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MCSCF study of polaron- and bipolaron-like defects in small *all-trans* conjugated polyenes*

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Summary. A Multiconfigurational Self-Consistent Field study of neutral, singly and doubly ionized C_4H_6, C_6H_8, C_8H_{10}, and $C_{10}H_{12}$ as model systems for polaron and bipolaron defects in polyacetylene has been carried out. In all computations a double zeta quality basis set was used. The post-Hartree–Fock computations were carried out in the complete active π subspace and the fully optimized structures are reported. Comparison with SCF results reveals that the inclusion of electron correlation attenuates the double bond/single bond alternancy in conjugated polyenes as well as the charge waves associated with the cations.

Key words: *All-trans* conjugated polyenes – Polyenes, *all-trans* conjugated – Polaron- and bipolaron-like defects

1. Introduction

Different chain defects have been proposed in recent years to explain the charge transport mechanism in doped conjugated polymers [1, 2]. These defects are perturbations which affect the regular periodic character of the undoped polymer electronic structure. Two groups of defects are defined depending on their spin, and they can be further subdivided according to their net charge. The first group includes charged solitons [3] and bipolarons [4], which are singly or doubly charged spinless defects, respectively. The second group is made of open shell systems called neutral solitons, for neutral species, or polarons, for charged species [5]. In chemical terminology, neutral solitons correspond to free radicals, while polarons are radical ions. The defects are, in fact, no more than reduced or oxidized forms of the materials and their nature depends on the dopant.

Doped polyacetylene is one of the better characterized conducting polymers, due to its structural simplicity. It has been the subject of numerous studies that encompass a wide range of experimental and theoretical methods, aimed at validating the various mechanistic models proposed for charge transport [6] in conducting polymers. Spinless defects in polyacetylene have been studied at the

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Hartree–Fock level of theory yielding a qualitative understanding of their structural and vibrational properties [7, 8]. Moreover, to accurately describe defects involving unpaired electrons, electronic correlation effects must be taken into account. Indeed, the unrestricted Hartree–Fock (UHF) formalism fails for long open-shell conjugated systems [9, 10] as the UHF wavefunction, through spin contamination, overestimates the correlation effects for stretched double bonds [10]. The overall result of this misrepresentation of the electron correlation is a nonalternant structure where all bonds are equal.

In this communication, we study twelve species: C_4C_6, C_6H_8, C_8H_{10}, and $C_{10}H_{12}$ in their neutral, singly and doubly ionized forms, as model systems for undoped polyacetylene, and of polaron and bipolaron defects as a step towards a more accurate characterization of these defects. Polaron defects are important not only as models to explain charge conduction [11] but they may also contribute to the design of novel conjugated ferromagnetic materials [12]. The present communication is organized as follows: in Sect. 2 we describe the methodology used; in Sect. 3 we describe the structural and electronic properties computed, together with an analysis of the influence of the electronic correlation effects on the description of the structures; finally in Sect. 4 the conclusions are given and their significance in the electron conduction mechanism in PA is discussed.

2. Methods

Ab initio calculations were carried out for C_4H_6, C_6H_8, C_8H_{10}, and $C_{10}H_{12}$, their radical cations and their dications, using a split valence 6-31G basis set [13]. The HONDO [14] package was used throughout this work. The closed-shell systems were studied within the restricted Hartree–Fock (RHF) formalism, while for the open-shell systems under UHF and restricted open-shell Hartree–Fock (ROHF) wavefunctions were used. The geometries were optimized for each ion or molecule and the force constants were calculated to characterize each point as a minimum on the hypersurface [15]. All structures were found to have C_{2h} symmetry.

In addition, electron correlation effects were taken into account using a complete active space (CAS) wavefunction [16] defined by distributing all π electrons of the system among all the π orbitals formally defined in a minimal basis set, in all possible ways consistent with spin and spatial symmetry. The geometries of all species were also fully optimized at this level of theory by analytical calculation of the energy gradients, using the same basis set. However, in this case the C_{2h} symmetry of all molecules and ions was maintained in the computations [17].

Only the ground state was studied for each system, i.e. ${}^1A_g$ for all the closed-shell structures, ${}^2A_u$ for $C_4H_a^{+\cdot}$ and $C_8H_{10}^{+\cdot}$, and ${}^2B_g$ for $C_6H_8^{+\cdot}$ and $C_{10}H_{12}^{+\cdot}$. In addition, the vertical excitations from the $1\,{}^1A_g$ ground state to the lowest lying excited states, $1\,{}^1B_u$ and $2\,{}^1A_g$, were computed for completeness.

3. Structural and electronic properties

Tables 1 to 4 give the optimized geometries for C_4H_6, C_6H_8, C_8H_{10}, and $C_{10}H_{12}$, their radical cations and dications obtained using the π-CAS-MCSCF approach. Carbon atoms were numbered starting at one end, while the hydrogen atoms have the number of the carbon atoms to which they are attached. For $C_{10}H_{12}$ and its ions the RHF, ROHF, and UHF results are also reported. Finally, Table 5 gives the occupation numbers for all systems obtained using the π-CAS-MCSCF representation.

Table 1. Geometrical parameters for C_4H_6, $C_4H_6^{+\cdot}$, and $C_4H_6^{++}$, clusters obtained from a π-CAS-MCSCF with 6-31G basis set (bond lengths are in angstroms, angles in degrees, energies in hartrees)

	C_4H_6	$C_4H_6^{+\cdot}$	$C_4H_6^{++}$
Energies	−154.9246	−154.6179	−154.0900
Distances			
C3 C2	1.463	1.400	1.382
C2 C1	1.349	1.390	1.451
C2 H2	1.076	1.074	1.076
C1 H1	1.075	1.073	1.080
C1 H	1.073	1.071	1.080
Angles			
C3 C2 C1	124.1	122.1	120.8
C3 C2 H2	116.4	119.0	121.7
C2 C1 H1	121.5	121.7	121.8
C2 C1 H	121.9	120.9	120.6

Table 2. Geometrical parameters for C_6H_8, $C_6H_8^{+\cdot}$, and $C_6H_8^{++}$, clusters obtained from a π-CAS-MCSCF with 6-31G basis set (bond lengths are in angstroms, angles in degrees, energies in hartrees)

	C_6H_8	$C_6H_8^{+\cdot}$	$C_6H_8^{++}$
Energies	−231.8147	−231.5348	−231.0796
Distances			
C4 C3	1.356	1.399	1.462
C3 C2	1.459	1.408	1.379
C2 C1	1.350	1.375	1.406
C3 H3	1.077	1.076	1.076
C2 H2	1.077	1.075	1.074
C1 H1	1.075	1.073	1.077
C1 H	1.072	1.071	1.076
Angles			
C4 C3 C2	124.3	123.1	122.2
C3 C2 C1	124.1	122.0	120.4
C4 C3 H3	119.2	118.5	117.6
C3 C2 H2	116.7	118.7	120.7
C2 C1 H1	121.6	121.3	121.8
C2 C1 H	121.8	121.7	120.9

3.1. Neutral system

For all the neutral systems studied, the results obtained using the CAS-MCSCF wavefunctions show a decrease in the single bond/double bond alternancy compared to the RHF results, as it can be seen in Table 4 for $C_{10}H_{12}$. Hence, the difference in bond length between a double and a single bond is now found closer

Table 3. Geometrical parameters for C_8H_{10}, $C_8H_{10}^{+\cdot}$, and $C_8H_{10}^{++}$, clusters obtained from a π-CAS-MCSCF with 6-31G basis set (bond lengths are in angstroms, angles in degrees, energies in hartrees)

	C_8H_{10}	$C_8H_{10}^{+\cdot}$	$C_8H_{10}^{++}$
Energies	−308.7050	−308.4419	−308.0340
Distances			
C5 C4	1.454	1.395	1.369
C4 C3	1.357	1.393	1.445
C3 C2	1.457	1.420	1.387
C2 C1	1.351	1.366	1.386
C4 H4	1.077	1.075	1.075
C4 H4	1.078	1.076	1.077
C2 H2	1.077	1.074	1.073
C1 H1	1.075	1.073	1.075
C1 H	1.073	1.071	1.074
Angles			
C5 C4 C3	124.2	122.6	122.0
C4 C3 C2	124.6	123.3	123.0
C3 C2 C1	124.1	122.7	120.4
C5 C4 H4	116.7	118.7	120.4
C4 C3 H3	119.0	118.5	118.0
C3 C2 H2	126.7	118.0	120.1
C2 C1 H1	121.7	121.1	121.3
C2 C1 H	121.7	121.9	121.8

to experimental values for polyacetylene, where the observed difference is 0.08 Å [18], in very good agreement with the computed values at the MCSCF level for the central unit of $C_{10}H_{12}$. The value for the difference represents a significant improvement over RHF results of 0.12 Å [7]. In contrast, angles are not significantly affected, as it could be expected since the σ subspace of orbitals and electrons is not included in the active space.

A reason for the decrease in alternancy when electron correlation is included can be found in Table 5. Significant effects of electron correlation are seen in the occupation numbers of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively). For all these conjugated alternant hydrocarbons, the LUMO has a node between any two carbon atoms engaged in bonding interactions in the HOMO. Similarly, any two atoms which are engaged in antibonding interaction in the HOMO have a bonding interaction in the LUMO. Occupation of the LUMOs results in an elongation of the double bonds and a shortening of the single bonds when the MCSCF wavefunction is considered.

3.2. Polaron defect

The structural defects associated with the polaron result directly from removing an electron from the HOMO, as noted in Table 5. Since the HOMO has maxima

Table 4. Geometrical parameters for $C_{10}H_{12}$, $C_{10}H_{12}^{+\cdot}$, and $C_{10}H_{12}^{++}$, clusters obtained from a π-CAS-MCSCF (MC), RHF, ROHF and UHF wavefunctions using a 6-31G basis set. (bond lengths are in angstroms, angles in degrees, energies in hartrees). The reported energies are for the MCSCF calculation

	$C_{10}H_{12}$		$C_{10}H_{12}^{+\cdot}$			$C_{10}H_{12}^{++}$	
Energies	−385.5954		−385.3434			−384.9693	
Distances	RHF	MC	ROHF	UHF	MC	RHF	MC
C6 C5	1.337	1.359	1.393	1.392	1.396	1.455	1.447
C5 C4	1.453	1.452	1.398	1.392	1.400	1.349	1.371
C4 C3	1.336	1.357	1.372	1.391	1.386	1.429	1.427
C3 C2	1.459	1.458	1.433	1.416	1.430	1.392	1.397
C2 C1	1.329	1.350	1.338	1.373	1.362	1.366	1.376
C5 H5	1.077	1.078	1.076	1.075	1.076	1.075	1.075
C4 H4	1.077	1.078	1.074	1.075	1.075	1.073	1.074
C3 H3	1.077	1.077	1.076	1.076	1.076	1.077	1.077
C2 H2	1.077	1.077	1.073	1.074	1.075	1.072	1.073
C1 H1	1.075	1.075	1.074	1.074	1.074	1.075	1.074
C1 H	1.072	1.072	1.072	1.073	1.072	1.073	1.073
Angles							
C6 C5 C4	124.3	124.2	122.6	123.0	123.4	122.6	122.8
C5 C4 C3	124.3	124.3	122.9	123.0	122.2	121.3	121.6
C4 C3 C2	124.3	124.1	123.7	123.3	124.2	123.7	123.6
C3 C2 C1	124.5	124.2	122.4	123.2	122.5	124.4	120.4
C6 C5 H5	119.2	118.9	118.6	118.4	118.3	117.0	117.5
C5 C4 H4	116.5	116.8	118.4	118.4	119.0	120.7	120.3
C4 C3 H3	119.3	119.1	118.9	118.5	118.3	117.8	118.0
C3 C2 H2	116.2	116.6	117.5	117.9	118.0	119.8	119.7
C2 C1 H1	121.8	121.7	122.1	121.7	121.7	122.3	121.9
C2 C1 H	121.9	121.8	121.4	121.2	121.4	121.1	121.4

at the double bonds and nodes at the single bonds, the removal of an electron from this orbital results in a disruption of the double bond/single bond alternancy characteristic of the polyenes. The disruption in the bond alternancy is more noticeable for the central units, in accord with the larger HOMO coefficients for the atoms in those units. Nevertheless, bonding alternancy is rapidly recovered towards the end units, since the HOMO coefficients at the terminal atoms are smaller than for the central atoms. Analysis of Table 5 also indicates that the largest contributions from electron correlation are due to changes in the occupation numbers for the frontier orbitals, similar to those found for the closed-shell systems.

When the geometries of the structures of the polarons obtained using the MCSCF wavefunction are compared to those obtained with the UHF and ROHF methods, different problems in the description of the structures can be detected. The UHF approach misrepresents the electron correlation effects as a function of the carbon-carbon distance, which results in the disappearance of the bond alternancy and to the equalization of carbon-carbon bonds everywhere, even for the end units. In contrast, the ROHF provides a qualitatively correct description of the structure of the polaron. However, the ROHF wavefunction

Table 5. Occupation numbers for C_4H_6 to $C_{10}H_{12}$ clusters obtained from a π-CASSCF with 6-31G basis set for the neutral singly and doubly charged species

	C_4H_6	$C_4H_6^{+\cdot}$	$C_4H_6^{++}$	C_6H_8	$C_6H_8^{+\cdot}$	$C_6H_8^{++}$
$1b_g$	1.926	1.918	1.858	1.934	1.936	1.913
$1a_u$	1.869	0.994	0.136	1.907	1.895	1.870
$2b_g$	0.135	0.066	0.004	1.846	0.990	0.133
$2a_u$	0.069	0.022	0.001	0.160	0.097	0.057
$3b_g$				0.091	0.057	0.030
$3a_u$				0.062	0.024	0.015

	C_8H_{10}	$C_8H_{10}^{+\cdot}$	$C_8H_{10}^{++}$	$C_{10}H_{12}$	$C_{10}H_{12}^{+\cdot}$	$C_{10}H_{12}^{++}$
$1b_g$	1.937	1.944	1.930	1.939	1.948	1.937
$1a_u$	1.922	1.918	1.912	1.929	1.930	1.928
$2b_g$	1.890	1.879	1.859	1.910	1.905	1.899
$2a_u$	1.828	0.989	0.146	1.875	1.865	1.850
$3b_g$	0.179	0.117	0.061	1.815	0.987	0.157
$3a_u$	0.110	0.079	0.046	0.193	0.133	0.076
$4b_g$	0.075	0.043	0.023	0.127	0.096	0.055
$4a_u$	0.058	0.031	0.022	0.088	0.058	0.049
$5b_g$				0.067	0.046	0.024
$5a_u$				0.057	0.033	0.023

exaggerates bond alternancy, in a manner similar to the RHF technique for the closed-shell systems. The discrepancies observed for the ROHF wavefunction are no worse than those noted for the MCSCF and the RHF calculations in the closed-shell systems.

In Fig. 1, the net charge per CH unit along the chain for $C_{10}H_{12}^{+\cdot}$ computed using the MCSCF and ROHF wavefunctions is shown, together with the charge wave associated to $C_9H_{11}^{+}$, which is presented for comparison purposes as a model for charged soliton defects [6]. The charge wave for the polaron is

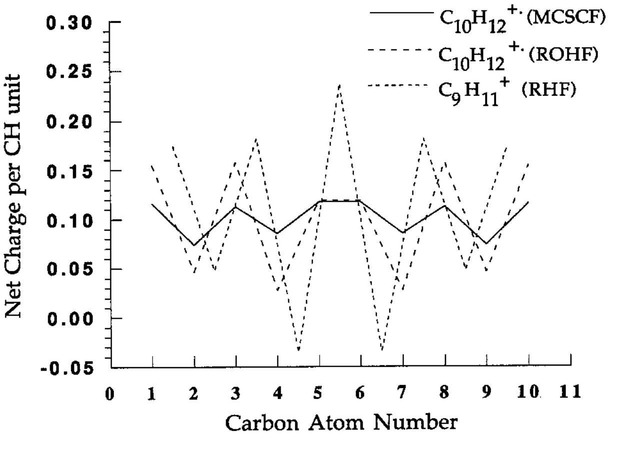

Fig. 1. Comparison of the net charge per CH unit for $C_{10}H_{12}^{+\cdot}$ computed using π-CAS-MCSCF and ROHF wavefunction. The net charge per CH unit for $C_9H_{11}^{+}$ using a RHF wavefunction is also shown [6]. The numeration starts at one end unit and increases towards the other end of the radical ion.
——— $C_{10}H_{12}^{+\cdot}$ (MCSCF);
- - - $C_9H_{11}^{+}$ (RHF);
– – – $C_{10}H_{12}^{+\cdot}$ (ROHF)

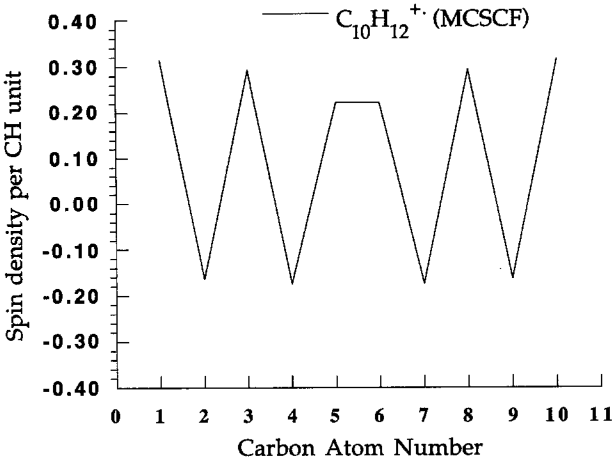

Fig. 2. Net spin density per CH unit computed using a MCSCF wavefunction, as a function of the atom number. The numeration starts at one end unit and increases towards the other end of the system. ——— $C_{10}H_{12}^{+\cdot}$ (MCSCF)

qualitatively similar to that observed for the charged soliton, having a maximum around the central units of the molecule. Quantitatively, the charge wave from the MCSCF wavefunction is less pronounced than from the ROHF or closed-shell wavefunctions of the soliton defects.

The results for the spin wave associated to $C_{10}C_{12}^{+\cdot}$ are shown in Fig. 2. Contrary to the charge wave, which shows a maximum, the spin wave does not significantly attenuate in any part of the system, although spin alternancy along the chain can be noted. The lack of a clear maximum may be due to the relatively small chain length considered in this study, particularly in light of previous results [12] indicating that the polaron defects have large spin polarization clouds and that their maxima are considerably apart from the charged center [12].

3.3. Bipolaron defect

The results for the doubly ionized polyenes parallel our findings for the closed-shell systems, as no qualitative changes are observed when electron correlation effects are included. The structures obtained by geometry optimization at the MCSCF or the RHF [6] levels of theory both show that the central part of the dication is alternant and there are two defects located in the proximity of the terminal bonds. Each of the two defects has a charge wave associated to it. These waves interfere destructively in the central part of the dication creating what has been described as a soliton antisoliton pair. However, the RHF calculations for dications overestimate the degree of alternancy in double and single bonds, as well as the net charges and the amplitude of the charge wave associated with the defect, as can be seen in Fig. 3.

In all cases the inclusion of electron correlation effects is more significant for the larger systems, as can be noted from the changes in occupation number with the chain length. This increase in electron correlation correction with the chain length can be attributed to the denser packing of molecular states in the proximity of the ground state for the longer polyenes.

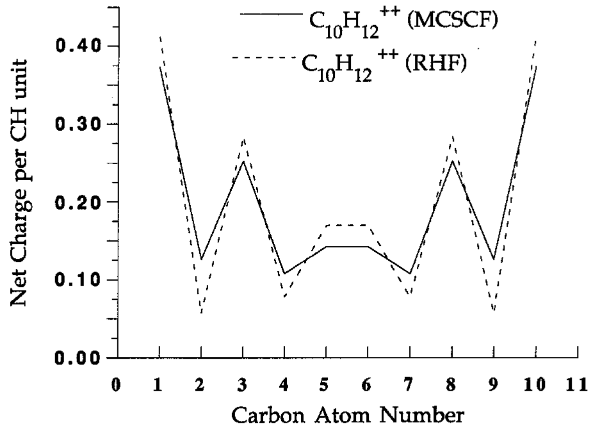

Fig. 3. Comparison of the net charge for $C_{10}H_{12}^{++}$ computed using a π-CAS-MCSCF and RHF wavefunctions [6]. The numeration starts at one end unit and increases towards the other end of the system.
—— $C_{10}H_{12}^{++}$ (MCSCF);
- - - $C_{10}H_{12}^{++}$ (RHF)

For completeness the vertical excitation energies for the neutral species, from the ground state to the 1 ^1B_u and 2 ^1A_g states using the same CAS-MCSCF and basis set described above have also been computed. The values for the transition from the ground state to the 1 ^1B_u state are 9.01, 6.71, 5.99, and 5.39 eV for C_4H_6, C_6H_8, C_8H_{10}, and $C_{10}H_{12}$, respectively, while for the transition from the ground state to the 2 ^1A_g state were 7.05, 5.90, 4.82, and 4.35 eV. These calculated values differ from the experimental results [19, 20] by as much as 3 eV. The discrepancy is to be attributed in part to the limited electron correlation treatment and, probably more importantly, to the inadequacy of the basis set used here for the evaluation of excitation energies, as it is known that these excited states have significant Rydberg character. Thus, Cave and Davidson in a series of studies [21] of the electronic structure of the same polyenes obtained values in closer agreement with experiment using a double zeta basis set augmented with diffuse p_π and d_π functions, even without optimizing the geometry of the ground state.

4. Conclusions

In this communication, the influence of electron correlation on the structural properties of polyenes has been analyzed. We have shown that a reduction in the double bond-single bond degree of alternancy of approximately 15% is observed when the results at the RHF level are compared to the π-CAS-MCSCF result. The degree of alternancy is now in better agreement with experimental data for polyenes. The significance of the improved description lies in considering the conducting properties of doped conjugated systems. Indeed, according to Peierls [22], the bond alternancy is responsible for the band gap observed in polyacetylene. If all carbon-carbon bonds were equal, polyacetylene would have metallic properties. Hence, a correct description of the alternancy is a key requirement in obtaining a reliable description of properties related to conductivity. Nonetheless, the geometries obtained without inclusion of electron correlation effects are appropriate for most purposes.

Finally, UHF wavefunctions cannot be used for open-shell polyenes, since they yield qualitatively incorrect structures. This finding supports earlier results for neutral open-shell polyacetylene, where the UHF formalism yields approximately equal bonds [6, 7, 9]. In the present work, we showed that UHF wavefunctions are also inadequate to describe open-shell conjugated polymers. The ROHF formalism provides a qualitatively satisfactory description of the polaron defect. Electron correlation brings only small changes to the ROHF results.

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