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# Singlet triplet gaps in polyacenes : A delicate balance of dynamic and static correlation investigated by spin flip methods

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## Abstract

Over the last few years people have been interested in the process of singlet fission, owing to its relevance in solar cell technology. The energetics of singlet fission is intimately related to singlet triplet (ST) gaps and energies of singlet excited states. However, accurate calculations of ST gaps in polyacenes are complicated due to near degeneracies in the $\pi$ orbitals, and therefore, have been quite challenging. Spin-flip equation-of-motion coupled-cluster (SF-EOM-CC) and its perturbative approximation have been shown to correctly treat situations involving electronic degeneracies and near degeneracies. In this work, we use various spin-flip methods to benchmark the ST gaps of small polyacenes and show that the error in the ST gaps with respect to experiment is small and does not increase appreciably with the system size. The diradical and polyradical character of the polyacene ground states increases with system size. However, for the small polyacenes the open-shell character of the ground state is still small enough to be treated with single reference methods.

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# 1 Introduction

Singlet fission is the process by which a singlet excited state decays into two triplet states. Detailed understanding of the mechanism of singlet fission has been the central goal of many recent studies, mainly because of its implications in solar cell technologies.[1–5] Polyacenes and substituted polyacenes have emerged as relevant candidates for singlet fission due to its interesting packing structures in materials as well as small ST gaps.[6,7] An intimate relationship between the di or polyradical nature and singlet fission process has been proposed.[8–10] There are two aspects to understanding singlet fission in polyacenes and designing new systems - (i) the accurate estimation of the singlet triplet (ST) gaps as well as other low lying singlet excited states; and (ii) calculations of electronic couplings and rates of non-adiabatic transitions.[2,11] In this work we focus on the first aspect. Estimation of ST gaps require a balanced description of both static and dynamic correlations, especially in the case of small ST gaps where the singlet states have considerable diradical or polyradical character.[12,13] Michl and co-workers argued that in systems with large diradical character the energetic conditions for singlet fission are easily satisfied[14] and based on this argument have proposed 1,3-diphenylisobenzofuran as a suitable candidate for singlet fission.[15] They have also tested these energetic criterion for many classes of compounds.[16] This gives further justification for studying the low-lying excited states of this class of compounds.

Polyacenes and patches of graphenes have been interesting systems for theoretical and experimental studies,[12,17–19] due to their highly conjugated nature. In their work, Angliker *et al* have experimentally probed polyacenes up to hexacene and extrapolated their UV-Vis spectra to suggest that there would be a singlet-triplet (ST) crossover at nonacenes, i.e., from nonacene onwards it would have a triplet ($1^3B_{2u}$) ground state.[20] This has also been supported by early density functional theory (DFT) calculations.[21] However, later theoretical calculations using density matrix renormalization group (DMRG) on Pariser-Parr-Pople (PPP) Hamiltonian[22] and ab initio Hamiltonian,[12] as well as later DFT calculations,[17] and valence bond[23] based description have challenged this prediction. Most of these calculations suggest an open-shell diradical singlet ($1^1A_g$) ground state. A recent optical absorption experiment on octacene and nonacene, successfully showed the absence of ST cross-over.[24]

However, a coupled-cluster based calculation by Hajgato *et al*,[13] while supporting the absence of ST cross-over, has suggested a predominantly closed shell ground state, with minimal static correlation. These events over the last few decades show the various controversies that have persisted about the ground state of the acenes as well as the importance of the theoretical predictions.

In order to estimate the relative importance of static and dynamic correlations, one needs to use a method that treats both static and dynamic correlations of the singlet and triplet states on an equal footing. However, consideration of static correlation in polyacenes in a consistent manner is difficult due to the ever increasing active space that needs to be considered for larger polyacenes (e.g., the full valence active space for benzene is (6e,6o) , naphthalene (10e,10o) , anthracene (14e,14o) and so on). With the increase in active space the number of configurations increases exponentially, thus making this approach unsustainable for large polyacenes. DMRG,[25–28] especially in its localized orbital basis[29] can be used to circumvent the exponential scaling with the active space problem. An alternative approach is to entirely circumvent the active space determination and use the spin-flip (SF) operator to treat the static correlation component.

Spin-flip based methods have been used as computationally affordable approach to treat both static and dynamic correlation in a balanced manner.[30–39] It is a size extensive approach. Spin-flip treatment can be viewed as a linear response solution from the triplet (high-spin) reference state. SF approach uses singlet and triplet states at an equal footing with importance to the possibility of both closed and open-shell character of the target states. The approach takes advantage of the fact that in the reference state (high-spin) the importance of static correlation is far less than the low spin (singlet) states. The reference state can be treated at various levels of complexity (DFT, CI, Moller-Plesset perturbation theory (MP2), coupled-cluster with singles and doubles substitution (CCSD) which includes dynamic correlation with increasing accuracy.[39–44] This also results in the increasing accuracy in the target state description.

There are some advantages of understanding the singlet states with SF-CCSD (relative to complete active space (CAS / DMRG based approaches). Firstly, the CAS based methods involves a choice of active space which can often be complicated. Also the full valence active space spanning over all the pi bonding and anti-bonding orbitals increases rapidly with the size of polyacenes and the number of configurations increase exponentially. The second advantage of the SF based approaches is that the states thus obtained have both dynamic and static correlation components in them. On the contrary, the CAS/DMRG based approaches (even when they consider perturbative way of correcting for the ST gaps), do not probe the nature of the excited states after the correction. CAS/DMRG based approaches (only on the $\pi$ type orbitals) reflect the static correlation and therefore, may be prone to over-estimation of the radical character of the states. RAS-2SF methods have already been used successfully to describe electronic structure in the acene dimers, including estimation of electronic coupling. However, this is the first study to evaluate the various single spin-flip approaches on monomers.

In this work, we have used spin-flip approach with the three variants (SF-CCSD, SF-MP2 and SF-TDDFT) to benchmark the ST gaps in small to medium polyacenes. Our results reveal the polyradical character of polyacenes. We also observe that while the ST gaps decrease, there is no ST cross-over. Section II explains the details of the theory used and in Section III we describe the computational protocols used in this study. Results and discussions are presented in Section IV which deals with the ST gaps, polyradical character of the singlet ground state and the low lying excited states of the polyacanes. We conclude in Section V.

## 2 Theory

### 2.1 Spin-flip approach

The central premise of spin-flip approach is starting from a high-spin reference state, which is inherently less multi-configurational and has less correlation. The target state can be defined by the following ansatz,

$$|\Psi_{\text{target}}\rangle = \hat{R}^{SF}|\Psi_{\text{ref}}\rangle, \tag{1}$$

where $\hat{R}^{SF}$ is the spin-flip operator which changes the spin of the system but does not change the number of particles. The $|\Psi_{ref}\rangle$ refers to the high spin reference state at the coupled-cluster, perturbative or DFT level of theory, depending on the flavor of spin flip method that is used. From the reference state, the $\hat{R}_{SF}$ operator moves one electron from $\alpha$ to $\beta$ spin, which changes the spin of the target state and thereby, considers various configurations. The $\hat{R}_{SF}$ is given by the equation,

$$\hat{R}^{\mathrm{SF}} = \sum_{i\uparrow,a\downarrow} R_{i\uparrow}^{a\downarrow}(k) a_{\downarrow}{}^{\dagger} i_{\uparrow} + \sum_{i\uparrow j\uparrow,a\downarrow b\uparrow} R_{i\uparrow j\uparrow}^{a\downarrow b\uparrow}(k) a_{\downarrow}{}^{\dagger} b_{\uparrow}{}^{\dagger} i_{\uparrow} j_{\uparrow} + \cdots, \tag{2}$$

where $a$ and $a^{\dagger}$ refer to the annihilation and creation operators respectively. The $i, j$ indices refer to the occupied orbitals and $a, b$ refer to the virtual orbitals in the HF reference. The $\hat{R}$ operator can be truncated at different levels of excitation thus giving rise to a hierarchy of accuracy, e.g., SF-CCSD, SF-CCSD(2,3) etc.[45] In $\hat{R}_{SF}$, the $\alpha$ and $\beta$ spins are denoted by ↑ and ↓ respectively, the equation shows the case where one starts with an excess $\alpha$ electrons (this can be easily generalized to the reference with excess $\beta$ electrons). The operator $\hat{R}$ is an excitation operator truncated at a certain order of excitation. Ref.[46] gives a detailed description of the method. It should be noted that in this work, we use the single spin-flip operator ($M_S$=-1), however, for dimers the same approach can be extended to double spin-flips ($M_S$=-2).

For a system with significant non-dynamic correlation, the target wavefunctions include multiple possible configurations with comparable weights. This can be achieved through the SF operator which changes the spin of the system ($\Delta M_s = \pm 1$) but not the number of particles ($\Delta N = 0$). One starts with a high spin triplet state (with excess $\alpha/\beta$ electrons) which is predominantly of a single-configurational character. From that reference, the $\hat{R}^{SF}$ operator moves one electron with $\alpha/\beta$ spin to $\beta$ /$\alpha$ spin, which changes the state from high spin ($M_s = 1$) to low spin (singlet and $M_s = 0$ triplet) and in the process considers various configurations.

## 2.2 Different spin-flip approach

The original implementation of SF approaches started as a modification of the traditional and highly successful equation-of-motion coupled-cluster (EOM-CC). The reference state in that case is given by the CC wavefunction,

$$|\Psi_{\mathrm{CC}}\rangle = \exp(\hat{T})|\Phi_0\rangle \tag{3}$$

where $\Phi_0$ is the uncorrelated Hartree Fock wavefunction. The operator $\hat{T}$ can be written as,

$$\hat{T} = \hat{T}_1 + \hat{T}_2 = \sum_{i,a} t_i^a a^\dagger i + \frac{1}{4} \sum_{i,j,a,b} t_{ij}^{ab} a^\dagger b^\dagger i j \tag{4}$$

in the traditional closed-shell CCSD form. This method of describing multi-configurational target states is called SF-CCSD.

CC theory and many body perturbation theory (MBPT) are closely related techniques for the calculation of many body effects.[47,48] Therefore, a natural way of analyzing and reducing the computational cost of CC based methods is to look at the possible perturbative approximations. One can express the effective Hamiltonian $\bar{H}$ as the connected terms in $[H\exp(\hat{T})]_c$. This effective Hamiltonian can also be expanded as a Baker-Campbell-Hausdorff (BCH) expansion

$$\bar{H} = H + [H,T] + \frac{1}{2}[[H,T],T] + \frac{1}{6}[[[H,T],T],T] + \cdots \tag{5}$$

and alternatively as a perturbative expansion,

$$\bar{H} = H^{[0]} + \bar{H}^{[1]} + \bar{H}^{[2]} + \bar{H}^{[3]} + \cdots \tag{6}$$

In case of truncated effective Hamiltonians (at the level of $H^{[2]}$), the CC amplitudes can be expressed as the MP2 amplitudes,[49]

$$\begin{aligned} \bar{H} &= (He^{T})_c \\ &\approx (He^{T'})_c \end{aligned} \tag{7}$$

where the perturbative approximation to the $T_2$ amplitudes can be written as,

$$\begin{aligned} T_i^{a\prime} &= \frac{f_{ia}}{\varepsilon_i - \varepsilon_a} \\ T_{ij}^{ab\prime} &= \frac{\langle ab||ij\rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}. \end{aligned} \tag{8}$$

$T_1$ is zero for restricted closed-shell and unrestricted MP2 reference. Using these $T'$ amplitudes one can calculate a modified effective $\bar{H}'$, which can be used as the reference for subsequent EOM calculation. Thus, this is necessarily an EOM calculation on a MBPT2 reference state. We refer to this as SF-MP2 or SF-CCSD(2)[50] and the details are given in Refs.[40] and.[51] Table 1 compares the various SF approaches. It should be noted that for many of the variants a two spin-flip is possible. However, all the operators that are shown in the table refer to only the single SF process, since we deal with only single SF computations in this work.

Table 1: Hierarchy of spin-flip methods. Some of the methods are described in Ref.[46]

| Reference | Method | Wavefunction |
|---|---|---|
| SCF | SF-CIS | $R_1\Phi_0$ |
| SCF | RAS-SF | $R_1\Phi_0$ + selected higher exc |
| DFT | SF-TDDFT | $R_1\Phi_{DFT}$ |
| SCF | SF-CIS(D) | $R_1\Phi_0$ + $R_2$ by PT |
| SCF | SF-CISD | $(R_1+R_2)\Phi_0$ |
| MP2 | SF-MP2 | $(R_1+R_2)\exp(T_1'+T_2')\Phi_0$ |
| CCSD | SF-CCSD | $(R_1+R_2)\exp(T_1+T_2)\Phi_0$ |

## 3 Computational details

The geometries of the polyacenes (1-13) have been optimized with the UB3LYP/6-31G(d) level of theory. The optimized geometries for the singlet and triplet states are given in the supplementary information. SF-CCSD, SF-MP2 and SF-DFT calculations with 6-311++G(d,p), 6-311G, 6-31+G(d,p) and 6-31G basis sets have been carried out with a locally modified version of the quantum chemistry software Q-Chem 4.2.[52–54] All SF-TDDFT calculations use collinear kernels and the recommended 50-50 functional. Frozen core orbitals are used to reduce the computational cost and UHF references are used for convergence issues. Here it should be noted that the error in $\langle S^2 \rangle$ for all reference states is always less that $< 0.2$. Frozen natural orbital (FNO)[55] approximation has been used to reduce the size of virtual space to cut the computational cost of larger polyacenes. The $R$ amplitudes of the SF operator have been analyzed to quantify the radical (di or higher) character of the singlet ground states.

The traditional equation-of-motion coupled-cluster (EOM-CCSD) has been used to calculate the low lying excitation energies of the smaller polyacenes with 6-311++G(d,p) basis set. These calculations were carried out to estimate the energetics of of the states relevant to singlet fission.

# 4 Results and discussion

## 4.1 Singlet triplet gaps

Fig 1 shows the plot of ST gap versus size of polyacenes calculated with SF-CCSD with different basis sets, compared to experimental values. Details of the effect of basis sets are further elucidated in the supplementary information. The electronic energy differences computed by SF-CCSD have been corrected for zero-point energies (ΔZPEs) computed at the UB3LYP/6-31G(d) level of theory. We observe that the ST gap plots for SF methods are parallel to the experimental results, i.e., the errors do not increase substantially with the increase in system size. We notice that due to different basis sets the ST gaps differ by $\approx 0.5$ kcal/mol. The effect of FNO (with population threshold 99.5% ) is 0.5-1.5 kcal/mol.

Table 2 shows the difference between the ST gaps calculated with various spin-flip methods from the experimental values for small polyenes. Comparing our results to the DMRG results by Hachmann *et al*,[12] it shows that while DMRG shows very good accuracy for the smaller polyacenes, the errors increase with system size. This is probably due to the lack of dynamic correlation in DMRG, as noted in Ref.,[13] comparing the CASSCF versus CASPT2 ST gaps. On the other hand the SF-CCSD, SF-MP2 and SF-TDDFT calculations contain both dynamic and static correlation and therefore, the errors do not increase substantially with system size. Supplementary information contains more details about other possible SF-TDDFT values including non-collinear kernels.

Fig 2 shows the comparison of different SF approaches - SF-CCSD, SF-MP2 and SF-TDDFT with respect to the ST gaps of polyacenes. The SF-TDDFT results for benzene starting from an unrestricted reference shows very high spin contamination and has therefore, not been considered.

We also notice that the ST gaps decrease exponentially, however, for the system sizes considered we do not notice any ST cross-over even after extrapolation. This is in accordance with the results by

Figure 1: ST gaps of different size polyacenes calculated with SF-CCSD method with different basis sets with or without FNO, compared to DMRG/STO-3G and experimental results.

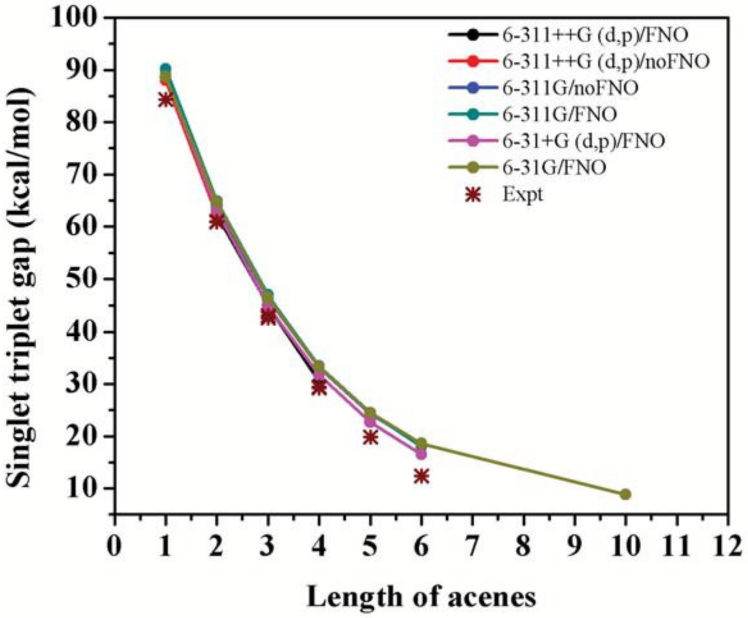


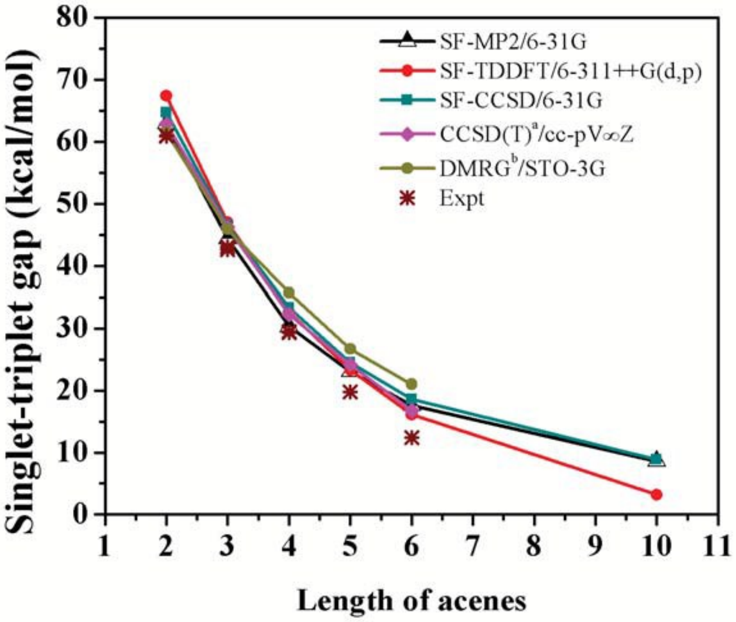
Table 2: Errors in the ST gaps with respect to experiment (in kcal/mol) of the SF-CCSD, SF-MP2 and SF-TDDFT at different basis sets.

| System | SF-MP2<br>6-31G | SF-MP2<br>6-31+G(d,p) | SF-CCSD<br>6-31G | SF-CCSD<br>6-31+G(d,p)/FNO | SF-TDDFT<br>6-311++G(d,p) |
|---|---|---|---|---|---|
| Naphthalene | 1.9-2.0 | 1.8-1.9 | 3.7-3.8 | 2.2-2.3 | 6.4-6.5 |
| Anthracene | 1.3-1.8 | 0.8-1.3 | 3.4-3.9 | 1.7-2.2 | 3.9-4.4 |
| Tetracene | 0.8-1.0 | 0-0.2 | 3.8-4.0 | 2.2-2.4 | 3.1-3.3 |
| Pentacene | 3.30 | - | 4.7 | 2.9 | 3.5 |
| Hexacene | 5.20 | - | 6.2 | 4.1 | 3.7 |

Hachmann *et al* and Bendikov and co-workers.

Since, accurate SF-CCSD calculations with large basis sets are computationally unfeasible for large polyacenes, SF-TDDFT with large basis set can be used with correction due to method calculated at a small basis set. Since from Fig 2, the SF-CCSD, SF-TDDFT and SF-MP2 plots are parallel to each other ( except in case of benzene), we can use a cheaper method, e.g., SF-TDDFT or SF-MP2 to calculate ST gaps of large polyacenes and add a correction due to method ($\Delta$method $=$ $E_{ST}^{\text{small polyacene}}(\text{method1}) - E_{ST}^{\text{small polyacene}}(\text{method2})$), where method1 refers to the more accurate (rigorous method), e.g., SF-CCSD and method2 refers to the less accurate but cheaper method, e.g.,

Figure 2: Adiabatic ST gaps calculated with SF-CCSD, SF-MP2 and SF-TDDFT, compared to CCSD(T)/cc-pV∞Z, DMRG/STO-3G and experimental results.[a]The CCSD(T)/cc-pV∞Z values are taken from Ref.[13] and [b]/STO-3G DMRG results are taken from Ref.[12]



SF-MP2 or SF-TDDFT. Thus, the best estimate for the ST gaps can be given as,

$$E_{ST}^{\text{large polyacene}}(\text{best estimate}) = E_{ST}^{\text{large polyacene}}(\text{SF}-\text{TDDFT}) + \Delta\text{method}, \tag{9}$$

where $\Delta\text{method} = E_{ST}^{\text{SF}-\text{CCSD}}(\text{small basis}) - E_{ST}^{\text{SF}-\text{TDDFT}}(\text{small basis})$.

To further analyze the ST gaps and estimate the errors for various methods, we have calculated the vertical ST gaps with all the flavors of SF methods with 6-31+G(d) basis set and tabulated them in Table 3. Comparing the SF-CCSD (most accurate) values with the other SF methods, we notice that the RMSDs are 1.57, 2.14, 1.06, 1.22 kcal/mol for SF-MP2, SF-CISD, SF-CIS(D) and SF-CIS respectively, and the RMSD is 1.46 for SF-TDDFT with respect to SF-CCSD. The leading amplitudes (given in parenthesis in Table 3) configuration is proportional to the closed-shell character of the ground state wavefunction and therefore, we see that all the methods show a similar trend. That is the closed-shell character decreases with size of polyacenes and therefore, open-shell or diradical character increases. Comparison between SF-CISD and SF-MP2 errors (with respect to SF-CCSD) shows the importance

Table 3: Vertical ST gaps (in kcal/mol) of the polyacenes calculated with different SF levels of theory with 6-31+G(d) basis set. The amplitudes for the leading configuration (closed-shell) is shown in parenthesis.

| Size | SF-TDDFT | SF-CIS | SF-CIS(D) | SF-CISD | SF-MP2 | SF-CCSD |
|---|---|---|---|---|---|---|
| 1 | n.a. | 100.93 | 103.94 | 111.29 | 101.98 | 106.7 |
| | n.a. | (0.9600) | (0.9600) | (0.9436) | (0.9437) | (0.9472) |
| 2 | 82.99 | 77.99 | 77.72 | 82.71 | 74.66 | 78.14 |
| | (0.9894) | (0.9510) | (0.9510) | (0.9307) | (0.9370) | (0.9347) |
| 3 | 58.26 | 55.09 | 53.39 | 61.17 | 52.72 | 56.76 |
| | (0.9832) | (0.9292) | (0.9292) | (0.9253) | (0.9148) | (0.9251) |
| 4 | 41.85 | 38.77 | 37.84 | 44.97 | 37.28 | 39.85 |
| | (0.9771) | (0.8998) | (0.8998) | (0.9136) | (0.8982) | (0.8940) |
| 5 | 30.67 | 28.94 | 26.45 | 33.78 | 26.58 | 28.62 |
| | (0.9679) | (0.8653) | (0.8653) | (0.9033) | (0.8740) | (0.8706) |

of dynamic correlation in the reference state. On the other hand, SF-CIS and SF-CIS(D) shows better ST gaps possibly because of error cancellation, although their leading amplitudes points towards errors in the wavefunction. It can also be seen that the SF-CIS leading amplitudes decrease much faster than any of the other wavefunctions originating from correlated reference states, e.g., SF-TDDFT, SF-MP2 and SF-CCSD. This also points towards a possible over-estimation of increase in open-shell character with methods such as CASSCF.

Table 4 tabulates the best estimates of the vertical and adiabatic ST gaps by applying method and basis set corrections.

Using the best estimate adiabatic ST gaps for polyacenes, we can fit this data to an exponential decay of the form $a + b\exp(-cx)$. Using this form of decay, the extrapolated ST gaps for infinitely long polyacenes are 5.06 and 5.37 kcal/mol for best estimate and SF-CCSD/6-31+G(d,p) values respectively. Thus, we see no ST cross-over. The fit is done using the data for benzene to decacene. The value of ST gap at infinite length can be compared to $\approx$4 kcal/mol from focal point analysis by Hajgato *et al*, 3.33 (cc-pVDZ) and 8.69 (STO-3G) kcal/mol from DMRG by Hachmann *et al* and 12.2 kcal/mol from semi-empirical Parr-Pariser-Pople Hamiltonian[62,63] study by Raghu *et al.*[22] It should be noted that from the analysis by Hajgato *et al*, estimates of vertical and adiabatic ST gaps at infinite polyacene length are very different if one keeps benzene in the fit (0.27 and -0.37 kcal/mol) vs if one removes benzene from the fit (3.75 and -0.22 kcal/mol). We notice no such large discrepancies in the

Table 4: Best estimates of vertical and adiabatic ST gaps compared to experimental ST gaps. Earlier theoretical values are also included for comparison.

| System | Vert. ST | Adia. ST | Expt. ST | Theory (vert.) | Theory (adia.) |
|---|---|---|---|---|---|
| Benzene | 102.8 | 88.0 | 84.3[a] | 100.79[h] | 87.02[g] |
| Naphthalene | 77.1 | 62.3 | 60.9-61.0[b] | 76.28[h] | 67.1[j], 61.5[i], 61.0[n], 56.9[l], 62.87[g] |
| Anthracene | 57.0 | 47.5 | 42.6-43.1[c] | 56.97[h] | 60.0[k], 45.9[i], 44.0[n], 46.1[m], 46.22[g] |
| Tetracene | 41.9 | 34.1 | 29.3-29.5[d] | 40.69[h] | 47.3[k], 34.7[i], 31.9[n], 34.8[m], 32.23[g] |
| Pentacene | 31.7 | 25.6 | 19.8[e] | 31.51[h] | 26.7[i], 23.4[n], 24.19[g] |
| Hexacene | 24.6 | 19.2 | 12.4[f] | 22.96[h] | 21.0[i], 17.5[n], 16.79[g] |
| Decacenes | 13.1 | 8.8 | n.a. | | 11.6[i] |
| 13-acene | ≈12 | ≈8 | n.a. | | |

[a] Ref;[56]
[b] Refs[56] and[57] ;
[c] Refs[56] and[58] ;
[d] Refs[56] and[59] ;
[e] Ref[60] ;
[f] Ref[20] ;
[g] FPA and ZPE corrected values from Ref[13] ;
[h] CCSD(T)/cc-pV∞Z values from Ref[13] ;
[i] DMRG/STO-3G values from Ref[12] ;
[j] CASSCF/DZP values from Ref[12] ;
[k] CASSCF/DZP values from Ref[61] ;
[l] CASPT2/DZP values from Ref[12] ;
[m] MRMP/DZP values from Ref[61] ;
[n] DMRG/DZ values from Ref.[12]

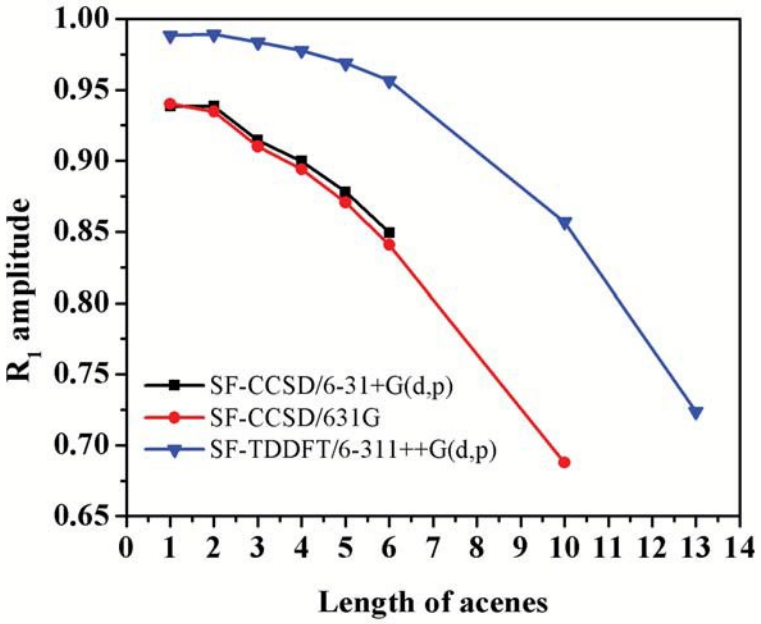
ST gap depending on inclusion of benzene in the fit.

## 4.2 Radical character of the singlet state

In order to elucidate the polyradical character of the singlet ground state (if any), we have looked at the $R_1$ amplitudes of the SF operator at the singlet optimized geometries for all polyacenes. The same trends hold for the amplitudes at the triplet optimized geometries. Fig 3 shows the $R_1$ amplitude that gives rise to the closed-shell configuration with respect to the system size. We notice that the amplitude decreases with the increase in the system size, thus showing that the closed-shell character decreases and therefore, the open-shell character of the ground state increases.

To further understand the specific character of the open-shell configurations of the ground state $S_0$,

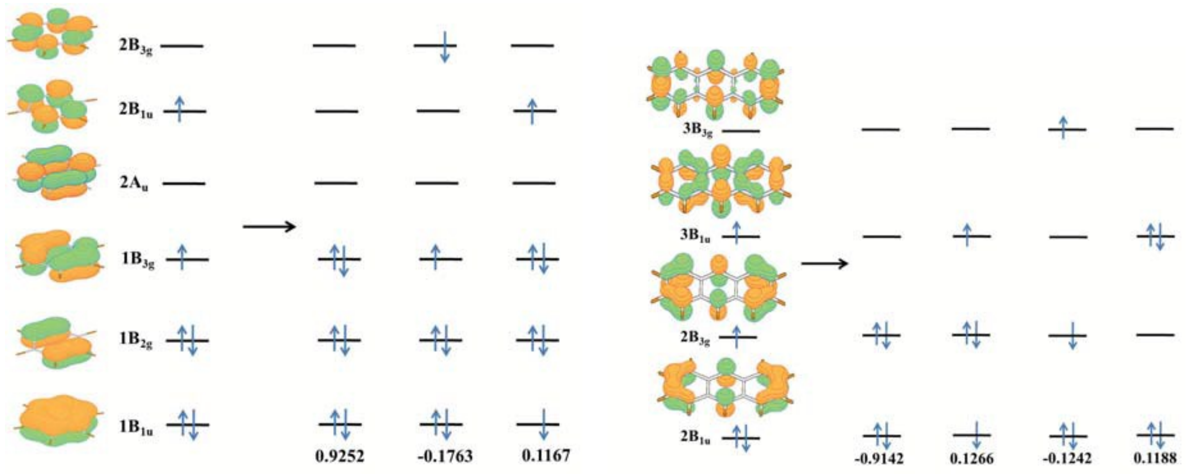
Figure 3: The value of $R_1$ amplitude corresponding to the most stable closed-shell configuration for the polyacenes plotted as a function of system size.



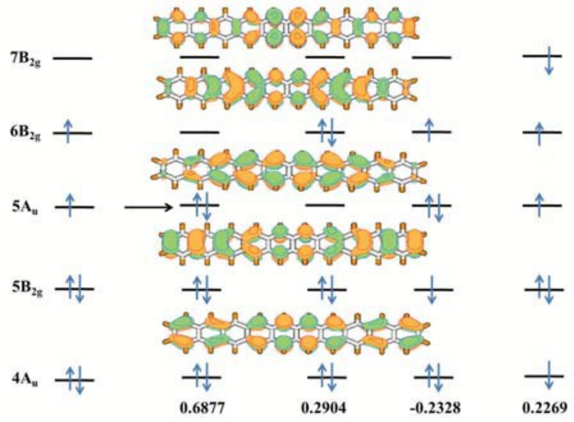
we have drawn the important configurations with the highest $R_1$ amplitudes. We notice that in case of benzene the ground state is almost entirely (>90%) of a closed-shell character (see Fig. 4). Benzene ground state is, thus, a combination of $R_1 = 0.9252$ amplitude of closed-shell ($(a_{2u})^2(e_{1g})^2(e_{1g})^2$ in $D_{6h}$ which corresponds to $(b_{1u})^2(b_{2g})^2(b_{3g})^2$ in $D_{2h}$) configuration, with small $R_1$ amplitudes of 0.1763 and 0.1167 for open-shell ($(b_{1u})^2(b_{2g})^2(b_{3g})^1(2b_{3g})^1$ and $(b_{1u})^1(b_{2g})^2(b_{3g})^2(2b_{1u})^1$) configurations. Notice that we have only mentioned the most important configurations that arise from highest $R_1$ amplitudes.

However, as we increase the system size to anthracene, we notice the appearance of more (10%) open-shell singlet configurations (see Fig. 4b). The anthracene ground state is, thus, a combination of $R_1 = 0.9142$ amplitude of closed-shell ($(b_{2u})^2(b_{2g})^2(b_{1g})^2(b_{1u})^2(a_u)^2(2b_{2g})^2(b_{3g})^2$) configuration, with small 0.1188 amplitude of the closed-shell ($(b_{2u})^2(b_{2g})^2(b_{1g})^2(b_{1u})^2(a_u)^2(2b_{2g})^2(2b_{1u})^2$) configuration. There are also small $R_1 = 0.1266$ and 0.1242 amplitude of open-shell ($(b_{2u})^2(b_{2g})^2(b_{1g})^2(b_{1u})^1(a_u)^2(2b_{2g})^2(b_{3g})^2(2b_{1u})^1$ and $(b_{2u})^2(b_{2g})^2(b_{1g})^2(b_{1u})^2(a_u)^2(2b_{2g})^2(b_{3g})^1(2b_{3g})^1$) configurations. The configurations II and III correspond to small amounts of diradical character in anthracene. Since the configurations II and III occur with small amplitudes, CCSD can in fact treat

Figure 4: Molecular orbitals corresponding to the highest amplitudes for the spin-flip operators.



(a) Benzene (b) Anthracene



(c) Decacene

these ground states quite accurately as shown by Hajgato *et al*.

Finally in case of decacene, we notice that there are presence of significant diradical as well as tetra-radical character (see Fig 4c). The decacene ground state is a combination of only $\mathrm{R}_1 = 0.6877$ amplitude of closed-shell $(\cdots(a_u)^2(b_{2g})^2(a_u)^2)$ configuration, with $R_1 = 0.2328$ amplitude of diradical $(\cdots(a_u)^2(b_{2g})^1(a_u)^2(b_{2g})^1)$ configurations, as well as $R_1 = 0.2269$ amplitude of tetra-radical configuration. We, therefore, notice the same kind of build up of polyradical character in the higher polyacenes as noticed by Hachmann *et al*.

Table 5: Vertical singlet excitation energies of the polyacenes (in eV) calculated with EOM-EE-CCSD/6-311++G(d,p) compared to the ST gaps. Earlier theoretical values using different methods are also included for comparison.

| System | $^1B_{2u}$ (bright) | $^1B_{3u}$ (dark) | ST gap | Earlier computed $^1B_{2u}$ | Earlier computed $^1B_{3u}$ |
|---|---|---|---|---|---|
| Benzene | 6.62 | 5.18 | 3.82 | | |
| Naphthalene | 5.16 | 4.41 | 2.70 | 4.68[c], 4.89[d], 5.09[e], 4.79[f] | 4.63[c],4.47[d], 4.43[e], 4.13[f] |
| Anthracene | 4.08 | 3.88 | 2.06 | 3.54[c], 3.70[d], 4.00[e], 3.69[f] | 4.04[c], 3.90[d], 3.90[e], 3.59[f] |
| Tetracene | 3.33 | 3.53 | 1.48 | 2.77[c], 2.90[d], 3.25[e], 2.94[f] | 3.66[c], 3.52[d], 3.54[e], 3.25[f] |
| Pentacene | 2.88[a] | 3.33[a] | 1.11 | 2.22[c], 2.35[d], 2.72[e], 2.42[f] | 3.40[c], 3.27[d], 3.30[e], 3.02[f] |
| Hexacene | 2.59[b] | 3.19[b] | 0.83 | 1.83[c], 1.95[d], 2.34[e], 2.05[f] | 3.21[c], 3.09[d], 3.12[e], 2.86[f] |

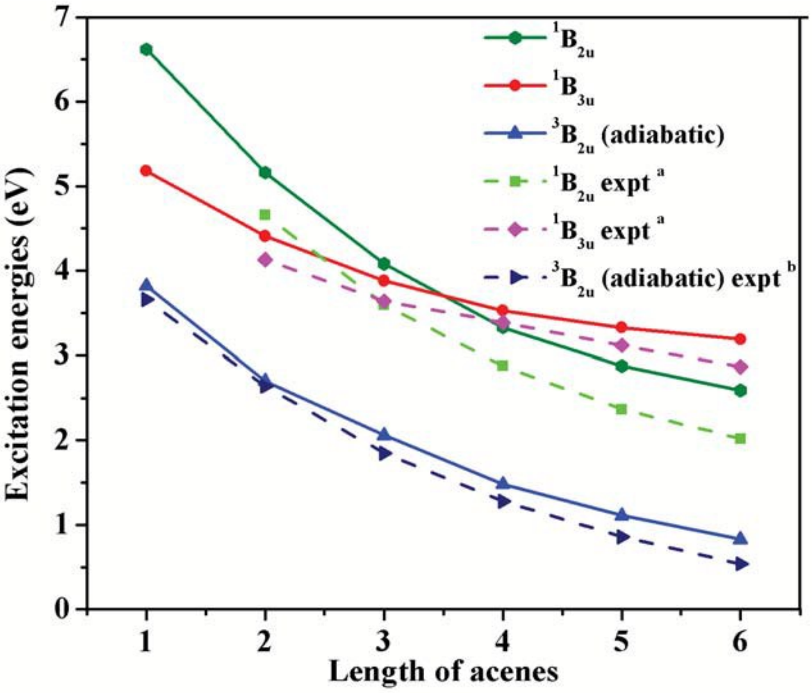
[a] FNO was used to reduce computational cost. ;
[b] FNO and H atoms with 6-31G basis set (keeping the bigger basis set for heavier atoms) were used to reduce computational cost. ;
[c] CAM-B3LYP values from Ref.[64] ;
[d] CC2 values from Ref.[64] ;
[e] EOM-CCSD from Ref.[65] ;
[f] CR-EOM-CCSD(T) from Ref.[65] .

## 4.3 Low lying singlet excitation energies

Since the diradical character of the ground state for small polyacenes are around 10%, the ground state can, in fact, be described with single reference methods such as CCSD. With this observation in mind, we have calculated with low-lying singlet excited states starting from a ground state CCSD reference with traditional EOM-CC method. Table 5 shows the low-lying excitation energies (vertical) of the singlet states of small polyacenes with EOM-CCSD/6-311++G(d,p) level of theory, as well as the transition dipole moments corresponding to these transitions. There is a cross-over between the $^1B_{2u}$ and $^1B_{3u}$ excited states from anthracene onwards. From the transition dipole moments, the excited state $^1B_{3u}$ is optically inactive, with the transition dipole along the long-axis, The excited state $^1B_{2u}$ is optically active, with the transition dipole along the short-axis.

Fig 5 compares the lowest singlet excitation energies with the ST gaps and we observe that singlet fission is feasible for higher polyacenes. We present a comprehensive methodology to quantify energetics of singlet fission for a range of compounds (with varying size and polyradical character) on an equal footing.

Figure 5: Two lowest VEEs (calculated with EOM-EE-CCSD) and adiabatic ST gaps (calculated with EOM-SF-CCSD) of polyacenes are plotted with respect to acene sizes. [a]The experimental values for $^1B_{2u}$ and $^1B_{3u}$ are taken from Refs.[66] and.[67] [b]The experimental values for $^3B_{2u}$ (adiabatic ST gap) is taken from Refs.,[56],[57],[58],[59 60] and.[20]



## 5 Conclusion

In this work, we have used various SF approaches to accurately calculate the ST gaps of polyacenes. The computed values are in good agreement with available experimental data. Since in most of the SF approaches, we start with a dynamically correlated reference state, the resulting wavefunctions contain both static and dynamic correlation. We notice a very delicate balance of both static and dynamic correlations is involved in the singlet and triplet states and therefore, in the ST gaps. We do not observe any ST cross-over in the polyacenes up to decacene. Using extrapolation of available data we predict that there are no ST cross-overs for any length of polyacenes.

As the system size increases the closed-shell character of the ground singlet state decreases as seen from the amplitudes. We also see there is a rise in diradical and polyradical character in the ground state. However, the substantial polyradical character is not observed for smaller polyacenes and therefore, gives a reason for the success of focal point analysis using single reference methods in earlier work. This also predicts that such single reference treatment will indeed become less reliable as the system sizes becomes larger than decacenes.

In the singlet excited states, we observe two low lying states $B_{2u}$ and $B_{3u}$ symmetries which are optically active and inactive respectively. There is a cross-over between these two states around anthracene. The success of SF approach in determining accurate ST gaps, opens up new avenues of understanding the mechanism of singlet fission.

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