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Determination of electronic couplings in the singlet fission process using a nonorthogonal configuration interaction approach

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Abstract

Singlet fission has been explored as an alternative mechanism to enhance the performance of solar cells. In this work, we use a nonorthogonal configuration interaction approach to study the singlet fission process in solid 2-methylene-2H-indene, an identified potential singlet fission molecule. Results of the electronic coupling calculations in pairs of molecules show that this molecule is suitable for the efficient formation of the 1TT state (≈ 40 meV). We report, for the first time, a comparison of the nonorthogonal configuration interaction approach with two other theoretical methodologies: restricted active space with two spin flips and the *ab initio* Frenkel–Davydov exciton model.

1. Introduction

Singlet fission (SF) is a multiexciton generation phenomenon that occurs in organic molecules and in which the first singlet excited state of a molecule splits into two triplets in an overall spin-allowed process by forming the so-called 1TT state (Fig. 1).^{1,2} Since SF may give rise to the generation of four charge carriers per absorbed photon, this multiexciton generation process has been explored as an alternative scheme to enhance the efficiency of current solar cells and overcome the so-called Shockley–Queisser limit.^{3,4} Nevertheless, the number of molecules known experimentally to exhibit this process is limited. Furthermore the mechanistic details of the process are not yet well-understood and are the subject of an active area of research.^{5–10} The lack of materials and poor understanding of the process have limited the technological development of SF-enhanced solar cells. Finding proper materials and obtaining a deeper comprehension of how SF occurs in organic solids may lead to its further implementation in solar cell technology¹¹.

In order for SF to be an efficient process, the following criteria must be fulfilled^{1,12}: (1) SF has to occur faster than any other competing process (e.g., radiative decay or intersystem crossing); (2) the process should preferably be isoergic or slightly exoergic (although endoergic SF has been observed in tetracene^{13–15}) which means fulfilling the energetic requirement

Fig. 1 Schematic representation of singlet fission. Upon absorption of a photon, a singlet excited molecule (S_1) transfers part of its energy to a neighbor to form two triplets (1TT) that are coupled into a singlet.

$E(S_1) \geq 2E(T_1)$; and (3) the T_2 state in the molecule should be higher in energy than S_1 , and at least twice the energy of T_1 to avoid triplet–triplet annihilation. Additionally, some properties are desired from these materials, such as high stability under continuous radiation, low cost associated to their production for practical applications and long-lived triplets to ensure that the charge carriers can be harvested. Theoretical simulations can assist the design of SF-enhanced solar cells and be used to optimize the SF process in organic solids that fulfill the above mentioned requirements.^{16,17} The mechanism underlying SF is still unclear;^{18,19} the schematic representation in Fig. 1 is generally accepted but the understanding of how the 1TT state is formed from the singlet excited state is still a matter for debate. Different mechanisms have been proposed: one in which the 1TT state is formed directly from the singlet excited state via a two-electron transfer (blue arrow in Fig. 2) or a transition in which the charge transfer (CT) states act as intermediates (red arrows in Fig. 2). Alternatively, if the CT states are too high in energy, a “mediated” mechanism (green arrows in Fig. 2) can occur in which CT configurations appear in the wave functions of the initial and final states facilitating the process. Therefore, studying the influence of the CT states in the mechanism of SF is essential. Additionally, vibrations and molecular motions have been suggested as playing active roles in SF.^{20–23}

Fig. 2 Direct (blue arrow), intermediate (red arrows), and mediated (green arrows) mechanisms between the different states (singlet excited, S_0S_1 ; charge transfer, $D_0^+D_0^-/D_0^-D_0^+$; and multiexciton state, 1TT) in singlet fission.

In order to study SF, a rate constant (k_E) associated with the process can be approximated by means of the Fermi's golden rule²⁴:

$$k_E \approx \frac{2\pi}{\hbar} |V_{\mu\nu}|^2 \rho(E) \quad (1)$$

where $V_{\mu\nu}$ represents the electronic coupling between two (diabatic) states, μ and ν , and $\rho(E)$ denotes the density of states per unit of energy E . Different ways to evaluate the electronic coupling exist,^{16,25} and in this work, we use a nonorthogonal configuration interaction (NOCI) approach;^{26–29} advantages of this method are that it is conceptually simple and yet considers orbital relaxation effects as well as (static) electron correlation. In cases where the orbitals of the excited states differ significantly (e.g., for CT states), lengthy CI expansions can be avoided using the NOCI approach and if the states of interest have multireference character, NOCI is expected to outperform methods based on single reference wave functions. With the NOCI approach, a solid is described in terms of molecular states. Therefore we calculate, for different electronic states of each molecule in an ensemble, molecular wave functions that are subsequently combined into basis functions which describe a particular combination of molecular states. The final wave function for the ensemble is then written as an expansion of these many-electron basis functions (MEBFs). The NOCI approach is attractive for the description of SF since the wave function is constructed with MEBFs that describe all the states involved and, moreover, the interaction between the photo excited state and the multiexciton state can be directly calculated. The molecular wave functions can be chosen to be complete active space self-consistent field (CASSCF) wave functions in which both the orbitals and CI coefficients are fully optimized. Each molecular wave function is optimized with its own set of orbitals and represents a specific electronic state I of molecule A (Ψ_A^I), such as the ground state ($\Psi_A^{S_0}$), the lowest singlet excited state ($\Psi_A^{S_1}$), the lowest triplet state (Ψ_A^T), the cationic ground state ($\Psi_A^{D_0^+}$), and the anionic ground state ($\Psi_A^{D_0^-}$). The MEBFs ($|\Phi_\mu\rangle$) are then constructed as spin-adapted antisymmetrized products of the molecular wave functions:

$$|\Phi_\mu\rangle = \sum_{\sigma} \kappa_{\sigma} \hat{A} \prod_A^N |\Psi_A^I\rangle_{\sigma} \quad (2)$$

where N is the number of molecules in the ensemble, κ_σ are the corresponding spin-coupling coefficients, and the summation over σ indicates that several antisymmetrized products of molecular wave functions with different M_s eigenvalues are combined such that the resulting MEBFs are spin eigenfunctions. In practice, for example for a pair of molecules, a MEBF is generated from the molecular CASSCF wave functions as:

$$\begin{aligned} \hat{A} \left(\sum_i C_i^A \Delta_i^A \right) \left(\sum_j C_j^B \Delta_j^B \right) &= \sum_{ij} C_i^A C_j^B \hat{A} | \phi_\mu^A \dots | | \phi_\nu^B \dots | \\ &= \sum_{ij} C_i^A C_j^B | \phi_\mu^A \dots \phi_\nu^B \dots |. \end{aligned} \quad (3)$$

In this notation, C_i and C_j denote the CI coefficients of the molecular CASSCF wave functions, Δ is a Slater determinant, and ϕ indicates the occupied spin orbitals in the Slater determinant for molecules A and B . In principle, the number of molecules included in the ensemble is not limited. However, our preliminary investigation following the protocol outlined in Ref. 26, for a pair of molecules taken from the structure reported in Ref. 26, resulted in an electronic coupling between the photo excited and the multiexciton state of 9 meV, compared to 12 meV reported for a cluster of three molecules; this indicates that the size of the ensemble only marginally affects the electronic coupling. Therefore, in this work we focus on the study of pairs of molecules.

In a pair of molecules named as A and B , several MEBFs can be constructed, e.g., one MEBF describing both molecules in their ground state ($|\Phi_{S_0 S_0}\rangle$); two MEBFs in which one of the molecules is in the lowest singlet excited state ($|\Phi_{S_0 S_1}\rangle$ and $|\Phi_{S_1 S_0}\rangle$); one MEBF representing the two triplets coupled into a singlet ($|\Phi_{TT}\rangle$); and two MEBFs describing the charge transfer states ($|\Phi_{D_0^+ D_0^-}\rangle$ and $|\Phi_{D_0^- D_0^+}\rangle$). The three spin singlet MEBFs constructed from the molecular wave functions with $S = 0$ are formed as:

$$|\Phi_{S_0 S_0}\rangle = \hat{A} |\Psi_A^{S_0} \Psi_B^{S_0}\rangle \quad (4a)$$

$$|\Phi_{S_0 S_1}\rangle = \hat{A} |\Psi_A^{S_0} \Psi_B^{S_1}\rangle \quad (4b)$$

$$|\Phi_{S_1 S_0}\rangle = \hat{A} |\Psi_A^{S_1} \Psi_B^{S_0}\rangle \quad (4c)$$

whereas the MEBFs constructed from the molecular wave functions with $S > 0$ (i.e., Ψ^T , $\Psi^{D_0^+}$, and $\Psi^{D_0^-}$) are expressed as linear combinations of the antisymmetrized products of those molecular functions, in such a way that the total M_s and S are equal to 0³⁰:

$$|\Phi_{TT}\rangle = \frac{1}{\sqrt{3}}\hat{A}\left|(\Psi_A^T)_{M_s=+1}(\Psi_B^T)_{M_s=-1}\right\rangle + \frac{1}{\sqrt{3}}\hat{A}\left|(\Psi_A^T)_{M_s=-1}(\Psi_B^T)_{M_s=+1}\right\rangle \\ - \frac{1}{\sqrt{3}}\hat{A}\left|(\Psi_A^T)_{M_s=0}(\Psi_B^T)_{M_s=0}\right\rangle \quad (5a)$$

$$\left|\Phi_{D_0^+D_0^-}\right\rangle = \frac{1}{\sqrt{2}}\hat{A}\left|(\Psi_A^{D_0^+})_{M_s=+1/2}(\Psi_B^{D_0^-})_{M_s=-1/2}\right\rangle \\ - \frac{1}{\sqrt{2}}\hat{A}\left|(\Psi_A^{D_0^+})_{M_s=-1/2}(\Psi_B^{D_0^-})_{M_s=+1/2}\right\rangle \quad (5b)$$

$$\left|\Phi_{D_0^-D_0^+}\right\rangle = \frac{1}{\sqrt{2}}\hat{A}\left|(\Psi_A^{D_0^-})_{M_s=+1/2}(\Psi_B^{D_0^+})_{M_s=-1/2}\right\rangle \\ - \frac{1}{\sqrt{2}}\hat{A}\left|(\Psi_A^{D_0^-})_{M_s=-1/2}(\Psi_B^{D_0^+})_{M_s=+1/2}\right\rangle. \quad (5c)$$

Then, the total NOCI wave function (Ψ_{NOCI}) describing the ensemble is expressed as a linear combination of the different MEBFs:

$$\Psi_{\text{NOCI}} = \sum_{\mu} C_{\mu} |\Phi_{\mu}\rangle \quad (6)$$

in which the coefficients C_{μ} are determined using variational theory and can be related to a weight for each MEBF that indicates the importance of a particular combination of molecular electronic states in the description of an electronic state of the ensemble. To perform such a calculation the Hamiltonian $\langle\Phi_{\mu}|\hat{H}|\Phi_{\nu}\rangle$ and overlap $\langle\Phi_{\mu}|\Phi_{\nu}\rangle$ matrix elements are needed. The MEBFs are mutually nonorthogonal, since they are constructed from independent and fully optimized molecular wave functions. Note that each $|\Phi_{\mu}\rangle$ consists of multiple determinants and therefore for the calculation of $\langle\Phi_{\mu}|\hat{H}|\Phi_{\nu}\rangle$ a large number of Hamiltonian matrix elements over determinant pairs has to be evaluated; this becomes the main computational challenge. The Hamiltonian and overlap matrix elements can be then used to calculate the electronic coupling, according to²⁶

$$V_{\mu\nu} = \frac{\langle\Phi_{\mu}|\hat{H}|\Phi_{\nu}\rangle - \frac{(\langle\Phi_{\mu}|\hat{H}|\Phi_{\mu}\rangle + \langle\Phi_{\nu}|\hat{H}|\Phi_{\nu}\rangle)}{2} \cdot \langle\Phi_{\mu}|\Phi_{\nu}\rangle}{1 - \langle\Phi_{\mu}|\Phi_{\nu}\rangle^2} \quad (7)$$

where Φ_μ and Φ_ν denote the initial and final (diabatic) states of interest, respectively, which in the case of SF correspond to the photo excited states and the two coupled triplets. The Hamiltonian in Eq. (7) is the Hamiltonian for the ensemble within the Born–Oppenheimer approximation. Please note that the MEBFs are denoted as $|\Phi\rangle$ whereas the electronic states are denoted by Φ .

The chapter is structured as follows: in Section 3.1, we compare the NOCI method with two other methodologies, restricted active space with two spin flips (RAS-2SF)^{31–33} and the *ab initio* Frenkel–Davydov exciton model (AIFDEM)^{34–36} for a tetracene dimer. Then in Section 3.2, we identify a potential SF molecule from a group of candidates and, finally, in Section 3.3 we perform a comparison of the NOCI, RAS-2SF and AIFDEM methods applied to the identified molecule. Our conclusions are given in Section 4.

2. Computational details

The identification of suitable SF molecules requires the evaluation of excitation energies. T_1 , S_1 , and T_2 (vertical) excitation energies for a set of candidates (Fig. S2) were calculated with various methodologies: (1) time-dependent density functional theory (TD-DFT);³⁷ (2) scaled-opposite-spin configuration interaction singles with a perturbative account of double excitations (SOS-CIS(D));³⁸ (3) CASSCF with correction to the energy using second-order perturbation theory (CASSCF/CASPT2),³⁹; and (4) the second-order algebraic diagrammatic construction scheme⁴⁰ (ADC(2)) of the polarization propagator. TD-DFT, SOS-CIS(D), and ADC(2) calculations were performed using Q-Chem 5.0,⁴¹ whereas the CASSCF/CASPT2 calculations with the MOLCAS 8.0⁴² code. The active spaces selected for each of the molecules are specified in Table S1. Unless otherwise stated, the basis set used is cc-pVDZ.

A crystal structure of the potential SF molecule is proposed, and all the relevant geometries of the identified pairs of molecules are given in Supplementary Materials in the online version at <https://10.1016/bs.aiq.2019.05.004>. Additionally, the molecules in the identified pairs in the optimized crystal structure were replaced by an optimized molecule at the ω B97X-D/cc-pVDZ level of theory, by arranging them as in the respective crystal structure distance and angle. Electronic couplings were

calculated for the pairs of molecules obtained by the periodic DFT calculations and for the pairs in which the molecules were replaced, in order to study the influence of different structural arrangements in the electronic couplings.

Molecular wave functions of the CASSCF-type with an active space of four electrons in four orbitals (CASSCF(4,4)) describing the S_0 , S_1 , T_1 , D_0^+ , and D_0^- states for the different molecules in each pair were calculated using the GAMESS-UK package.⁴³ MEBFs representing the following electronic states of the pairs of molecules were generated: $|\Phi_{S_0S_0}\rangle$, $|\Phi_{S_1S_0}\rangle$, $|\Phi_{S_0S_1}\rangle$, $|\Phi_{1TT}\rangle$, $|\Phi_{D_0^+D_0^-}\rangle$ and $|\Phi_{D_0^-D_0^+}\rangle$. Two diabatic states, $\Phi_{S_{[1]}}$ and $\Phi_{S_{[2]}}$, were constructed from a 2×2 NOCI calculation in the basis of the $|\Phi_{S_0S_1}\rangle$ and $|\Phi_{S_1S_0}\rangle$ MEBFs, whereas the diabatic state Φ_{1TT} corresponds to the $|\Phi_{1TT}\rangle$ MEBF. The influence of the charge transfer states is explored by adding the corresponding MEBFs to the $\Phi_{S_{[1]}}$ and $\Phi_{S_{[2]}}$ states (resulting in 4×4 NOCI calculations) and to the Φ_{1TT} (resulting in a 3×3 NOCI calculation). To investigate the importance of each MEBF in the diabatic $\Phi_{S_{[1]}}$, $\Phi_{S_{[2]}}$, and Φ_{1TT} states, the weights (ω_i) of the MEBFs were calculated using the Gallup and Norbeck scheme,⁴⁴ $\omega_i = |C_i|^2 / (S^{-1})_{ii}$, where C_i corresponds to the CI coefficient of the i th MEBF and $(S^{-1})_{ii}$ denotes the ii th element of the inverse of the overlap matrix in the MEBF basis. The NOCI methodology has been implemented in the package GronOR.⁴⁵ The calculation of the Hamiltonian matrix elements is performed by means of the factorized cofactor method which is described in Ref. 46.

For the RAS-2SF and AIFDEM methodologies we follow the protocols as outlined in Refs. 47 and 36, respectively. The RAS-2SF calculations for the dimer arrangements were performed with an active space of four electrons in four orbitals (RAS(4,4)-2SF) using a high-spin quintet as the initial reference.³³ The resulting dimer wave functions ($|\Phi\rangle$) are then described in terms of different configurations: local excited ($|\Psi_{LE}\rangle$), multiexcitonic ($|\Psi_{1TT}\rangle$), and charge transfer states or charge-resonance ($|\Psi_{CT}\rangle$);

$$|\Phi\rangle = C^{LE}|\Psi_{LE}\rangle + C^{1TT}|\Psi_{1TT}\rangle + C^{CT}|\Psi_{CT}\rangle \quad (8)$$

where C^{LE} , C^{1TT} , and C^{CT} are the corresponding amplitudes of the LE, CT, and $1TT$ configurations. The importance of each configuration in the different states is described by the corresponding weights (ω_i), calculated as the square of their amplitudes ($\omega_{LE} = |C^{LE}|^2$, $\omega_{1TT} = |C^{1TT}|^2$, and $\omega_{CT} = |C^{CT}|^2$). Based on these weights, $\Phi_{S_{[1]}}$ and $\Phi_{S_{[2]}}$ states are assigned to those wave functions with large ω_{LE} , whereas the Φ_{1TT} corresponds to the one

with large ω_{1TT} . Then, the norm of the one-particle transition density matrix ($||\gamma||^2$) is used to estimate the couplings between singlet excited and 1TT states.⁴⁸

The nonorthogonal AIFDEM methodology follows, in principle, the same protocol as the NOCI approach. For each pair of molecules, molecular wave functions are generated and then, MEBFs describing the electronic states of the ensemble are constructed as direct products of those molecular wave functions. In AIFDEM, Hartree–Fock wave functions are used for the description of the S_0 , D_0^+ , and D_0^- states and CIS wave functions for the S_1 and T_1 states.³⁴ As in NOCI, six different MEBFs were generated: $|\Phi_{S_0S_0}\rangle$, $|\Phi_{S_1S_0}\rangle$, $|\Phi_{S_0S_1}\rangle$, $|\Phi_{1TT}\rangle$, $|\Phi_{D_0^+D_0^-}\rangle$, and $|\Phi_{D_0^-D_0^+}\rangle$. Then, the total wave function of the ensemble is expanded as a linear combination of the MEBFs, and the CI coefficients (C_μ in Eq. (6)) are determined using variational theory. The resulting CIS and Hartree–Fock energies were corrected, as outlined in the protocol in Ref. 36, by shifting the diagonal elements of the Hamiltonian matrix in the orthogonalized⁴⁹ basis to match reference values calculated for an optimized molecule at the ω B97X-D/cc-pVDZ level of theory. The $\langle\Phi_{S_0S_1}|\hat{H}|\Phi_{S_0S_1}\rangle$ and $\langle\Phi_{S_1S_0}|\hat{H}|\Phi_{S_1S_0}\rangle$ elements were shifted to match the vertical S_1 excitation energy, whereas the $\langle\Phi_{1TT}|\hat{H}|\Phi_{1TT}\rangle$ element was shifted to twice the T_1 excitation energy. It has been shown in a benchmark study that among various popular functionals, the ω B97X-D functional gives the best description of excited state properties when compared to high-level wave function methods.^{50–52} The $\Phi_{D_0^+D_0^-}$ and $\Phi_{D_0^-D_0^+}$ energy reference values were approximated as the sum of three terms: ionization potential (IP), electron affinity (EA), and the Coulombic attraction (CA). IP and EA were calculated from the energies of the neutral, cationic, and anionic form of a molecule at the ω B97X-D/cc-pVDZ level of theory, whereas the CA was determined as the electrostatic attraction between the centers of mass of the molecules in the corresponding cationic and anionic ground states. The weights of each MEBF were calculated similarly to the NOCI approach. The RAS-2SF and AIFDEM calculations were carried out using Q-Chem 5.0.⁴¹

3. Results and discussion

3.1 Comparing NOCI, RAS-2SF, and AIFDEM for tetracene

A pair of tetracene molecules, an extensively studied singlet fission molecule,^{53,54} has been used to compare the NOCI approach with RAS-2SF and AIFDEM before studying unexplored systems. Fig. 3 shows the

Fig. 3 Tetracene dimer arrangement; d = centers of masses distance, θ = angle between the molecular planes.

Table 1 State energies (in eV) of the different electronic states for a pair of tetracene molecules.

Method	Φ_{TT}	$\Phi_{S_{[1]}}$	$\Phi_{S_{[2]}}$	$\Phi_{D_0^+D_0^-}$	$\Phi_{D_0^-D_0^+}$
NOCI:CASSCF(4,4)	3.96	4.30	4.41	4.71	5.42
NOCI:CASCI ²⁶	4.12	4.45	4.49	4.94	5.03
RAS(4,4)-2SF	3.52	4.11		5.00	
AIFDEM	3.20(4.39)	3.20(3.78)	3.26(3.86)	3.50(3.42)	3.52(4.13)
Experimental	2.54 ⁵⁵	2.62 ⁵⁶	2.62 ⁵⁶	2.90 ⁵⁷	2.90 ⁵⁷

For AIFDEM, the unshifted values are reported in parenthesis. The calculated $\Phi_{S_{[2]}}$ state with RAS-2SF is dominated by the $|\Phi_{S_1S_1}\rangle$ configuration and is not included.

orientation of the tetracenes in the tetracene dimer arrangement. The methods are compared in three aspects: (1) the calculated state energies in order to determine whether the charge transfer states act as real or virtual intermediate states, (2) the calculated weights of the different MEBFs in order to determine if the methods can predict similar character for the electronic states, and (3) we compare the calculated electronic couplings. The calculated state energies and the individual contributions for the tetracene dimer arrangement are shown in [Tables 1](#) and [2](#), respectively. The energies in [Table 1](#) were calculated in the gas-phase, whereas the reported experimental values correspond to determinations in solution^{55,56} for S_1 and T_1 and in the crystal structure for the CT states⁵⁷.

3.1.1 Excited state energies

The energies calculated with the NOCI approach are reported in [Table 1](#). For the sake of computational cost, we have restricted the active space of the molecular wave functions to four electrons in four orbitals (denoted NOCI:

Table 2 Comparison of the individual weights of MEBFs obtained for a pair of tetracene molecules.

State	Φ_{1TT}			$\Phi_{S_{[1]}}$			$\Phi_{S_{[2]}}$		
Configuration	NOCI	RAS-2SF	AIFDEM	NOCI	RAS-2SF	AIFDEM	NOCI	RAS-2SF	AIFDEM
$ \Phi_{S_0S_0}\rangle$	0.000	0.001	0.000	0.001	0.017	0.002	0.000		0.000
$ \Phi_{S_0S_1}\rangle$	0.000	0.001	0.005	0.999	0.642	0.929	0.000		0.009
$ \Phi_{S_1S_0}\rangle$	0.001	0.001	0.027	0.000	0.063	0.016	0.978		0.867
$ \Phi_{1TT}\rangle$	0.999	0.935	0.894	0.000	0.001	0.009	0.020		0.007
$ \Phi_{D_0^+D_0^-}\rangle$	0.000	0.008	0.014	0.000	0.023	0.038	0.001		0.112
$ \Phi_{D_0^-D_0^+}\rangle$	0.000	0.054	0.060	0.000	0.003	0.006	0.000		0.005

The main contributions are highlighted as bold numbers. The calculated $\Phi_{S_{[2]}}$ state with RAS-2SF is dominated by the $|\Phi_{S_1S_1}\rangle$ configuration and is not included.

CASSCF(4,4)). The NOCI energies are overestimated when compared to the experimental values. The energies might be improved by adding the remaining π - and π^* -like orbitals to the active space. RAS-2SF also overestimates the energies of the electronic states because of an incomplete account of dynamic correlation,⁵⁸ and as in the NOCI approach, the energies are expected to improve by increasing the active space. The energies calculated with AIFDEM have been corrected as explained in Section 2; these energy values are also overestimated. The overestimation of the energies for the three methods might be due to the fact that the calculations are performed without the environment effects, neither the solvent nor the surrounding crystal structure. Despite this overestimation, the results suggest that the CT states are too high in energy to be accessed but perhaps act as virtual states promoting a mediated mechanism. The calculated state energies in this work are compared with previously reported values²⁶ in which a NOCI calculation was performed for a cluster of three tetracene molecules (values denoted as NOCI: CASCI in Table 1). Unlike here, where we generate proper spin-adapted, antisymmetrized products of molecular wave functions as the MEBFs, in that work MEBFs were approximated by CASCI wave functions: the orbital sets resulting from molecular CASSCF(4,4) wave functions were projected on the basis of the trimer, followed by orthogonalization and a CASCI(12,12) calculation. This procedure results in MEBFs, contaminated with small contributions of (unwanted) CT states. Differences between the results in state energies and electronic couplings in this work and Ref. 26 can be attributed to differences in the geometry of the ensemble (Ref. 26 used a B3LYP/6-21G optimized geometry and here the pair of molecules was taken from Supplementary Materials in the online version at <https://10.1016/bs.aiq.2019.05.004> of Ref. 36 from a plane-wave DFT optimized structure).

3.1.2 Weights of MEBFs

The weights of the individual contributions of the different MEBFs to the Φ_{1TT} , $\Phi_{S[1]}$, and $\Phi_{S[2]}$ states are listed in Table 2. The dominant contributions to the electronic states are highlighted as bold numbers; the Φ_{1TT} state corresponds mainly to the $|\Phi_{1TT}\rangle$ MEBF for the three methodologies. The AIFDEM predicts a contribution from the $|\Phi_{D_0^-D_0^+}\rangle$ state that is not observed in the NOCI approach. In order to shed more light on the origin of this discrepancy, we have applied the same shift to NOCI. The NOCI results (Tables S2 and S3) predict also a contribution from $|\Phi_{D_0^+D_0^-}\rangle$ and $|\Phi_{D_0^-D_0^+}\rangle$ after applying the shift. From the shiftings applied to NOCI and AIFDEM,

we have observed two opposite trends; in the case of NOCI, the CT states become more important (higher weights) since the CT energies are lowered, whereas in the case of AIFDEM, the CT weights decrease since the CT states are shifted to the reference value which is higher (see Tables S2 and S3 for shifted and unshifted NOCI and AIFDEM individual weights of MEBFs). For the $\Phi_{S_{[1]}}$ and $\Phi_{S_{[2]}}$ states, the main contributions obtained with NOCI and AIFDEM correspond to the $|\Phi_{S_0S_1}\rangle$ and $|\Phi_{S_1S_0}\rangle$ MEBFs, respectively. For the $\Phi_{S_{[1]}}$ state, the configuration $|\Phi_{S_1S_1}\rangle$ was found to have a large weight in the RAS-2SF calculations, however, this particular configuration is not of interest for the SF process. The calculated $\Phi_{S_{[2]}}$ state with RAS-2SF is dominated by the $|\Phi_{S_1S_1}\rangle$ configuration and it is not included for comparison. In fact, differences in calculated weights with NOCI and AIFDEM and those obtained with RAS-2SF are attributed to the fact that additional configurations, such as $|\Phi_{S_1S_1}\rangle$, are considered in RAS-2SF. In sum, the methods show similar contributions of the different electronic states, despite the differences in the numerical values.

3.1.3 Electronic couplings

Electronic couplings between $\Phi_{S_{[1]}}$ and $\Phi_{S_{[2]}}$ with the Φ_{1TT} states calculated with the NOCI approach for the tetracene pair are reported in Table 3. In the primed wave functions, the CT states were allowed to mix with the wave functions of the singlet excited and 1TT states. The results indicate that the electronic coupling is enhanced from 2.2 to 37.6 meV when the CT states are allowed to mix; this enhancement is in line with a previous NOCI study of a cluster of three tetracene molecules.²⁶ A similar trend is observed in the electronic couplings that we calculated with AIFDEM; the values are enhanced when the CT configurations are included in the calculation (see Table S4). The increase in the coupling can be then attributed to the mixing in of the CT states with both photo excited states and the multiexcitonic state.

Table 3 Electronic couplings (in meV) between the (diabatic) states $\Phi_{S_{[1]}}$ and $\Phi_{S_{[2]}}$ with Φ_{1TT} for the tetracene pair.

States	$\Phi_{S_{[1]}}$	$\Phi_{S_{[2]}}$	$\Phi'_{S_{[1]}}$	$\Phi'_{S_{[2]}}$
Φ_{1TT}	4.0	2.2	2.2	58.9
Φ'_{1TT}	7.9	19.6	4.0	37.6

In the primed wave functions the CT states were included in the NOCI calculation.

3.1.4 Comparison

All three methods show a similar qualitative trend for the tetracene dimer; they predict that the CT states are too high in energy to be accessed. However, the discrepancies between numerical values are evident. The three methods overestimate the state energies when compared with the experimental values. The NOCI and AIFDEM approaches are conceptually similar. (Static) electron correlation and (local) orbital relaxation effects can be included in the NOCI approach but our current implementation in the GronOR package is able to treat only small clusters of small molecules. The current AIFDEM implementation is able to handle large clusters and molecules. Additionally, analytical gradients and nonadiabatic couplings are available for the AIFDEM method³⁶ but not implemented in GronOR so far. Electronic couplings can be directly calculated for NOCI and AIFDEM but for RAS-2SF it is only possible to estimate the coupling based on $||\gamma||^2$ values.

3.2 Identification of a SF molecule based on excitation energies

In this chapter, a group of SF candidates has been selected (Fig. S2). (Vertical) excitation energies of the T_1 , S_1 , and T_2 states calculated with different levels of electronic structure theories are reported in Table S5 together with E_{stt} , which is defined as $E_{stt} = E(S_1) - 2E(T_1)$. SF should be, in principle, an isoergic process which means that E_{stt} must be ideally close to zero. Nevertheless, experimental values (Table S5) suggest that the process also occurs if it is slightly endo or exoergic. Therefore, for potential SF molecules E_{stt} should lie roughly in the -0.1 to 0.1 eV range. From the results in Table S5, the isobenzofulvene derivative 2-methylene-2H-indene (named as M2I for the upcoming discussion) is selected for further evaluation as a promising SF molecule.

3.3 Comparing NOCI, RAS-2SF, and AIFDEM for 2-methylene-2H-indene

3.3.1 Pairs of molecules

In the optimized crystal structure of M2I, four different pairs of molecules were identified (Fig. 4A). Two of them show a π -like stacking (slip-stacked) and have been named I-A and I-C, whereas the other two correspond to structural arrangements that differ in the angle between the molecular planes of the molecules, and they are denoted for the upcoming discussion I-B ($\theta = 131^\circ$) and I-D ($\theta = 49^\circ$) (Fig. 4B and Fig. S3 for further information).

Fig. 4 (A) Identified pairs of molecules of M2I; from a central molecule (black) the I-A (red), I-B (pink), I-C (green), and I-D (blue) conformations are depicted. (B) The angle between the molecular planes in each pair is depicted. Crystal structure optimized at the PBE/6-31G(d,p) level of theory.

3.3.2 Excited state analysis

The first singlet excited and lowest triplet states of M2I correspond mainly to a single excitation with $\pi \rightarrow \pi^*$ character as can be seen from the frontier orbitals depicted in Fig. S4. The biradicaloid character of M2I has been reported,⁵⁹ but a CASSCF(10,10) calculation on the ground state shows 1.83 and 0.20 as the natural orbital occupation numbers for the HOMO and LUMO, respectively, suggesting a closed shell character for the molecule.

3.3.3 Excited state energies

The energies of the Φ_{1TT} , $\Phi_{S_{[1]}}$, $\Phi_{S_{[2]}}$, $\Phi_{D_0^+D_0^-}$, and $\Phi_{D_0^-D_0^+}$ states for the four pairs of molecules are shown in Table 4. The RAS-2SF energies are lower than those obtained with the NOCI approach and the shifted energies in AIFDEM. A close look at the hole and particle contributions in the RAS active space reveals that the HOMO-1 should have been included as an active orbital; the underestimation of the excitation energies in this case suggests that RAS-2SF is suitable for the description of molecules in which it is sufficient to consider the frontier orbitals in the active space, e.g., tetracene. State energies are improved by including the required orbitals in the active space (see RAS(8,6)-2SF and RAS(8,8)-2SF calculations in Table S6). For I-B and I-D, the $\Phi_{S_{[2]}}$ state is dominated by the $|\Psi_{S_1S_1}\rangle$ configuration which suggests a double excitation character. Therefore, these states were not included in the comparison. The NOCI energies of the $\Phi_{S_{[1]}}$ and $\Phi_{S_{[2]}}$ states

Table 4 State energies (in eV) for the different electronic states for the four pairs of molecules of M2I.

Pair	Method	Φ_{1TT}	$\Phi_{S_{[1]}}$	$\Phi_{S_{[2]}}$	$\Phi_{D_0^+D_0^-}$	$\Phi_{D_0^-D_0^+}$
I-A	NOCI	2.15	2.47	2.49	4.27	4.32
	RAS(4,4)-2SF	1.33	1.97	2.08	3.29	3.32
	AIFDEM	2.29(3.38)	2.43(3.53)	2.50(4.05)	5.03(2.68)	5.13(2.99)
I-B	NOCI	2.12	2.41	2.42	4.69	5.07
	RAS(4,4)-2SF	1.28	1.96		4.05	
	AIFDEM	2.33(2.95)	2.39(3.02)	2.53(3.17)	5.00(2.78)	5.11(3.11)
I-C	NOCI	2.12	2.41	2.42	4.69	5.07
	RAS(4,4)-2SF	1.27	1.96	1.98	4.11	4.25
	AIFDEM	2.34(2.72)	2.41(3.02)	2.47(3.07)	5.00(2.92)	5.12(2.94)
I-D	NOCI	2.11	2.39	2.42	4.36	4.92
	RAS(4,4)-2SF	1.26	1.97		3.64	
	AIFDEM	2.33(2.97)	2.43(3.01)	2.46(3.19)	5.00(2.40)	5.12(2.90)

For AIFDEM, the unshifted values are shown in parenthesis. $\Phi_{S_{[2]}}$ states calculated with RAS-2SF are dominated by the $|\Phi_{S_1S_1}\rangle$ configuration and are not included.

are close to the Φ_{1TT} energy deviating by only ~ 0.3 meV, showing that the system almost fulfills the requirement $E_{stt} = 0$. The NOCI $\Phi_{D_0^+D_0^-}$ and $\Phi_{D_0^-D_0^+}$ energies are 2.0 eV or more above the $\Phi_{S_{[1]}}$ and $\Phi_{S_{[2]}}$ energies indicating that these states are too high in energy to be accessed but might act as virtual states mediating the SF process; the same trend holds for RAS-2SF and AIFDEM CT state energies.

3.3.4 Weights of MEBFs

Table 5 shows a comparison between the weights of the MEBFs to the Φ_{1TT} , $\Phi_{S_{[1]}}$, and $\Phi_{S_{[2]}}$ states in the pairs of molecules. The dominant contributions, highlighted as bold numbers, show that for the four pairs of molecules the Φ_{1TT} states have almost pure $|\Phi_{1TT}\rangle$ character, whereas $\Phi_{S_{[1]}}$ and $\Phi_{S_{[2]}}$ are described mainly by the singlet excited MEBFs; the weights suggest that the excitation is localized on one of the two molecules for all the cases. A similar trend is observed with the RAS-2SF and AIFDEM methodologies, although in RAS-2SF the $|C|^2$ values are lower than those calculated with

Table 5 Comparison of the individual weights of MEBFs in the four pair arrangements of M2I.

Configuration	Φ_{1TT}			$\Phi_{S_{[1]}}$			$\Phi_{S_{[2]}}$		
	NOCI	RAS-2SF	AIFDEM	NOCI	RAS-2SF	AIFDEM	NOCI	RAS-2SF	AIFDEM
<i>Pair I-A</i>									
$ \Phi_{S_0S_0}\rangle$	0.001	0.001	0.000	0.000	0.066	0.014	0.000	0.000	0.007
$ \Phi_{S_0S_1}\rangle$	0.014	0.013	0.041	0.982	0.665	0.889	0.000	0.000	0.000
$ \Phi_{S_1S_0}\rangle$	0.000	0.013	0.059	0.000	0.000	0.000	0.999	0.828	0.929
$ \Phi_{1TT}\rangle$	0.985	0.885	0.539	0.018	0.060	0.000	0.000	0.000	0.000
$ \Phi_{D_0^+D_0^-}\rangle$	0.000	0.037	0.000	0.000	0.019	0.096	0.000	0.008	0.063
$ \Phi_{D_0^-D_0^+}\rangle$	0.000	0.037	0.360	0.000	0.019	0.000	0.000	0.008	0.000
<i>Pair I-B</i>									
$ \Phi_{S_0S_0}\rangle$	0.000	0.000	0.000	0.000	0.009	0.001	0.000		0.004
$ \Phi_{S_0S_1}\rangle$	0.000	0.000	0.001	1.000	0.675	0.995	0.000		0.003
$ \Phi_{S_1S_0}\rangle$	0.000	0.000	0.000	0.000	0.000	0.003	1.000		0.991
$ \Phi_{1TT}\rangle$	1.000	1.000	0.999	0.000	0.000	0.000	0.000		0.000
$ \Phi_{D_0^+D_0^-}\rangle$	0.000	0.000	0.000	0.000	0.000	0.001	0.000		0.002
$ \Phi_{D_0^-D_0^+}\rangle$	0.000	0.000	0.000	0.000	0.000	0.000	0.000		0.000

Continued

Table 5 Comparison of the individual weights of MEBFs in the four pair arrangements of M2I.—cont'd

Configuration	Φ_{1TT}			$\Phi_{S_{[1]}}$			$\Phi_{S_{[2]}}$		
	NOCI	RAS-2SF	AIFDEM	NOCI	RAS-2SF	AIFDEM	NOCI	RAS-2SF	AIFDEM
<i>Pair I-C</i>									
$ \Phi_{S_0S_0}\rangle$	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.015	0.001
$ \Phi_{S_0S_1}\rangle$	0.000	0.000	0.000	1.000	0.853	0.996	0.000	0.000	0.003
$ \Phi_{S_1S_0}\rangle$	0.000	0.000	0.000	0.000	0.000	0.003	1.000	0.822	0.996
$ \Phi_{1TT}\rangle$	1.000	1.000	1.000	0.000	0.000	0.000	0.000	0.000	0.000
$ \Phi_{D_0^+D_0^-}\rangle$	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$ \Phi_{D_0^-D_0^+}\rangle$	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
<i>Pair I-D</i>									
$ \Phi_{S_0S_0}\rangle$	0.000	0.000	0.000	0.000	0.226	0.001	0.000		0.001
$ \Phi_{S_0S_1}\rangle$	0.000	0.000	0.000	1.000	0.572	0.999	0.000		0.000
$ \Phi_{S_1S_0}\rangle$	0.000	0.000	0.000	0.000	0.000	0.000	1.000		0.999
$ \Phi_{1TT}\rangle$	1.000	0.996	0.998	0.000	0.000	0.000	0.000		0.000
$ \Phi_{D_0^+D_0^-}\rangle$	0.000	0.003	0.001	0.000	0.004	0.000	0.000		0.000
$ \Phi_{D_0^-D_0^+}\rangle$	0.000	0.001	0.001	0.000	0.002	0.000	0.000		0.000

The main contributions are highlighted as bold numbers. $\Phi_{[2]}$ states calculated with RAS-2SF are dominated by the $|\Phi_{S_1S_1}\rangle$ configuration and are not included.

NOCI and AIFDEM since additional configurations, such as double excitations ($|\Phi_{S_1S_1}\rangle$), contribute. NOCI shows that the states in I-B, I-C, and I-D retain mostly a pure character, which is also observed in the individual contributions calculated with RAS-2SF and AIFDEM. However, the contributions for the Φ_{1TT} state in dimer I-A are different between the methods; the weights from the NOCI calculation predict that Φ_{1TT} has mainly a contribution from the $|\Phi_{1TT}\rangle$ MEBF with a small contribution from $|\Phi_{S_0S_1}\rangle$, whereas RAS-2SF and the weights obtained with AIFDEM predict a contribution from the CT states. After applying the same shift to NOCI, contributions from the CT states are also observed (see Table S8). When we shift NOCI and AIFDEM (see Tables S8 and S9), we observed the same trends in the weights as in tetracene.

3.3.5 Electronic couplings

In Table 6, electronic couplings are reported for the four pairs of molecules between the $\Phi_{S_{[1]}}$ and $\Phi_{S_{[2]}}$ states with the Φ_{1TT} state. The largest coupling values are observed in I-A, whereas the lower values are obtained for I-B and I-C. For I-A, the inclusion of the CT states to the $\Phi_{S_{[1]}}$ state enhances the electronic coupling from 21.4 to 42.2 meV. The electronic coupling is also enhanced if the CT states are allowed to interact only with the Φ_{1TT} state. For the $\Phi_{S_{[2]}}$ state, no significant enhancement is observed. The most plausible determination of the electronic coupling in I-A corresponds to that

Table 6 Electronic couplings (in meV) between the (diabatic) states $\Phi_{S_{[1]}}$ and $\Phi_{S_{[2]}}$ with Φ_{1TT} for the dimer arrangements of M2I.

Pair	States	$\Phi_{S_{[1]}}$	$\Phi_{S_{[2]}}$	$\Phi'_{S_{[1]}}$	$\Phi'_{S_{[2]}}$
I-A	Φ_{1TT}	21.4	0.4	42.2	0.4
I-B		0.2	0.1	0.2	0.2
I-C		0.0	0.3	0.0	0.4
I-D		0.6	0.6	0.4	1.3
I-A	Φ'_{1TT}	38.0	1.1	39.8	0.4
I-B		0.2	0.3	0.2	0.2
I-C		0.0	0.4	0.0	0.4
I-D		0.1	1.2	0.3	1.3

In the primed wave functions the CT states were included in the NOCI calculation.

in which the CT states are allowed to mix with both the $\Phi_{S_{[1]}}$ and Φ_{1TT} states, with a value of 39.8 meV. The magnitude of the electronic coupling suggests that the formation of the 1TT state could occur efficiently. We performed the same analysis for the four pairs of molecules in which the molecules were replaced by optimized molecules (Tables S10–S12). Originally, the pairs of molecules from the periodic DFT optimization were slightly bent, and after the replacement they became planar. Although the quantitative results changed, the same observations as discussed above (regarding the excitation energies of the states, the individual contributions of the MEBFs and the electronic couplings) are observed; the highest electronic coupling is found for I–A and the lowest for I–B and I–C. It is apparent that the electronic couplings strongly depend on the orientation of the molecules in the cluster.

Table 7 shows the configurational analysis of the RAS-2SF wave functions of the pairs of molecules showing their local excited (LE), multiexcitonic (ME) and CT character, and the $||\gamma||^2$ values between the Φ_{1TT} with $\Phi_{S_{[1]}}$ and $\Phi_{S_{[2]}}$ states are also listed. The $||\gamma||^2$ values indicate that the transition is most probable to occur when the molecules are disposed as in arrangement I–A (0.25 and 0.30), for I–D also a transition is expected to occur (0.09), whereas for I–B and I–C no transition would be observed. The $||\gamma||^2$ values obtained with the RAS(8,6)–2SF and RAS(8,8)–2SF calculations (see Tables S13 and S14) show the same trend. The differences in

Table 7 Configuration analysis of the RAS-2SF wave functions for the pair arrangements of M2I using localized orbitals within the DMO-LCFMO framework.

Pair	State	LE	ME	CT	$ \gamma ^2$	Pair	State	LE	ME	CT	$ \gamma ^2$
I–A	Φ_{1TT}	0.03	0.89	0.07		I–B	Φ_{1TT}	0.00	1.00	0.00	
	$\Phi_{S_{[1]}}$	0.83	0.15	0.02	0.25		$\Phi_{S_{[1]}}$	0.67	0.32	0.00	0.01
	$\Phi_{S_{[2]}}$	0.66	0.23	0.04	0.30		$\Phi_{S_{[2]}}$				
I–C	Φ_{1TT}	0.00	1.00	0.00		I–D	Φ_{1TT}	0.00	0.99	0.00	
	$\Phi_{S_{[1]}}$	0.85	0.15	0.00	0.02		$\Phi_{S_{[1]}}$	0.57	0.20	0.01	0.09
	$\Phi_{S_{[2]}}$	0.82	0.16	0.00	0.02		$\Phi_{S_{[2]}}$				

The values of $||\gamma||^2$ between the Φ_{1TT} and each of the local excited states $\Phi_{S_{[1]}}$ and $\Phi_{S_{[2]}}$ are shown. $\Phi_{S_{[2]}}$ states calculated with RAS-2SF are dominated by the $|\Phi_{S_1S_1}\rangle$ configuration, and are not included for comparison.

the $||\gamma||^2$ values can be associated to the degree of contribution of the CT states to the singlet excited and 1TT states. CT contributions are predicted for I-A and I-D whereas they are negligible for I-B and I-C. Remarkably, the electronic couplings calculated with NOCI and AIFDEM (Table S15) follow the qualitative behavior predicted by the RAS-2SF method, in which the highest values are observed for I-A; this implies that if the molecules are disposed as in this conformation in the crystal structure, the SF process might occur efficiently.

4. Conclusions

We report a comparison of the NOCI approach with two theoretical approaches, RAS-2SF and AIFDEM used for the study of SF, and we propose 2-methylene-2H-indene as a potential SF molecule. The comparison of the methods indicate that for tetracene, NOCI, RAS-2SF, and AIFDEM overestimate the energies of the states when compared with the experimental values. Despite this overestimation, our results suggest that the CT states act as virtual states in the SF process. The three methods agree on the character of the excited states, however, more configurations were found to be important in the RAS-2SF calculations, which were not included in the NOCI and AIFDEM calculations. The major difference between the NOCI and AIFDEM approaches, despite being conceptually similar, are that electron correlation and orbital relaxation effects can be included in the NOCI approach, but currently only small clusters of small molecules can be treated, whereas the AIFDEM approach can handle large clusters and molecules. Calculated electronic couplings for four pairs of the 2-methylene-2H-indene with the NOCI and AIFDEM approaches, and $||\gamma||^2$ values calculated with RAS-2SF show that the formation of the 1TT state could occur efficiently in the crystal when the molecules are oriented as in conformation I-A. NOCI and AIFDEM overestimate the state energies, whereas RAS-2SF underestimates them; however, the three methods predict similar character for the relevant electronic states. The CT state energies are too high to be accessible, and a mediated mechanism is proposed for the SF process in 2-methylene-2H-indene. Finally, the methodologies are able to distinguish between configurations with low and high SF probabilities. A further comparison beyond these two systems has to be done in order to establish and generalize the predictive power of the methodologies.

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