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**Local Electron Correlation Treatment in Extended Multireference Calculations: Effect of
Acceptor-Donor Substituents on the Biradical Character of the Polycyclic Aromatic
Hydrocarbon Heptazethrene**

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Abstract

The implementation of a local correlation (LC) treatment of multireference (MR) configuration interaction approaches within the COLUMBUS program system is reported. The LC treatment is based on the weak pairs approximation of Sæbø and Pulay (*Ann. Rev. Phys. Chem.* **1993**, *44*, 213) and a geometrical analysis of Walter et al. (*Chem. Phys. Lett.* **2001**, *346*, 177). The removal of simultaneous single excitations out of the weak pairs is based on the reference doubly occupied space only, leading to a straightforward program implementation and a conceptual simplicity in terms of well-defined localized orbitals. Reductions of up to an order of magnitude in the configuration space expansion and in computer time for the Davidson diagonalization step are found. The selection of the active and the virtual orbital spaces is not affected by this procedure. This treatment is successfully applied to the singlet biradical heptazethrene and its different acceptor-donor substituents: 4,12-dicyanoheptazethrene, 4,12-diaminoheptazethrene, and 4-amino-12-cyanoheptazethrene. Simultaneous insertion of pairs of donor and acceptor groups increases the biradical character; for push-pull substitution this effect is significantly smaller. In addition, results obtained from spin-corrected unrestricted density functional theory calculations are supported by our MR calculations.

1. INTRODUCTION

Over the last couple of years, zethrenes and their derivatives¹⁻⁷ have attracted significant interest because of the potential applications in the field of organic electronics,⁸⁻¹¹ non-linear optics,¹²⁻¹³ energy storage devices¹⁴ and spintronics.¹⁵⁻¹⁶ This interest is derived from the fact that this class of compounds, starting with heptazethrene, possesses small excitation energies, a fact which can be rationalized in the framework of valence bond theory by a stabilization of the non-Kekulé biradical form with respect to the closed-shell Kekulé structure (see Chart 1 and discussion below). However, the presence of partial odd-electron character¹⁷ or density of effectively unpaired electrons¹⁸ associated with this small energy gap makes these compounds highly reactive and, therefore, difficult to synthesize. Because of its intrinsic high reactivity, the synthesis of the parent heptazethrene is not feasible.¹⁹ Incorporation of different substituents like electron-withdrawing groups²⁰⁻²² or bulky groups at the reactive sites have made it possible to increase the thermodynamic or kinetic stability of these materials. By introducing different substituents, it is also possible to tune their properties and extend the range of possible applications.

Clar's aromatic sextet rule²³⁻²⁵ provides a useful qualitative approach for assessing the aforementioned stability changes between a closed-shell quinoidal form and an open-shell biradical form. For quantitative characterization, quantum chemical calculations are indispensable for providing detailed descriptions of the unique electronic properties of polycyclic aromatic hydrocarbons (PAHs).²⁶⁻³¹ Because several configurations of comparable importance are involved in the electronic configuration of the singlet biradicals, straightforward application of single-reference methods will not describe their electronic structure properly. Among the theoretical methods available,³²⁻⁴¹ broken-symmetry (BS) density functional theory (DFT) is effective, especially because of its computational efficiency. But, the low-spin BS solution has two crucial drawbacks; (a) it suffers from the problem of spin contamination⁴²⁻⁴³ and (b) DFT itself strongly depends on the choice of an appropriate exchange-correlation functional. On the other hand, multireference (MR) methods, especially the multireference configuration interaction with single and double excitations (MR-CISD)⁴⁴⁻⁴⁶ and the multireference averaged quadratic coupled cluster (MR-AQCC)⁴⁷ approaches offer appropriate ways to treat spin states for which more than one configuration is needed to describe the electronic structure in a qualitatively correct way. The MR methods do not have the spin contamination problem and simultaneously include both static and

dynamic correlation. The multireference averaged coupled pair functional (MR-ACPF) method,⁴⁸ and in particular the related MR-AQCC approach used in this work consider consistently important size-extensivity corrections at the MR level. It was shown by us in recent publications on zethrenes and non-Kekulé structures⁴⁹ and dimethylenepolycyclobutadienes,⁵⁰ that the MR-AQCC method can be applied successfully to capture the bi- or polyradical character of PAHs. However, these MR methods are computationally very expensive. One interesting approach to decrease the computational cost in an efficient way in cases of increasing sizes of molecular systems is to use a local correlation (LC) treatment. Although a large number of LC techniques and applications⁵¹⁻⁶¹ are available in the literature, they are mostly applied to the simpler closed-shell cases. The applicability of LC in the multireference case has been successfully taken up in the investigations of the group of Carter⁵⁸⁻⁶¹ in the framework of their TIGERCI code.^{41, 62} The strategy followed in that work is to fully exploit localization in the reference-occupied and virtual orbital spaces using the concept of the weak pairs approximation developed by Sæbø and Pulay (SP).^{54-56, 63} Based on the concepts developed in this just-mentioned work, we report in this paper a somewhat simpler but nevertheless also quite effective strategy based on the multireference program system COLUMBUS.⁶⁴⁻⁶⁶ We focus on eliminating weak pairs within the reference doubly occupied space only, because orbital localization is more challenging within the active and virtual spaces. As a result, the active and the virtual orbital spaces remain the same in this procedure and all flexibility included there will remain unaffected by the localization procedure. These relatively simple measures already allow efficient MR-CISD and MR-AQCC calculations on systems of the size of heptazethrene and more, as will be demonstrated below. In the present implementation (see below), the Pipek-Mezey localization procedure⁶⁷ will be used. However, we want to note that other localization schemes such as the Foster-Boys localization⁶⁸ could be used also. The two localization methods generate qualitatively the same orbitals except for cases like double bonds for which two equivalent banana orbitals are generated in Boys localization whereas Pipek-Mezey localization preserves the symmetry of σ and π orbitals of these bonds.⁶⁷ Since we include all valence doubly occupied orbitals in the MR-CISD wavefunction, the full calculations without the weak pairs approximation will be invariant to different unitary transformations in that space. Since only distant pairs are neglected we do not expect significant differences from using the two localization methods.

Recent theoretical studies^{12, 69-70} have predicted that making charge distributions asymmetric through the introduction of electron-donating and electron-withdrawing groups into the open-shell PAHs significantly enhances the second hyperpolarizability and the two-photon absorption cross-sections. From both experimental² as well as DFT studies,⁵ it has also been observed that substitution of hydrogen atoms in heptazethrene with the triisopropylsilylethynyl group stabilizes the closed-shell quinoidal structure whereas introduction of the diimide group favors the open-shell biradical structure.

Because the open-shell singlet density is mostly located at the position of C4/12 of heptazethrene⁴⁹ (see Chart 1 for numbering), these two positions of the heptazethrene core provide a very good basis for the introduction of acceptor/donor substituents. Therefore, in this work, the parent heptazethrene (**1**) and substitutions with respective donor and acceptor amino and cyano groups, 4,12-dicyanoheptazethrene (**2**), 4,12-diaminoheptazethrene (**3**), and 4-amino-12-cyanoheptazethrene (**4**) (see Chart 1), were investigated. Because of the relatively small size of the substituents, steric repulsion with the heptazethrene core will be very small and should not distort the heptazethrene framework significantly. The influence of these substituents on already discussed questions of biradical character will be investigated here by means of high-level MR calculations. In addition to these *ab initio* MR results, DFT is also tested to obtain further insight regarding its applicability to this interesting class of compounds.

Chart 1. Heptazethrene (**1**) and different substituted versions: 4,12-dicyanoheptazethrene (**2**); 4,12-diaminoheptazethrene (**3**) and 4-amino-12-cyanoheptazethrene (**4**), showing the quinoid Kekulé and non-Kekulé biradical resonance forms. The benzene rings in red represent Clar's aromatic sextet rings.

2. COMPUTATIONAL DETAILS

Multiconfiguration self-consistent field (MCSCF), mostly in the form of complete active space (CAS) self-consistent field (CASSCF) calculations with four electrons in four π orbitals, state-averaged (SA) over the lowest singlet and triplet state, denoted SA-CASSCF(4,4), and single-state (SS) CASSCF denoted as SS-CASSCF(4,4) were performed to obtain molecular orbitals for the subsequent localization procedure and the MR calculations. It was shown before for the unsubstituted heptazethrene⁴⁹ that this CAS is well suited to describe the quasi-degeneracies due to the biradical structure and to act as a starting point for the subsequent MR calculations that include the dynamic electron correlation. However, significantly extended active reference spaces (up to 16 active orbitals and 12 electrons) were investigated in order to support our original choice. A full CAS(12/16) reference for the MR-CISD/AQCC calculations would be prohibitive. Thus, a RAS(m)/CAS(4,4)/AUX(n) scheme was constructed where RAS(m) stands for restricted active space containing m orbitals which were initially doubly occupied. Auxiliary active orbitals (AUX) were moved from the virtual space or from weakly occupied natural orbitals into the active space. From the RAS only single or single and double excitations into the other spaces were allowed and only single or single and double occupations of AUX orbitals were permitted. In the following, the single-excitation case is denoted as 1-ex and the double-excitation case as 2-ex. These labels are added to the RAS(m)/CAS(4,4)/AUX(n) scheme when needed. In summary, the entire orbital space consists of a set of frozen core (FRZC), reference doubly occupied (REFDOCC), active (ACT) and virtual (VIRT) orbitals. The doubly occupied internal orbitals of the SA-CASSCF(4,4) calculation were localized by the Pipek-Mezey localization procedure.⁶⁷ MR-CISD and MR-AQCC calculations were performed subsequently to account for static and dynamic electron correlation effects. The interacting space approach⁷¹ was used in constructing all single and double excitations for each reference configuration individually. Core orbitals were kept frozen. For comparison purposes, in addition to MR-AQCC calculations, MR-CISD and size-extensivity corrections are included by means of the extended Davidson correction^{46, 72-73}

$$E_Q = \frac{(1 - C_0^2)(E_{CI} - E_{REF})}{(2C_0^2 - 1)} \quad (1)$$

denoted as +Q (MR-CISD+Q). C_0^2 is the sum of squared coefficients of the reference configurations in the MR-CISD expansion and E_{REF} denotes the reference energy. The approaches

concerning the implementation of the local correlation will be discussed in a separate subsection below.

The reference spaces for the MR-CISD and MR-AQCC calculations usually were kept the same as the CAS in the SA-CASSCF calculations. The contributions of the singly and doubly substituted configurations were monitored; in the case of a weight larger than 1%, extensions of the active space were made in order to eliminate intruder states in the MR-AQCC calculations. Because in most cases configuration state functions (CSFs) containing excitations from the CAS to the virtual orbital space were affected, an auxiliary orbital space as part of the reference space was introduced to which such virtual orbitals were moved. An occupation of at most one electron was allowed in the AUX at the reference level. This procedure allowed for an effective removal of these intruder states without increasing the computational cost too much. For the MR calculations, the 6-31G* basis set⁷⁴ was used throughout.

All the structures collected in Chart 1 were optimized using DFT with the CAM-B3LYP⁷⁵ exchange-correlation functional and the 6-31G** basis set. A wave function stability analysis calculation⁷⁶ based on the Kohn-Sham determinant⁷⁷ was performed and it was found that the optimized singlet state of structures **1-4** have triplet instabilities. Thus, all DFT calculations were performed at unrestricted (UDFT) level with a broken symmetry (BS) solution. None of the structures showed any imaginary frequencies, i.e., they all correspond to minimum energy structures and all the structures have a low-spin ground state. To correct for spin contamination, the spin correction approach proposed by Yamaguchi et al.^{43, 78} was employed, where the vertical singlet-triplet gap is given by

$$\Delta E_{proj} = E_{T^i} - E_{S^i} = \frac{\langle S_{T^i}^2 \rangle (E_{T^i} - E_{BS^i})}{\langle S_{T^i}^2 \rangle - \langle S_{BS^i}^2 \rangle}. \quad (2)$$

E_{T^i} , E_{S^i} and E_{BS^i} represent the energy of the triplet, singlet, and BS solutions and $\langle S_{T^i}^2 \rangle$ and $\langle S_{BS^i}^2 \rangle$ are the expectation value of the square of the total spin operator for the triplet and BS solutions.

For the MR calculations, along with the LC treatment, the parallel version⁷⁹⁻⁸⁰ of the COLUMBUS program system^{64-65, 81} was used. DFT and stability analysis calculations were performed with the Gaussian 09 package.⁸²

3. PROGRAM IMPLEMENTATION

The concept of strong and weak pairs was introduced by Saebø and Pulay^{54-56, 63} in connection with their local electron correlation treatment based on pair energies, which was successfully implemented into Møller-Plesset perturbation theory⁸³ and coupled cluster theory.⁸⁴⁻⁸⁵ In the present work, which is dedicated to application of local electron correlation within multireference methods, we follow an alternative strategy proposed by Carter and coworkers⁵⁸⁻⁶¹ that utilizes a distance analysis of localized orbitals. The present approach restricts the general formalism developed and applied previously to the application of doubly occupied orbitals. In the first step, the doubly occupied orbitals are localized by a Pipek-Mezey localization procedure.⁶⁷ Then, a Mulliken population analysis is performed for each localized orbital in order to determine the atoms contributing predominantly to this orbital. A group of most important atoms is selected according to an accumulated Mulliken population which should exceed a certain threshold (default 0.8 e). A maximum distance $r_{\max}$ between this set of selected atoms and a charge-weighted average position r_c is used to draw a sphere with radius $\alpha r_{\max}$ centered at r_c . α is an adjustable parameter (default value 1.0) which can be used to adjust the radius $r_{\max}$. In case of an orbital localized entirely on a single atom, a radius of 0.8 bohr is chosen. Those pairs of localized orbitals whose assigned spheres overlap with each other are referred to as the strong pairs. Weak pairs are then defined as those pairs of localized orbitals for which their assigned spheres do not overlap. Following the work of Carter and coworkers,⁵⁸⁻⁶¹ all double excitations derived from simultaneous single excitations out of weak orbital pairs into the active and virtual spaces are completely neglected.

The implementation of the local MR-CISD scheme within COLUMBUS is straightforward. COLUMBUS is based on the graphical unitary group approach (GUGA)^{65, 86} which encodes the configuration space in terms of a distinct row table (DRT) whose graphical representation is shown in Figure 1. The figure shows the orbitals (also termed levels) arranged vertically in the order used in COLUMBUS.⁸⁶⁻⁸⁷ On top are the inactive (reference doubly occupied) followed by the active orbitals. Inactive and active orbitals constitute the internal orbitals. Frozen core orbitals do not show up in this scheme. The external orbitals are located at the bottom and usually form the largest fraction of the total number of orbitals. Horizontally, for

each orbital different nodes (vertices) are found connected by arcs. They arise from the spin coupling scheme within GUGA. The four possible step vectors connecting nodes between different levels are shown in the inset of Figure 1. Each distinct strictly ascending walk from the bottom to the top of the graph represents one CSF. The walks in red represent the reference CSFs. The example given in this figure refers to a doublet state with five internal orbitals, two of them inactive. It is assumed in this example that the two inactive orbitals are represented by localized orbitals forming a weak pair.

Figure 1 shows the complicated structure of the walks through the active part of the DRT whereas the pattern belonging to the external part is regular. Therefore, the DRT is explicitly coded only up to the level of internal orbitals (nodes W, X, Y and Z in Figure 1). Classes of configurations are defined as specific walks through the internal orbital occupation pattern (internal walk) down to the border vertices W, X, Y and Z plus all possible extensions into the external (virtual) orbital space. Only the internal walk is considered explicitly. The contribution of the external continuation is added on-the-fly during the matrix-vector product of the Hamiltonian matrix times trial vector required in the direct CI iterative Davidson subspace method.⁸⁸⁻⁸⁹ The external part of the matrix-vector multiplication can be formulated in terms of dense matrix-vector operations⁹⁰ in spite of the overall pronounced sparsity of the Hamiltonian matrix. This formulation allows an efficient numerical processing of the external orbital space. For efficiency reasons, in this matrix formulation the size of the external space is kept the same for all internal paths of a walk. It is only possible to freeze external orbitals completely or consider them in all CSFs. No individual selection scheme (cutoff) can be adopted. Moreover, in the context of the LC approach, no localization of the external orbitals is performed.

In view of the just-described structure of paths (CSFs) in the DRT, the task of eliminating weak orbital pair contributions is quite simple. It is reduced to identifying and marking the respective internal walks as invalid during the CSF space construction phase. The actual MR-CISD code of computing the roots of the eigenvalue problem remains unaffected. Figure 1 shows as an example two walks (broken lines) corresponding to weak pair interactions. Any of these walks arriving at the boundary between reference doubly occupied and active orbitals (node A in the present example) will continue through the subgraph of the active orbitals in many ways and will give rise to a multitude of walks connecting to the boundary nodes W, X, Y and Z. The set of weak

pair walks passing through W and X and all extensions into the external space will be always removed completely. The set of corresponding Z and Y walks can be removed optionally. In the present calculations, the weak pair walks through all four vertices W, X, Y and Z were deleted. Any weak pair occurring in the reference doubly occupied orbitals will be processed in the same, just-described way. Removal of the internal part of a CSF is achieved by setting a flag in an index vector. A pruning process is initiated at the end of the removal of the weak pair configurations to eventually remove arc and nodes in the DRT.

Figure 1. Graph describing a DRT for an MR-CISD wavefunction of a state with $N = 2a + b = 7$ electrons and spin $S = b/2 = 1/2$. Each distinct strictly ascending walk from the bottom to the top

of the graph represents one CSF. The walks in red represent the reference CSFs. The inset shows the four possible step vectors connecting two nodes. $d = 3$ and 0 denote doubly occupied and empty orbitals, $d = 1$ and $d = 2$ correspond to low-spin and high-spin coupling, respectively. The red lines show the eight reference configurations, a CAS based on the three active orbitals and seven electrons. Node A is located at the boundary between inactive (reference doubly occupied) and active orbitals and nodes Z, Y, X and W are located at the boundary between internal and external (virtual) orbitals. Walks from Z to the bottom of the graph represent CSFs with zero occupation in the external space, walks from Y down to the bottom of the graph correspond to single occupation in the external space; X and W walks represent double occupation in the external space with triplet and singlet coupling, respectively. The two walks denoted as weak pairs in the inactive orbitals space and all continuations from A to the bottom of the DRT will be omitted in the LC approach.

The overall scheme of a typical calculation is represented by the block diagram displaying the different steps of the calculation shown in Figure 2. After an initial self-consistent field (SCF) calculation, the core orbitals are frozen by folding their effect into an effective one-electron Hamiltonian as has been formulated for example by Shavitt and coworkers.⁹¹ The original basis set is transformed into the basis of the remaining non-frozen orbitals. Following the MCSCF step, the resulting doubly occupied orbitals are localized and used for the determination of weak pairs. In addition to the LC treatment and the removal of weak pairs, selected orbitals can be frozen completely after the localization step. Because this freezing scheme is based on localized orbitals, specific bond orbitals not relevant to a certain question investigated can be identified and removed, which decreases the computational cost without losing a significant amount of accuracy. At the end of the MR-CISD calculation, the orbitals are transformed back to the original AO basis.

Figure 2. Block diagram representation for the different steps of the calculation.

4. RESULTS

In Figure 3 selected bond distances of the optimized geometries for the low-spin state of structures **1-4** computed at the UDFT/CAM-B3LYP/6-31G** level are shown. The bond length alternation of the central p-quinodimethane subunit of structure **1** indicates that it has an intermediate geometry between the closed-shell quinoid Kekulé and the biradical resonance forms. The introduction of the electron-withdrawing $-CN$ groups or the electron-donating $-NH_2$ groups or both (Chart 1) at the two radical centers leads to a reduction of the single-double bond alternation of the central p-quinodimethane subunit (distances a , b , and c in Figure 3) by ~ 0.01 Å and to a concomitant increase of the aromatic character of the central benzene ring. In agreement with this picture is the increase of the distance d (Chart 1) with respect to the unsubstituted heptazethrene structure. These factors indicate that singlet biradical character becomes more pronounced for structures **2** and **3**. The reduction in the distance d for structure **4** in comparison to **2** and **3** indicates a decreased efficiency in formation of biradical character by means of the push-pull substitution as compared to the symmetric substitution in the former two cases.

Figure 3. UDFT/CAM-B3LYP/6-31G** optimized geometries with selected bond distances for the singlet ground state of (a) heptazethrene (1), (b) 4,12-dicyanoheptazethrene (2), (c) 4,12-diaminoheptazethrene (3) and (d) 4-amino-12-cyanoheptazethrene (4).

A. Selection of the Reference Space

In our previous investigation on heptazethrene,⁴⁹ a CAS(4,4) reference space had been selected, which was well-suited for the calculation of the changes in the series of singlet-triplet splittings along the different heptazethrenes and the other compounds investigated there. In this section, the validity of this choice of reference space is re-examined with special emphasis on the calculation of singlet-triplet splittings under various conditions. Since these investigations involved significant extensions of the active space (up to 16 active orbitals) with concomitant increases of the configuration space, we restricted these calculations to the π system with the σ system frozen. It had been shown previously^{27, 49} that this approach gave very good results in comparison to the full calculations. State-averaged (SA) over the singlet and triplet states and single-state (SS) CASSCF calculations have been performed in order to investigate in detail the influence of different orbital choices on the splittings. NOs derived from the AQCC(4,4) calculation based on SA-CASSCF(4,4) and SS-CASSCF(4,4) orbitals have been used to test the influence of improved orbitals sets.

Table 1 first shows the basic data obtained from the AQCC(4,4) calculation by using MOs computed from SS and SA-CASSCF(4,4) calculations, respectively. Subsequently, several active space extensions have been used to test the sensitivity of the singlet-triplet splittings with respect to these changes. To maintain a uniform set of orbitals, the NOs computed from these two calculations were used as molecular orbitals in the subsequent AQCC calculations. These NOs, which are obtained from an extended correlated wavefunction, are also expected to give better correlating orbitals than those computed from a CASSCF calculation, which includes only a small fraction of dynamic electron correlation. Using these NOs at the AQCC(4,4) level does not change the singlet-triplet splitting as compared to the use of the original CASSCF(4,4) orbitals. Increasing the active space to various levels of RAS/CAS/AUX schemes as shown in Table 1 decreases the singlet-triplet splitting. We compute a best estimate of 0.70 eV from the RAS(4)/CAS(4,4)/AUX(4)-2ex calculation containing in total 12 active orbitals corrected by the difference of the RAS(4)/CAS(4,4)/AUX(4)-1ex and RAS(6)/CAS(4,4)/AUX(6)-1ex value. The latter calculation contains 16 active orbitals. Best estimates obtained from SA and SS MOs agree very well. These best estimates differ only by ~ 0.09 eV from our original procedure given in the two top result lines.

For better comparison, the same NOs derived from the AQCC calculations (Table 1) are used for the MR-CISD and MR-CISD+Q results presented in Table 1S and Table 2S of the supporting information (SI). For the MR-CISD calculations (Table 1S), best estimates are also almost the same for the two MO choices and are smaller by ~ 0.09 eV than the original MR-CISD(4,4) results. For the MR-CISD+Q results presented in Table 2S, best estimates agree very well. They are about 0.04 eV smaller than the respective AQCC best estimates. In view of the simplicity of the standard approach of using CASSCF orbitals, we decided to stay with the CAS(4,4) active space. Both the obtained AQCC(4,4) and MR-CISD(4,4) splittings are estimated to be about 0.09 eV too high than the best estimates obtained at AQCC and MR-CISD level, respectively. In the case of the MR-CISD(4,4)+Q calculations, a slightly larger orbital dependence is observed. Using SA-CASSCF orbitals, MR-CISD(4,4)+Q singlet-triplet splittings are too large by ~ 0.2 eV whereas using SS-CASSCF(4,4) orbitals, the agreement with the AQCC reference values is significantly better. For the full calculations considering both the σ and π orbitals, although the two possibilities for all three methods (MR-CISD, MR-CISD+Q and MR-AQCC) are

very close to each other, the SA approach was found to be more consistent (for both the π and $\pi+\sigma$ space) than the SS approach and, thus, has been used in the subsequent calculations.

Table 1. Reference space dependence of heptazethrene vertical singlet-triplet splittings $\Delta E(S-T)$ using the MR-AQCC method (performed only in the π orbital space with the σ orbitals frozen) and the 6-31G* basis set.^a

Reference space	$\Delta E(S-T)$ (eV)
Orbital basis: SA-CASSCF MOs	
CAS(4,4)	0.791
Orbital basis: SS-CASSCF MOs	
CAS(4,4)	0.781
Orbital basis: NOs from AQCC(4,4)/SA-CASSCF(4,4)	
CAS(4,4)	0.806
RAS(2)/CAS(4,4)/AUX(2)-1ex	0.680
RAS(4)/CAS(4,4)/AUX(4)-1ex	0.644
RAS(6)/CAS(4,4)/AUX(6)-1ex	0.727
RAS(2)/CAS(4,4)/AUX(2)-2ex	0.674
RAS(4)/CAS(4,4)/AUX(4)-2ex	0.621
Best estimate	0.704
Orbital basis: NOs from AQCC(4,4)/SS-CASSCF(4,4)	
CAS(4,4)	0.797
RAS(2)/CAS(4,4)/AUX(2)-1ex	0.681
RAS(4)/CAS(4,4)/AUX(4)-1ex	0.642
RAS(6)/CAS(4,4)/AUX(6)-1ex	0.717
RAS(2)/CAS(4,4)/AUX(2)-2ex	0.675
RAS(4)/CAS(4,4)/AUX(4)-2ex	0.618
Best estimate	0.693

B. Computational Aspects of the Local Correlation Implementation

SA-CASSCF(4,4) calculations with frozen core orbitals using the 6-31G* basis set were performed for all the structures shown in Chart 1 to create the orbitals for the subsequent MR

calculations. The doubly occupied SA-CASSCF(4,4) orbitals, which not only include the σ orbitals but also the reference doubly occupied π orbitals, were localized by the Pipek-Mezey localization procedure. This procedure does not mix the σ and π orbitals. Figure 4 displays the doubly occupied localized π orbitals of heptazethrene (**1**). For the purpose of comparison, the corresponding canonical delocalized π -orbitals are presented in Figure 1S of the SI. The balanced occurrence of bonding and antibonding π orbitals allows also their partial localization in space even though no two-electron two-center bonds are formed as in the case of the σ orbitals. Note that the localized orbitals do not transform according to irreducible representations but are obtained as symmetry-equivalent orbitals. Since the symmetry treatment in COLUMBUS is based on irreducible representations, the calculations were performed in C_1 symmetry, i.e., without utilization of symmetry. It is clear that in many practical applications, larger molecules or clusters will have either low or no symmetry anyway.

Figure 4. The Pipek-Mezey doubly occupied localized π -orbitals of heptazethrene (**1**) (isovalue is $\pm 0.03 e/\text{bohr}^3$) calculated at the SA2-CASSCF(4,4)/6-31G* method with frozen core orbitals.

Table 2 shows a comparison of the recovery of the amount of the MR-CISD(4,4)/6-31G* stabilization energy $\Delta E_{\text{MR-CISD}} = E_{\text{MR-CISD}} - E_{\text{CASSCF}}$ as a function of the radius multiplier α of the LC approach for heptazethrene based on a SA-CASSCF(4,4) calculation. In addition to the core orbitals, all the C-H bonds are frozen at the multireference correlation level. This is the optimal freezing scheme, which has been used here to test the effect of the scaling factor α . It should be noted, though, that the total savings with respect to a standard full calculation in C_1 symmetry with no C-H bonds frozen are much larger, as can be seen from the discussion of the statistics given in Table 3. The average recovered energy (for the vertical singlet and the triplet state) reaches 100% for $\alpha=2.0$. Even the value $\alpha=1.6$ gives a good recovery at 99.8%. The corresponding number of CSFs with respect to the full list is only about 64% and 53%, respectively. Due to error compensation, the vertical singlet-triplet splitting $\Delta E(S-T)$ is almost independent of α , even for small values such as $\alpha=0.6$. This error compensation depends on the orbitals chosen. In the case of choosing SS-CASSCF orbitals, i.e., different orbitals for the singlet and triplet state, such error compensation was not observed. Similarly, the corresponding adiabatic singlet-triplet splitting is strongly dependent on α . For results within a range of 0.05 eV, α values of 1.3 and larger are appropriate. α values of 1.3 – 1.6 lead to configuration spaces of 44%-53% with respect to the full space; these reductions are converted directly to analogous decreases in computer time. These trends, i.e., the variation in number of CSFs, recovered energy, vertical and adiabatic singlet-triplet gap with increasing α are also the same for MR-CISD+Q calculations. Thus, from this table one can conclude that if ultra-high accuracy is not needed, as for adiabatic singlet-triplet splittings, smaller alpha values (for example, $\alpha=1.0$ where 98.4% stabilization energy is recovered) can be used, leading to even larger reductions in computer time.

Table 2. Dependence of the number of configurations (in millions), average percentage of the MR-CISD energy difference $\Delta E_{\text{MR-CISD}} = E_{\text{MR-CISD}} - E_{\text{CASSCF}}$ recovered for singlet and triplet state and vertical and adiabatic (in parentheses) singlet-triplet splittings $\Delta E(S-T)$ on the value of the radius multiplier α for heptazethrene.^a

α	Spin multiplicity	no. of CSFs (millions)	% of no. full config.	Recovered energy (%)	$\Delta E(S-T)$ (eV) Vert. (Adiab.)
0.6	Singl.	389	16.1	91.0	0.967
	Tripl.	338	18.1		(0.336)

0.8	Singl.	566	23.4		0.963
	Tripl.	472	25.3	96.5	(0.487)
1.0	Singl.	770	31.8		0.964
	Tripl.	625	33.5	98.4	(0.706)
1.3	Singl.	1033	42.7		0.964
	Tripl.	823	44.1	99.4	(0.777)
1.6	Singl.	1261	52.1		0.963
	Tripl.	995	53.3	99.8	(0.806)
2.0	Singl.	1535	63.4		0.964
	Tripl.	1201	64.3	100	(0.824)
2.5	Singl.	1796	74.2		0.964
	Tripl.	1397	74.8	100	(0.831)
Full	Singl.	2420	100		0.963
	Tripl.	1867	100	100	(0.831)

^aA SA-CASSCF(4,4) calculation with a CAS(4,4) reference space and the 6-31G* basis were used. In addition to the core orbitals, all C-H bonds were frozen at the multireference level.

Table 3 compares the number of CSFs for structures **1-4** in different computational schemes at the MR-CISD level using the 6-31G* basis set. The table shows the reduction in the number of configurations in the full calculation (all valence electrons) without symmetry (C_1) either by making use of existing symmetry or by introducing the LC scheme. The LC scheme is performed always in C_1 symmetry. It should be emphasized that the LC scheme not only gives the possibility of reducing the number of configurations by means of the weak pairs approximation, but includes also complete freezing of localized orbitals not relevant for a certain question. In the present case, such candidates are obviously the C-H bonds. For example, the vertical and adiabatic singlet-triplet splitting for structure **1** computed at the MR-CISD/6-31G* level is 0.964 eV and 0.837 eV, respectively, whereas if we freeze all C-H bonds, these energies become 0.963 eV and 0.831 eV (Table 2), respectively. This means that the vertical and adiabatic splittings are independent of the freezing of all the C-H bonds. The LC treatment with $\alpha=1.0$ including all the C-H bonds frozen yields a vertical singlet-triplet splitting of 0.964 eV. Table 3 shows that C_{2h} symmetry for structures **1** and **2** decreases the number of CSFs nearly by a factor of 6 - 7. The LC treatment performed in C_1 symmetry ($\alpha = 1.0$) is not as efficient in reducing the number of CSFs compared to C_{2h} symmetry, but with all C-H bonds frozen, this treatment results in CSF numbers

comparable to those of C_{2h} symmetry. The full advantage of the LC approach, however, comes into play in cases of low (structure **3**) or no symmetry (structure **4**) where especially in the last example the LC treatment with freezing all the C-H bonds, decreases the number of configurations by a factor of ~ 6 . This strong reduction comes from the fact that, e.g., when freezing all the C-H bonds in structure **1**, out of the 1081 localized pairs, only 282 pairs are strong pairs and the remaining 799 (73.9%) are weak pairs. The reduction in the CSF expansion size is not only important for decreasing the computer time, but also for reducing the memory requirements since the subspace expansion vectors and the matrix-vector products of the Hamiltonian matrix with the trial vectors need to be kept in memory.

Table 3. Comparison of the number of CSFs (in millions) at full MR-CISD level with that of the full LC approach (all valence orbitals included) and with the C-H bonds frozen (C-H(frz)) for structures **1-4** using a CAS(4,4) reference space and the 6-31G* basis set.^a

System	Full calc.: C_1 symm.	Full calc.: full symm.	LC: all valence orb. ^b	LC: C-H(frz) ^{b,c}
1	$C_1 (1^1A)$: 4 348	$C_{2h} (1^1A_g)$: 705	$C_1 (1^1A)$: 1 127	$C_1 (1^1A)$: 770
	$C_1 (1^3A)$: 3 334	$C_{2h} (1^3B_u)$: 486	$C_1 (1^3A)$: 910	$C_1 (1^3A)$: 625
2	$C_1 (1^1A)$: 6 938	$C_{2h} (1^1A_g)$: 1 117	$C_1 (1^1A)$: 1 551	$C_1 (1^1A)$: 1 174
	$C_1 (1^3A)$: 5 308	$C_{2h} (1^3B_u)$: 767	$C_1 (1^3A)$: 1 254	$C_1 (1^3A)$: 953
3	$C_1 (1^1A)$: 6 000	$C_i (1^1A_g)$: 1 841	$C_1 (1^1A)$: 1 387	$C_1 (1^1A)$: 976
	$C_1 (1^3A)$: 4 593	$C_i (1^3A_u)$: 1 272	$C_1 (1^3A)$: 1 121	$C_1 (1^3A)$: 796
4	$C_1 (1^1A)$: 6 456	$C_1 (1^1A)$: 6 456	$C_1 (1^1A)$: 1 460	$C_1 (1^1A)$: 1059
	$C_1 (1^3A)$: 4 941	$C_1 (1^3A)$: 4 941	$C_1 (1^3A)$: 1 181	$C_1 (1^3A)$: 863

^aOrbital spaces in C_1 symmetry: **1** FRZC: 28, REFDOCC: 62, ACT: 4, VIRT: 330; **2** FRZC: 32, REFDOCC: 70, ACT: 4, VIRT: 370; **3** FRZC: 30, REFDOCC: 68, ACT: 4, VIRT: 354; **4** FRZC: 31, REFDOCC: 69, ACT: 4, VIRT: 362

^bRadius multiplier $\alpha = 1.0$, ^cAll C-H bonds are frozen

B. Singlet-Triplet Splittings

Vertical (Table 4) and adiabatic (Table 3S) singlet-triplet splittings $\Delta E(S-T) = E(T) - E(S)$ were computed for structures **1-4** at the MR-CISD, MR-CISD+Q and MR-AQCC levels. In all cases, $\Delta E(S-T)$ is positive, i.e., the ground state is a singlet. In both the MR-CISD as well as in the Davidson-corrected methods, the differences in the vertical $\Delta E(S-T)$ values calculated with the full and local correlation schemes available for structures **1-3** are negligible. The adiabatic $\Delta E(S-T)$ values differ only by 0.06 eV at most (Table 3S). Because of the occurrence of several intruder states for both the singlet and the triplet states, MR-AQCC calculations for the full treatment were not feasible. On the other hand, MR-AQCC calculations with the LC treatment were better behaved and the weak intruder states could be removed. To our knowledge, no experimental single-triplet splittings are available for heptazethrene.

Table 4. Vertical singlet-triplet splitting energies $\Delta E(S-T)$ (eV) computed at different MR levels, expectation values of the square of the total spin operator for the broken symmetry solution at UDFT/CAM-B3LYP/6-31G** level, and the vertical singlet-triplet gap, ΔE_{proj} , using the uncorrected and the spin- corrected formula (Eq. 2) for structures **1-4**.

System	MR-CISD		MR-CISD+Q		MR-AQCC LC ^a	UDFT/ CAM-B3LYP	$\langle S_{BS}^2 \rangle$	ΔE_{proj}
	Full	LC ^a	Full	LC ^a				
1	0.964	0.964	0.948	0.943	0.837	0.512	0.940	0.909
2	0.733	0.733	0.735	0.732	0.685	0.397	0.996	0.739
3	0.746	0.744	0.741	0.736	0.712	0.389	0.971	0.713
4	-	0.979	-	0.906	0.733	0.478	0.836	0.785

^a Radius multiplier $\alpha = 1.0$. A SA-CASSCF(4,4) calculation, a CAS(4,4) reference space and the 6-31G* basis were used. The core orbitals and in the LC treatment all C-H bonds, were frozen at the multireference level.

Introduction of either two electron-withdrawing or two electron-donating groups (structures **2** and **3**) respectively decreases the vertical singlet-triplet splitting $\Delta E(S-T)$ by 0.13 to 0.15 eV at the MR-AQCC level, as compared to the splitting for the unsubstituted structure **1**. Somewhat larger shifts of ~ 0.2 eV are obtained at the MR-CISD and +Q level. For the push-pull structure **4**, the vertical $\Delta E(S-T)$ increases compared to structures **2** and **3** by about 0.17 eV at the MR-CISD+Q level and approaches the value of structure **1**. For the MR-AQCC calculations, a

somewhat smaller increase in the singlet-triplet splitting for structure **4** is observed. For the adiabatic $\Delta E(S-T)$ (Table 3S) a similar trend as for the vertical $\Delta E(S-T)$ values is observed.

The singlet-triplet splitting, along with the expectation values of S^2 for the BS state computed at the UDFT level with CAM-B3LYP, is given in Table 4 as well. In all cases the S^2 values are close to unity, i.e., the BS state is highly spin-contaminated. Because of this, $\Delta E(S-T)$ was computed also with the spin-corrected formula (Eq. 2, ΔE_{proj}). Because of the spin-projection, ΔE_{proj} increases significantly and is quite close to the MR-AQCC results.

5. CONCLUSIONS

The possibilities afforded by implementation of the concept of localized orbitals according to the geometrical analysis developed by Carter and coworkers⁵⁸⁻⁵⁹ into the COLUMBUS program system is reported. The resulting computational savings due to the omission of weak pairs and the excellent agreement between results computed at full and LC level, respectively, were demonstrated for the computation of substituent effects on singlet-triplet splittings for heptazethrenes, a prominent example of low-energy gap PAHs. Only the doubly occupied orbitals were involved in the localization procedure. It was shown that the LC treatment is able to reproduce even subtle changes in the singlet-triplet splittings. In case of C_1 symmetry, which is the actual reference case we have in mind, reductions in the CI expansion size by a factor of six and similar savings in computer time have been achieved. In favorable cases, of quasi-linear polyenes or carotenoids much larger savings can be expected. The parameter α can be conveniently used to switch continuously between different accuracy requirements. Thus, MR calculations of quite extended systems of lower symmetry are becoming feasible which, otherwise, would have been tedious or not at all possible.

The insertion of both electron withdrawing and donating groups in the position of maximum open-shell singlet density leads to a reduction of the singlet-triplet gap. However, the effects of electron donating, accepting, and push-pull groups is relatively small in these cases. In more complex situations that arise just by simple extensions of the present heptazethrene, e.g., to 5,6:13,14-dibenzoheptazethrene,⁴⁹ the biradical character is enhanced further and several substituent positions seem feasible, which can be tested by the present methods. Since the basic logic of the LC approach is restricted to doubly occupied orbitals, its application within the

multireference scheme is straightforward and the extension to a wide range of applications much beyond the current example of the biradical character of PAH systems is directly available.

ASSOCIATED CONTENT

Supporting Information

Vertical singlet-triplet splitting for MR-CISD and MR-CISD+Q methods, adiabatic singlet-triplet splittings, canonical doubly occupied π orbitals of heptazethrene, and Cartesian coordinates of all optimized structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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References:

- (1) Wu, T. C.; Chen, C. H.; Hibi, D.; Shimizu, A.; Tobe, Y.; Wu, Y. T. Synthesis, Structure, and Photophysical Properties of Dibenzo[De,Mn]Naphthacenes. *Angew. Chem., Int. Ed.* **2010**, *49*, 7059-7062.
- (2) Li, Y.; Heng, W. K.; Lee, B. S.; Aratani, N.; Zafra, J. L.; Bao, N.; Lee, R.; Sung, Y. M.; Sun, Z.; Huang, K. W.; Webster, R. D.; Navarrete, J. T. L.; Kim, D.; Osuka, A.; Casado, J.; Ding, J.; Wu, J. S. Kinetically Blocked Stable Heptazethrene and Octazethrene: Closed-Shell or Open-Shell in the Ground State? *J. Am. Chem. Soc.* **2012**, *134*, 14913-14922.

- (3) Sun, Z.; Lee, S.; Park, K. H. e. a. Dibenzoheptazethrene Isomers with Different Biradical Characters: An Exercise of Clar's Aromatic Sextet Rule in Singlet Biradicaloids. *J. Am. Chem. Soc.* **2013**, *135*, 18229–18236.
- (4) Sun, Z.; Zeng, Z.; Wu, J. Zethrenes, Extended P-Quinodimethanes, and Periacenes with a Singlet Biradical Ground State. *Acc. Chem. Res.* **2014**, *47*, 2582–2591.
- (5) Zafra, J. L.; Cano, R. C. G.; Delgado, M. C. R.; Sun, Z.; Li, Y.; Navarrete, J. T. L.; Wu, J. S.; Casado, J. Zethrene Biradicals: How Pro-Aromaticity Is Expressed in the Ground Electronic State and in the Lowest Energy Singlet, Triplet, and Ionic States. *J. Chem. Phys.* **2014**, *140*, 054706.
- (6) Hibi, D.; Kitabayashi, K.; Shimizu, A.; Umeda, R.; Tobe, Y. Synthesis and Physical Properties of Zethrene Derivatives Bearing Donor/Acceptor Substituents at 7,14-Positions. *Org. Biomol. Chem.* **2013**, *11*, 8256-8261.
- (7) Hsieh, Y. C.; Fang, H. Y.; Chen, Y. T.; Yang, R.; Yang, C. I.; Chou, P. T.; Kuo, M. Y.; Wu, Y. T. Zethrene and Dibenzozethrene: Masked Biradical Molecules? *Angew. Chem., Int. Ed.* **2015**, *54*, 3069-3073.
- (8) Chikamatsu, M.; Mikami, T.; Chisaka, J.; Yoshida, Y.; Azumi, R.; Yase, K.; Shimizu, A.; Kubo, T.; Morita, Y.; Nakasuji, K. Ambipolar Organic Field-Effect Transistors Based on a Low Band Gap Semiconductor with Balanced Hole and Electron Mobilities. *Appl. Phys. Lett.* **2007**, *91*, 043506.
- (9) Feringa, B. L. In Control of Motion: From Molecular Switches to Molecular Motors. *Acc. Chem. Res.* **2001**, *34*, 504-513.
- (10) Bendikov, M.; Wudl, F.; Perepichka, D. F. Tetrathiafulvalenes, Oligoacenenenes, and Their Buckminsterfullerene Derivatives: The Brick and Mortar of Organic Electronics. *Chem. Rev.* **2004**, *104*, 4891-4945.
- (11) Balzani, V.; Credi, A.; Venturi, M. Molecular Machines Working on Surfaces and at Interfaces. *ChemPhysChem* **2008**, *9*, 202-220.
- (12) Nakano, M.; Kishi, R.; Takebe, A.; Nate, M.; Takahashi, H.; Kubo, T.; Kamada, K.; Ohta, K.; Champagne, B.; Botek, E. Second Hyperpolarizability of Zethrenes. *Computing Letters* **2007**, *3*, 333-338.
- (13) Kamada, K.; Ohta, K.; Kubo, T.; Shimizu, A.; Morita, Y.; Nakasuji, K.; Kishi, R.; Ohta, S.; Furukawa, S.; Takahashi, H.; Nakano, M. Strong Two-Photon Absorption of Singlet Diradical Hydrocarbons. *Angew. Chem., Int. Ed.* **2007**, *46*, 3544-3546.
- (14) Morita, Y.; Nishida, S.; Murata, T.; Moriguchi, M.; Ueda, A.; Satoh, M.; Arifuku, K.; Sato, K.; Takui, T. Organic Tailored Batteries Materials Using Stable Open-Shell Molecules with Degenerate Frontier Orbitals. *Nat. Mater.* **2011**, *10*, 947-951.
- (15) Dediu, V. A.; Hueso, L. E.; Bergenti, I.; Taliani, C. Spin Routes in Organic Semiconductors. *Nat. Mater.* **2009**, *8*, 707-716.
- (16) Coronado, E.; Epsetin, A. J. Molecular Spintronics and Quantum Computing. *J. Mater. Chem.* **2009**, *19*, 1670-1671.
- (17) Takatsuka, K.; Fueno, T.; Yamaguchi, K. Distribution of Odd Electrons in Ground-State Molecules. *Theor. Chim. Acta* **1978**, *48*, 175–183.
- (18) Staroverov, V. N.; Davidson, E. R. Distribution of Effectively Unpaired Electrons. *Chem. Phys. Lett.* **2000**, *330*, 161-168.
- (19) Clar, E.; Macpherson, I. A. The Significance of Kekulé Structures for the Stability of Aromatic Systems-II. *Tetrahedron* **1962**, *18*, 1411-1416.

- (20) Weil, T.; Vosch, T.; Hofkens, J.; Peneva, K.; Mullen, K. The Rylene Colorant Family-Tailored Nanoemitters for Photonics Research and Applications. *Angew. Chem., Int. Ed.* **2010**, *49*, 9068-9093.
- (21) Anthony, J. E. Functionalized Acenes and Heteroacenes for Organic Electronics. *Chem. Rev.* **2006**, *106*, 5028-5048.
- (22) Anthony, J. E. The Larger Acenes: Versatile Organic Semiconductors. *Angew. Chem., Int. Ed.* **2008**, *47*, 452-483.
- (23) Clar, E. In *The Aromatic Sextet*, John Wiley & Sons Ltd: London, New York, Sydney, Toronto, 1972.
- (24) Wassmann, T.; Seitsonen, A. P.; Saitta, A. M.; Lazzeri, M.; Mauri, F. Clar's Theory, Pi-Electron Distribution, and Geometry of Graphene Nanoribbons. *J. Am. Chem. Soc.* **2010**, *132*, 3440-3451.
- (25) Balaban, A. T.; Klein, D. J. Claromatic Carbon Nanostructures. *J. Phys. Chem. C* **2009**, *113*, 19123-19133.
- (26) Plasser, F.; Pasalic, H.; Gerzabek, M. H.; Libisch, F.; Reiter, R.; Burgdörfer, J.; Müller, T.; Shepard, R.; Lischka, H. The Multiradical Character of One- and Two-Dimensional Graphene Nanoribbons. *Angew. Chem., Int. Ed.* **2013**, *52*, 2581-2584.
- (27) Horn, S.; Plasser, F.; Müller, T.; Libisch, F.; Burgdörfer, J.; Lischka, H. A Comparison of Singlet and Triplet States for One- and Two-Dimensional Graphene Nanoribbons Using Multireference Theory. *Theor. Chem. Acc.* **2014**, *133*, 1-9.
- (28) Horn, S.; Lischka, H. A Comparison of Neutral and Charged Species of One- and Two-Dimensional Models of Graphene Nanoribbons Using Multireference Theory. *J. Chem. Phys.* **2015**, *142*, 054302.
- (29) Lambert, C. Towards Polycyclic Aromatic Hydrocarbons with a Singlet Open-Shell Ground State. *Angew. Chem., Int. Ed.* **2011**, *50*, 1756-1758.
- (30) Jiang, D. E.; Sumpter, B. G.; Dai, S. Unique Chemical Reactivity of a Graphene Nanoribbon's Zigzag Edge. *J. Chem. Phys.* **2007**, *126*, 134701.
- (31) Barone, V.; Hod, O.; Peralta, J. E.; Scuseria, G. E. Accurate Prediction of the Electronic Properties of Low-Dimensional Graphene Derivatives Using a Screened Hybrid Density Functional. *Acc. Chem. Res.* **2011**, *44*, 269-279.
- (32) Krylov, A. I. Spin-Flip Configuration Interaction: An Electronic Structure Model That Is Both Variational and Size-Consistent. *Chem. Phys. Lett.* **2001**, *350*, 522-530.
- (33) Casanova, D.; Head-Gordon, M. Restricted Active Space Spin-Flip Configuration Interaction Approach: Theory, Implementation and Examples. *Phys. Chem. Chem. Phys.* **2009**, *11*, 9779-9790.
- (34) Jimenez-Hoyos, C. A.; Henderson, T. M.; Tsuchimochi, T.; Scuseria, G. E. Projected Hartree-Fock Theory. *J. Chem. Phys.* **2012**, *136*, 164109.
- (35) Gidofalvi, G.; Mazziotti, D. A. Active-Space Two-Electron Reduced-Density-Matrix Method: Complete Active-Space Calculations without Diagonalization of the N-Electron Hamiltonian. *J. Chem. Phys.* **2008**, *129*, 134108.
- (36) Pelzer, K.; Greenman, L.; Gidofalvi, G.; Mazziotti, D. A. Strong Correlation in Acene Sheets from the Active-Space Variational Two-Electron Reduced Density Matrix Method: Effects of Symmetry and Size. *J. Phys. Chem. A* **2011**, *115*, 5632-5640.
- (37) Hachmann, J.; Dorando, J. J.; Aviles, M.; Chan, G. K. L. The Radical Character of the Acenes: A Density Matrix Renormalization Group Study. *J. Chem. Phys.* **2007**, *127*, 134309.

- (38) Mizukami, W.; Kurashige, Y.; Yanai, T. More Pi Electrons Make a Difference: Emergence of Many Radicals on Graphene Nanoribbons Studied by Ab Initio DMRG Theory. *J. Chem. Theory Comput.* **2013**, *9*, 401-407.
- (39) Hajgato, B.; Szieberth, D.; Geerlings, P.; De Proft, F.; Deleuze, M. S. A Benchmark Theoretical Study of the Electronic Ground State and of the Singlet-Triplet Split of Benzene and Linear Acenes. *J. Chem. Phys.* **2009**, *131*, 224321.
- (40) Luzanov, A. Effectively Unpaired Electrons in Bipartite Lattices within the Generalized Tight-Binding Approximation: Application to Graphene Nanoflakes. *Funct. Mater.* **2014**, *21*, 437-447.
- (41) Valentine, A. J. S.; Mazziotti, D. A. Theoretical Prediction of the Structures and Energies of Olympicene and Its Isomers. *J. Phys. Chem. A* **2013**, *117*, 9746-9752.
- (42) Jiang, D. E.; Dai, S. Electronic Ground State of Higher Acenes. *J. Phys. Chem. A* **2008**, *112*, 332-335.
- (43) Yamaguchi, K.; Jensen, F.; Dorigo, A.; Houk, K. N. A Spin Correction Procedure for Unrestricted Hartree-Fock and Moller-Plesset Wavefunctions for Singlet Diradicals and Polyradicals. *Chem. Phys. Lett.* **1988**, *149*, 537-542.
- (44) Siegbahn, P. E. M. Generalizations of the Direct CI Method Based on the Graphical Unitary Group-Approach II. Single and Double Replacements from Any Set of Reference Configurations. *J. Chem. Phys.* **1980**, *72*, 1647-1656.
- (45) Shavitt, I. In *Methods of Electronic Structure Theory*, Schaefer III, H.F., Ed. Plenum: New York, 1977.
- (46) Szalay, P. G.; Müller, T.; Gidofalvi, G.; Lischka, H.; Shepard, R. Multiconfiguration Self-Consistent Field and Multireference Configuration Interaction Methods and Applications. *Chem. Rev.* **2012**, *112*, 108-181.
- (47) Szalay, P. G.; Bartlett, R. J. Multireference Averaged Quadratic Coupled-Cluster Method - a Size-Extensive Modification of Multireference CI. *Chem. Phys. Lett.* **1993**, *214*, 481-488.
- (48) Gdanitz, R. J.; Ahlrichs, R. The Averaged Coupled-Pair Functional (ACPF) - a Size-Extensive Modification of MR CI(SD). *Chem. Phys. Lett.* **1988**, *143*, 413-420.
- (49) Das, A.; Müller, T.; Plasser, F.; Lischka, H. Polyradical Character of Triangular Non-Kekule Structures, Zethrenes, P-Quinodimethane-Linked Bisphenalenyl, and the Clar Goblet in Comparison: An Extended Multireference Study. *J. Phys. Chem. A* **2016**, *120*, 1625-1636.
- (50) Vazdar, M.; Eckert-Maksic, M.; Lischka, H. The Antiferromagnetic Spin Coupling in Non-Kekule Acenes-Impressive Polyradical Character Revealed by High-Level Multireference Methods. *ChemPhysChem* **2016**, *17*, 2013-2021.
- (51) Kapuy, E.; Csépes, Z.; Kozmutza, C. Application of the Many-Body Perturbation Theory by Using Localized Orbitals. *Int. J. Quantum Chem.* **1983**, *23*, 981-990.
- (52) Ahlrichs, R.; Lischka, H.; Zurawski, B.; Kutzelnigg, W. PNO-CI (Pair-Natural-Orbital Configuration Interaction) and CEPA-PNO (Coupled Electron Pair Approximation with Pair Natural Orbitals) Calculations of Molecular Systems .4. Molecules N₂, F₂, C₂H₂, C₂H₄, and C₂H₆. *J. Chem. Phys.* **1975**, *63*, 4685-4694.
- (53) Köhler, H. J.; Lischka, H. Theoretical Investigations on Carbocations - Structure and Stability of C₃H₅⁺, C₄H₉⁺ (2-Butyl Cation), C₅H₅⁺, C₆H₇⁺ (Protonated Benzene), and C₇H₁₁⁺ (2-Norbornyl Cation). *J. Am. Chem. Soc.* **1979**, *101*, 3479-3486.
- (54) Pulay, P. Localizability of Dynamic Electron Correlation. *Chem. Phys. Lett.* **1983**, *100*, 151-154.

- (55) Sæbø, S.; Pulay, P. Local Configuration Interaction: An Efficient Approach for Larger Molecules. *Chem. Phys. Lett.* **1985**, *113*, 13-18.
- (56) Saebo, S.; Pulay, P. Local Treatment of Electron Correlation. *Annu. Rev. Phys. Chem.* **1993**, *44*, 213-236.
- (57) Fink, R.; Staemmler, V. A Multi-Configuration Reference CEPA Method Based on Pair Natural Orbitals. *Theor. Chim. Acta* **1993**, *87*, 129-145.
- (58) Walter, D.; Carter, E. A. Multi-Reference Weak Pairs Local Configuration Interaction: Efficient Calculations of Bond Breaking. *Chem. Phys. Lett.* **2001**, *346*, 177-185.
- (59) Walter, D.; Venkatnathan, A.; Carter, E. A. Local Correlation in the Virtual Space in Multireference Singles and Doubles Configuration Interaction. *J. Chem. Phys.* **2003**, *118*, 8127-8139.
- (60) Venkatnathan, A.; Szilva, A. B.; Walter, D.; Gdanitz, R. J.; Carter, E. A. Size Extensive Modification of Local Multireference Configuration Interaction. *J. Chem. Phys.* **2004**, *120*, 1693-1704.
- (61) Krisiloff, D. B.; Carter, E. A. Approximately Size Extensive Local Multireference Singles and Doubles Configuration Interaction. *Phys. Chem. Chem. Phys.* **2012**, *14*, 7710-7717.
- (62) Krisiloff, D. B.; Dieterich, J. M.; Libisch, F.; Carter, E. A. Numerical Challenges in a Cholesky-Decomposed Local Correlation Quantum Chemistry Framework. In *Mathematical and Computational Modeling: With Applications in Natural and Social Sciences, Engineering, and the Arts*, Melnik, R., Ed. John Wiley and Sons, Inc.: Hoboken, NJ, 2015.
- (63) Saebo, S.; Pulay, P. 4th-Order Møller-Plessett Perturbation-Theory in the Local Correlation Treatment .1. Method. *J. Chem. Phys.* **1987**, *86*, 914-922.
- (64) Lischka, H.; Shepard, R.; Pitzer, R. M.; Shavitt, I.; Dallos, M.; Müller, T.; Szalay, P. G.; Seth, M.; Kedziora, G. S.; Yabushita, S.; Zhang, Z. Y. High-Level Multireference Methods in the Quantum-Chemistry Program System Columbus: Analytic MR-CISD and MR-AQCC Gradients and MR-AQCC-LRT for Excited States, GUGA Spin-Orbit CI and Parallel CI Density. *Phys. Chem. Chem. Phys.* **2001**, *3*, 664-673.
- (65) Lischka, H.; Müller, T.; Szalay, P. G.; Shavitt, I.; Pitzer, R. M.; Shepard, R. Columbus-a Program System for Advanced Multireference Theory Calculations. *WIREs Comput Mol Sci* **2011**, *1*, 191-199.
- (66) Lischka, H.; Shepard, R.; Shavitt, I.; Pitzer, R.; Dallos, M.; Müller, T.; Szalay, P., G.; Brown, F.; Ahlrichs, R.; Boehm, H. J.; Chang, A.; Comeau, D.; Gdanitz, R.; Dachsel, H.; Ehrhardt, C.; Ernzerhof, M.; Höchtel, P.; Irle, S.; Kedziora, G.; Kovar, T.; Parasuk, V.; Pepper, M.; Scharf, P.; Schiffer, H.; Schindler, M.; Schuler, M.; Seth, M.; Stahlberg, E.; Zhao, J.-G.; Yabushita, S.; Zhang, Z.; Barbatti, M.; Matsika, S.; Schuurmann, M.; Yarkony, D.; Brozell, S.; Beck, E.; Blaudeau, J.-P.; Ruckebauer, M.; Sellner, B.; Plasser, F.; Szymczak, J. J.; Spada, R. F. K. Columbus, an Ab Initio Electronic Structure Program, Release 7.0. **2016**.
- (67) Pipek, J.; Mezey, P. G. A Fast Intrinsic Localization Procedure Applicable for Abinitio and Semiempirical Linear Combination of Atomic Orbital Wave-Functions. *J. Chem. Phys.* **1989**, *90*, 4916-4926.
- (68) Foster, J. M.; Boys, S. F. Canonical Configurational Interaction Procedure. *Rev Mod Phys* **1960**, *32*, 300-302.
- (69) Nakano, M.; Minami, T.; Yoneda, K.; Muhammad, S.; Kishi, R.; Shigeta, Y.; Kubo, T.; Rougier, L.; Champagne, B.; Kamada, K.; Ohta, K. Giant Enhancement of the Second

Hyperpolarizabilities of Open-Shell Singlet Polyaromatic Diphenalenyl Diradicaloids by an External Electric Field and Donor-Acceptor Substitution. *J. Phys. Chem. Lett.* **2011**, *2*, 1094-1098.

(70) Nakano, M.; Yoneda, K.; Kishi, R.; Takahashi, H.; Kubo, T.; Kamada, K.; Ohta, K.; Botek, E.; Champagne, B. Remarkable Two-Photon Absorption in Open-Shell Singlet Systems. *J. Chem. Phys.* **2009**, *131*, 114316.

(71) Bunge, A. Electronic Wavefunctions for Atoms. III. Partition of Degenerate Spaces and Ground State of C. *J. Chem. Phys.* **1970**, *53*, 20-28.

(72) Luken, W. L. Unlinked Cluster Corrections for Configuration Interaction Calculations. *Chem. Phys. Lett.* **1978**, *58*, 421-424.

(73) Langhoff, S. R.; Davidson, E. R. Configuration Interaction Calculations on Nitrogen Molecule. *Int. J. Quantum Chem.* **1974**, *8*, 61-72.

(74) Hehre, W. J.; Ditchfield, R.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian-Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. *J. Chem. Phys.* **1972**, *56*, 2257-2261.

(75) Yanai, T.; Tew, D. P.; Handy, N. C. A New Hybrid Exchange-Correlation Functional Using the Coulomb-Attenuating Method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, *393*, 51-57.

(76) Cizek, J.; Paldus, J. The Stability Conditions for the Solutions of the Hartree-Fock Equations for Atomic and Molecular Systems. Application to the Pi-Electronic Model of Cyclic Polyenes. *J. Chem. Phys.* **1967**, *47*, 3976-3985.

(77) Bauernschmitt, R.; Ahlrichs, R. Stability Analysis for Solutions of the Closed Shell Kohn-Sham Equation. *J. Chem. Phys.* **1996**, *104*, 9047-9052.

(78) Yamaguchi, K.; Takahara, Y.; Fueno, T.; Houk, K. N. Extended Hartree-Fock (EHF) Theory of Chemical-Reactions. 3. Projected Moller-Plesset (PMP) Perturbation Wavefunctions for Transition Structures of Organic-Reactions. *Theor. Chim. Acta* **1988**, *73*, 337-364.

(79) Dachsel, H.; Lischka, H.; Shepard, R.; Nieplocha, J.; Harrison, R. J. A Massively Parallel Multireference Configuration Interaction Program: The Parallel Columbus Program. *J. Comput. Chem.* **1997**, *18*, 430-448.

(80) Müller, T. Large-Scale Parallel Uncontracted Multireference-Averaged Quadratic Coupled Cluster: The Ground State of the Chromium Dimer Revisited. *J. Phys. Chem. A* **2009**, *113*, 12729-12740.

(81) Szalay, P. G.; Müller, T.; Lischka, H. Excitation Energies and Transition Moments by the Multireference Averaged Quadratic Coupled Cluster (MR-AQCC) Method. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2067-2073.

(82) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision E.01*, Gaussian, Inc.: Wallingford, CT, USA, 2013.

- (83) Schütz, M.; Hetzer, G.; Werner, H. J. Low-Order Scaling Local Electron Correlation Methods. I. Linear Scaling Local MP2. *J. Chem. Phys.* **1999**, *111*, 5691-5705.
- (84) Hampel, C.; Werner, H. J. Local Treatment of Electron Correlation in Coupled Cluster Theory. *J. Chem. Phys.* **1996**, *104*, 6286-6297.
- (85) Schütz, M.; Werner, H. J. Low-Order Scaling Local Electron Correlation Methods. IV. Linear Scaling Local Coupled-Cluster (LCCSD). *J. Chem. Phys.* **2001**, *114*, 661-681.
- (86) Shavitt, I. The Graphical Unitary Group Approach and Its Application to Direct Configuration Interaction Calculations. In *Lecture Notes in Chemistry*, Hinze, J., Ed. Springer: Berlin Heidelberg New York, 1981.
- (87) Lischka, H.; Shepard, R.; Brown, F. B.; Shavitt, I. New Implementation of the Graphical Unitary-Group Approach for Multi-Reference Direct Configuration-Interaction Calculations. *Int. J. Quantum Chem.* **1981**, *S15*, 91-100.
- (88) Roos, B. O.; Siegbahn, P. E. M. In *Methods of Electronic Structure Theory*, Schaefer III, H. F., Ed. Plenum, New York: 1977.
- (89) Davidson, E. R. Iterative Calculation of a Few of Lowest Eigenvalues and Corresponding Eigenvectors of Large Real-Symmetric Matrices. *J. Comput. Phys.* **1975**, *17*, 87-94.
- (90) Shepard, R.; Shavitt, I.; Pitzer, R. M.; Comeau, D. C.; Pepper, M.; Lischka, H.; Szalay, P. G.; Ahlrichs, R.; Brown, F. B.; Zhao, J. G. A Progress Report on the Status of the Columbus MRCI Program System. *Int. J. Quantum Chem.* **1988**, *S22*, 149-165.
- (91) Hosteny, R. P.; Dunning, T. H.; Gilman, R. R.; Pipano, A.; Shavitt, I. Abinitio Study of Pi-Electron States of Trans-Butadiene. *J. Chem. Phys.* **1975**, *62*, 4764-4779.

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