPT2/ANO-L using the same CASSCF orbitals from Ref. 80
<sup>h</sup>state averaged MS-CASPT2/ANO-L from Ref. 89
<sup>i</sup>CASSCF(6-31G(d) with CAS(8,8) from Ref. 96
<sup>j</sup>CASPT2/6-31G(d) with CASSCF orbitals with CAS(8,8) from Ref. 94
<sup>k</sup>EOM-SF-CCSD/6-31G(d) from Ref. 92
<sup>l</sup>Multi-reference second-order Møller-Plesset/ang-cc-pVTZ from Ref. 93
<sup>m</sup>LCCQMC/6-311++g(d,p) from Ref. 93
TABLE III: Adiabatic singlet-triplet energy gap for ortho-, meta- and para-benzyne using the RAS-1SF and RAS-1SF-PDFT method. All results with aug-cc-pVDZ basis set and natural orbitals truncated with a threshold of 0.0001. Units are in kcal/mol.

|         | \(\text{o-benzyne}\) | \(\text{m-benzyne}\) | \(\text{p-benzyne}\) |
|---------|---------------------|---------------------|---------------------|
| CAS-1SF | 16.7                | 2.3                 | 0.6                 |
| CAS-1SF-tPBE | 30.2                | 14.1                | 3.4                 |
| CASSCF\(^a\) | 27.6                | 10.1                | 1.5                 |
| CASSCF-tPBE\(^a\) | 39.0                | 23.4                | 5.4                 |
| RAS(S)-1SF | 38.0                | 22.1                | 3.8                 |
| RAS(S)-1SF-tPBE | 34.9                | 20.0                | 5.8                 |
| RAS(S)-1SF-rPBE | 33.0                | 17.7                | 5.4                 |
| RAS(S)-1SF-tBLYP | 35.5                | 19.0                | 6.0                 |
| RAS(S)-1SF-tBLYP | 33.7                | 17.0                | 5.6                 |
| expt.\(^b\) | 37.5                | 21.0                | 3.8                 |
| expt.−ZPE\(^c\) | 38.1                | 20.0                | 3.3                 |

Literature

|         | S−T gap (kcal/mol) |
|---------|--------------------|
| 35.1\(^d\) | 16.4               |
| 32.6\(^e\), 36.8\(^f\) | 19.0               |
| 37.3\(^g\) | 20.1               |

\(^a\)using CAS(2,2) active space
\(^b\)expt. value from Ref. \(^{97}\)
\(^c\)ZPE correction with SF-DFT/6-311G* from Ref. \(^{75}\)
\(^d\)CASSCF using CAS(8,8) active space from Ref. \(^{98}\)
\(^e\)CASPT2 using CASSCF(8,8) orbitals from Ref. \(^{98}\)
\(^f\)ic-MRCCSD(T) based on CAS(2,2) from Ref. \(^{99}\)
\(^g\)SF-CCSD(T) from Ref. \(^{100}\)

Counts for some dynamical correlations but we emphasise again that the MC-PDFT method avoids double counting of electron correlation. Comparing to literature, we find that for the ortho- and meta-benzyne radicals, RAS(S)-1SF-tPBE is more accurate than CASPT2 (based on CASSCF orbitals with CAS(8,8) active space)\(^ {98}\) which is often a method of choice for including dynamical correlations in modelling strongly correlated systems.

The para-benzyne radical presents as a more challenging case and has been the focus in comparing the ST gap obtained from various highly accurate theoretical methods to the available experimental result\(^ {98–100,103}\). Kohn and co-workers have pointed out the possibility of wrong assignments of the singlet and triplet states in the experiment\(^ {99,103}\). The ST gap for the diradical presented in Table III further supports this possibility. The ST gap for CAS-1SF-tPBE in which the bare CAS-1SF does not account for any external relaxation agrees well within 0.1 kcal/mol of the experimental result in contrast to RAS(S)-1SF-tPBE. This would mean that CAS-1SF provides a more accurate one- and two-RDMS than the RAS(S)-1SF in the MC-PDFT equation in contrast to the results obtained for the other radicals discussed before. Furthermore, the ST gap form RAS(S)-1SF agrees well with other literature values obtained from CASPT2 (based on CASSCF orbitals with CAS(8,8) active space)\(^ {98}\) and ic-MRCCSD(T)\(^ {99}\). The ST gap also agrees well with the CASSCF-tPBE.

FIG. 4: Adiabatic singlet-triplet gap with increasing length of acenes.

C. Polyacenes

In the previous sections, we have shown that the RAS-nSF(-IP/EA)-PDFT approach can describe challenging medium-sized biradical and triradical molecular systems with good accuracy. In this section, we demonstrate the performance of our approach for larger systems: the polyacenes, ranging from naphthalene to dodecacene. The polyacenes have a singlet ground state, with the open shell character increasing as the number of the benzene ring increases. The singlet-triplet (ST) gap in this case correlates with the acene length which exponentially decreases.

Table IV reports the adiabatic singlet-triplet gaps of the polyacenes obtained from RAS-1SF and RAS-1SF-PDFT. Here, the on-top tPBE functional was employed. Using the triplet state \((m_s=1)\) as the reference, the singlet state is accessed by performing only a single SF operation on the reference state. The external RAS(S) excitations were carried out from all the valence \(\pi\) orbitals. The ST gap for the diradical presented in Table III further supports this possibility. The ST gap from CAS-1SF-tPBE in which the bare CAS-1SF does not account for any external relaxation agrees well within 0.1 kcal/mol of the experimental result in contrast to RAS(S)-1SF-tPBE. This would mean that CAS-1SF provides a more accurate one- and two-RDMS than the RAS(S)-1SF in the MC-PDFT equation in contrast to the results obtained for the other radicals described before. Furthermore, the ST gap form RAS(S)-1SF agrees well with other literature values obtained from CASPT2 (based on CASSCF orbitals with CAS(8,8) active space)\(^ {98}\) and ic-MRCCSD(T)\(^ {99}\). The ST gap also agrees well with the CASSCF-tPBE.

![Graph](image-url)
TABLE IV: Adiabatic singlet-triplet energy gap \((E_{\text{triplet}} - E_{\text{singlet}})\) for polyacenes. aug-cc-pVDZ basis set are used upto Hexacene and cc-pVDZ basis set for the remainder. RAS(S)-1SF-PDFT results are obtained using tPBE functional. Units are in kcal/mol.

| Acene       | CAS-1SF  | CASSCF\textsuperscript{a} | RAS(S)-1SF | expt. | expt. |
|-------------|----------|---------------------------|------------|-------|-------|
|             | bare -PDFT | bare -PDFT | bare -PDFT |       | −ZPE\textsuperscript{b} |
| Naphthalene | 52.7     | 57.4                      | 64.7       | 56.2  | 62.3  |
|             |          |                           | 76.8       | 60.4\textsuperscript{109} | 61.1\textsuperscript{107} | 64.1, 64.3 |
| Anthracene  | 31.4     | 36.7                      | 48.7       | 33.8  | 40.4  |
|             |          |                           | 51.9       | 42.1\textsuperscript{109} | 43.3\textsuperscript{108} | 45.0, 45.4 |
| Tetracene   | 26.4     | 26.6                      | 41.8       | 27.7  | 28.5  |
|             |          |                           | 29.1       | 29.3\textsuperscript{109} | 31.4 |
| Pentacene   | 14.5     | 18.1                      | 29.4       | 15.4  | 19.2  |
|             |          |                           | 24.1       | 19.4\textsuperscript{109} | 20.9 |
| Hexacene    | 10.8     | 12.2                      | 23.2       | 11.5  | 13.3  |
|             |          |                           | 13.7       | 12.3\textsuperscript{110} | 13.9 |
| Heptacene   | 5.9      | 8.6                       | 14.1       | 10.6  | 7.8   |
| Octacene    | 3.4      | 5.6                       | 10.1       | 10.0  | 4.8   |
| Nonacene    | 1.3      | 4.1                       | 5.0        | 7.1   | 3.3   |
| Decacene    | -0.2     | 1.9                       | 3.2        | 5.6   | 2.0   |
| Undecacene  | -1.8     | 2.6                       | 0.1        | 4.8   | 2.3   |
| Dodecacene  | -3.0     | 1.2                       | -1.1       | 3.9   | 2.1   |

\textsuperscript{a}using CAS(2,2)

\textsuperscript{b}ZPE correction with B3LYP/6-31G(d,p) from Ref. \[70\]

Several other literature values are available, a detailed analysis of the available ST gaps in literature are provided in Ref. \[113\] and \[114\]. The RAS(S)-1SF-PDFT adiabatic ST gaps have a good agreement with the corresponding experimental values as compared to the RAS(S)-1SF values. Although the bare RAS(S)-1SF includes some dynamical correlation, RAS(S)-1SF-PDFT improves over the bare RAS(S)-1SF method.

Here, a delicate balance between the dynamic and the static correlation exist in the singlet and triplet state \[115\]. From Table IV, it can be seen that the larger acenes agree very well with the experimental value whereas available while for anthracene the difference is \(\sim 5\) kcal/mol. However, we note that the experimental values were obtained from measurements in solutions or as solids unlike the theoretical results from gas phase calculation \[109\]. Table IV also presents ST gaps obtained from bare CAS-1SF, CASSCF(2,2) and the corresponding MC-PDFT approaches. In both the cases, including the PDFT correction improves upon the bare method for the ST gaps. However, the RAS(S)-1SF-PDFT performs better in comparison to CAS-1SF-PDFT and CASSCF-PDFT for the polyacene chains. This shows that RAS(S)-1SF provides a more accurate 1- and 2-RDMs entering the MC-PDFT equation (Equation \[4\] and \[5\]) than CAS-1SF and CASSCF based on minal CAS(2,2) active space.

For the acenes where experimental values are not available, the RAS-1SF-PDFT values are lower than the available literature values shown in Figure 4, although in some cases good agreements can be seen. The CCSD(T) as well as the Monte Carlo values tend to overestimate the available experimental values while it can be seen that the largest reported acenes with these methods agrees well with the RAS-1SF-PDFT values. The values reported for the v2RDM-CASSCF-PDFT differ between 1.8 to 5.7 kcal/mol while the difference is between 0.3 to 3.1 kcal/mol with the GAS-PDFT method.

Another feature that can be observed in Figure 4 is the smoothly decaying exponential curve for the RAS-1SF-PDFT ST gaps which can be fitted to the form \(a \exp(-bx) + c\). The fit then can be used to estimate an extrapolated ST gap for polyacene with infinite length. Using the fitting formula,

\[
E_{\text{ST}}(x) = 138.14 e^{(-0.40x)} + 0.10
\]

The adiabatic ST gap estimated for an infinitely long linear polyacene chain is 0.10 kcal/mol. The value is in very good agreement with the ST gap of 0.18 kcal/mol from CCSD(T)/cc-pV\(\infty\)Z reported in Ref. \[111\] and with pp-RPA/cc-pVDZ with a value between 0.0 and 2.3 kcal/mol reported in Ref. \[116\]. The later however is estimated using vertical ST gaps. The ST gap is directly related to the HOMO-LUMO gap and the obtained result suggest a closure for the HOMO-LUMO gap for infinitely long polyacene chains. Note that the result is in contrast to Ref. \[71\] where the ST gap for the infinite chain is reported to be 4.87 kcal/mol with the v2RDM-CASSCF-PDFT/cc-pVTZ method and Ref. \[115\] with a value of 5.06 and 5.37 kcal/mol obtained as their best estimate and from SF-CCSD/6-31+G(d,p) method respectively. With GAS-PDFT/6-31+G(d,p) (WFP-3 partitioning), the ST gap is reported to be 1.9 kcal/mol which is roughly half way between our value and the ones obtained from v2RDM-CASSCF-PDFT and SF-CCSD method \[69\].

Although the theoretical results presented above show
quantitative consistency, the basis sets used to compute the ST gaps differ for the various approaches and so comparison with the available literature values does not account for basis set effects.

V. SUMMARY

In this work, we have presented a practical approach for treating large multiconfigurational molecular system with a low computational cost. The new method, spin-flip pair-density functional theory (SF-PDFT) uses a spin-flip or a redox spin-flip operator to account for the static correlation while the dynamical correlation is described with DFT using the MC-PDFT approach. The SF-PDFT method improves upon the result of bare spin-flip or a redox spin-flip pair-density functional theory (SF-PDFT) uses a low computational cost. The new method, spin-flip pair-density functional theory (SF-PDFT) improves upon the result of bare spin-flip approach, thereby capturing the missing dynamical correlations in the spin-flip approach. In cases where the spin-flip results are already close to the available experimental results, the SF-PDFT only changes the spin-flip results slightly ascertaining the reliability of SF-PDFT. The reason is because in such cases, the static correlation dominates the electron correlation. The method yields good accuracy for energy gaps between ground and the low-lying excited states for challenging open-shell molecular systems. The applicability range of the method was demonstrated by computing the singlet-triplet gap in linear polyacene chains ranging from naphthalene to dodecacene. The SF-PDFT predicts a closing singlet-triplet gap for an infinitely long linear polyacene chain.

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