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Polarizability and second hyperpolarizability of open-shell π-conjugated compounds from spin projection method calculations

Benoît Champagne [a,*], Edith Botek [a], Olivier Quinet [a], Masayoshi Nakano [b], Ryohei Kishi [b], Tomoshige Nitta [b], Kizashi Yamaguchi [c]

[a] *Laboratoire de Chimie Théorique Appliquée, Facultés Universitaires Notre-Dame de la Paix, rue de Bruxelles, 61, 5000 Namur, Belgium*
[b] *Division of Chemical Engineering, Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan*
[c] *Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan*

Abstract

The Löwdin spin projection technique has been applied to the calculation of the polarizability (α) and second hyperpolarizability (γ) of polyacetylene (PA) chains bearing neutral soliton or charged polaron defects. For both types of systems, α and γ smoothly evolve when successive spin contaminations are removed and converge towards a non-spin-contaminated value. Comparisons between the α and γ of these open-shell systems and their corresponding closed-shell analogs, i.e. regular PA chains and PA chains bearing a positively charged soliton, demonstrate the dual role of spin pairing and charge on the linear and non-linear responses of π-conjugated systems.
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1. Introduction

A multidisciplinary approach has been developed over the last decades in view of developing very fast optical devices for the treatment and transport of information. Such approach encompasses the design of new non-linear optical (NLO) materials from a mixed theoretical–experimental point of view [1]. Up to now, almost all investigations have focused on closed-shell systems – and in particular π-conjugated systems with different substituents – and have addressed the structure–property relationships between, on the one hand, the microscopic or macroscopic NLO responses and, on the other hand, structural and electronic parameters like the nature and length of the π-segment, the nature and position of the donor/acceptor substituents [2–4],

the presence of charge defects [5,6], as well as the dimensionality and shape of the chromophores [7,8]. In addition, theoretical investigations have dealt with both the electronic and the vibrational NLO responses [9], the NLO responses of isolated molecules, molecules in solution [10], as well as molecular crystals [11]. For small systems quantum chemistry methods can estimate the hyperpolarizability values with equal or better accuracy than the experimental techniques [12,13]. On the other hand, for systems of interest in NLO, because of the substantial computational needs, semi-quantitative accuracy can only be reached but this is often sufficient for deducing structure–property relationships.

Quite recently, the design of NLO materials has focused on open-shell systems because of the possibility of fabricating multi-functional compounds. Indeed, upon switching the spin state by suitable application of an external magnetic field, the molecular properties are expected to change. Although fewer than for

* Corresponding author. Fax: +32 81 724567.
E-mail address: benoit.champagne@fundp.ac.be (B. Champagne).

closed-shell systems, experimental and theoretical works addressing the NLO properties of open-shell systems have appeared in the literature. A pioneering study on open-shell NLO systems was reported by Nakano et al. [14], who investigated theoretically the γ values of ionic radical states of π-conjugated condensed-ring systems with the aim of designing unique NLO compounds presenting negative γ values. Subsequent experimental investigations [15–17] mainly tackled compounds containing one or more transition metal atoms while several theoretical investigations were carried out on small systems with a hierarchy of quantum chemical methods [18,19]. During the last decades, some of us have studied the hyperpolarizabilities of medium-size open-shell systems including nitronyl nitroxide radical [20] and tetrathiapentalene [21]. More recently, in relation with the doping enhancement of the molecular hyperpolarizabilities [5,6], our groups have begun an investigation of the linear and non-linear responses of model polyene chains bearing a radical or a cation radical with the aim of providing an understanding of the underlying phenomena as well as accurate data for validating simplified approaches that could be used to study larger systems [22,23]. Although NLO experimental characterizations have not yet been reported for such compounds, some of these were synthesized while their UV/vis absorption spectra recorded [24]. These investigations reported on the effects of spin multiplicity upon the second hyperpolarizability, on the spatial description of the non-linear polarization, on the effects of electron correlation and atomic basis set upon the estimated linear and non-linear responses, as well as on the effect of the charge [22,23].

Two aspects are addressed in this Letter. The polarizability and second hyperpolarizability of small neutral or charged open-shell π-conjugated polyacetylene (PA) chains are evaluated and compared to those of the corresponding closed-shell systems. This is achieved by using, for the open-shell systems, the spin projection technique of Löwdin [25], which therefore corresponds to an extension to the previous study [26] adopting an approximate spin projection technique. Since this is the first application of this method to determining the (hyper)polarizabilities, the first part of the Letter addresses its performance with respect to more elaborated schemes.

2. Methodology and computational procedure

2.1. Structures

Fig. 1 displays the geometrical structures of the C_5H_7 and C_9H_{11} radicals and of the C_6H_8 and $C_{10}H_{12}$ radical cations in their doublet ground state, which have been optimized at the UB3LYP level of approximation using the 6-311G* basis set. For C_5H_7 and C_6H_8, the geometries are characterized by bond length alternations (BLA) of 0.050 and 0.026 Å whereas the expectation values of $\langle S^2 \rangle$ amount to 0.795 and 0.779, respectively. For validation purpose, the C_5H_7 geometry was also optimized at the UQCISD/6-311G* level. The external and internal CC bond lengths attain 1.367 and 1.422 Å, i.e. they differ from the B3LYP data by 0.01 Å or less. For C_9H_{11} and $C_{10}H_{12}$, the corresponding BLA amount to 0.052 and 0.030 Å while the expectation values of $\langle S^2 \rangle$ to 0.822 and 0.792, respectively. The neutral and
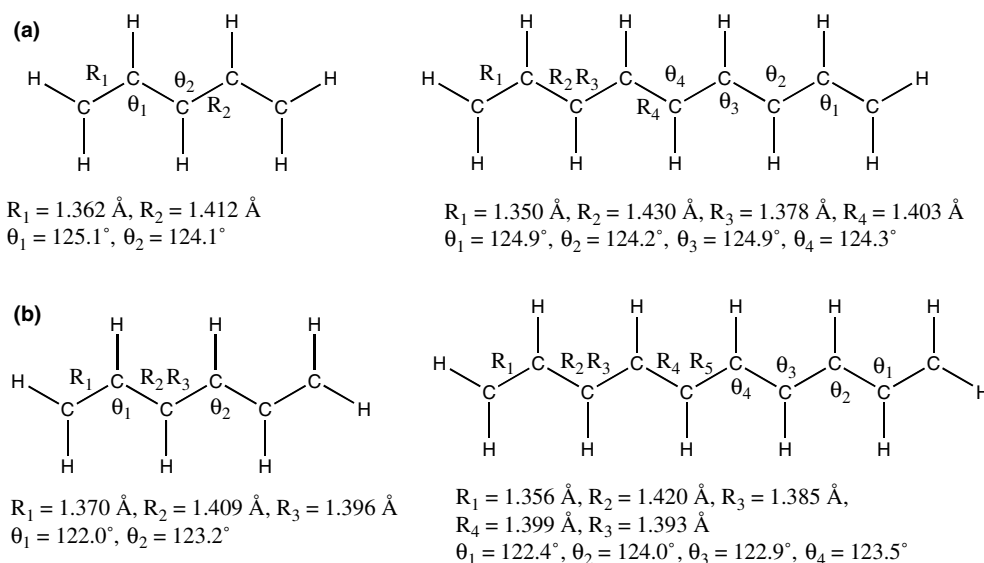

$R_1 = 1.362$ Å, $R_2 = 1.412$ Å
$\theta_1 = 125.1°$, $\theta_2 = 124.1°$

$R_1 = 1.350$ Å, $R_2 = 1.430$ Å, $R_3 = 1.378$ Å, $R_4 = 1.403$ Å
$\theta_1 = 124.9°$, $\theta_2 = 124.2°$, $\theta_3 = 124.9°$, $\theta_4 = 124.3°$

$R_1 = 1.370$ Å, $R_2 = 1.409$ Å, $R_3 = 1.396$ Å
$\theta_1 = 122.0°$, $\theta_2 = 123.2°$

$R_1 = 1.356$ Å, $R_2 = 1.420$ Å, $R_3 = 1.385$ Å,
$R_4 = 1.399$ Å, $R_3 = 1.393$ Å
$\theta_1 = 122.4°$, $\theta_2 = 124.0°$, $\theta_3 = 122.9°$, $\theta_4 = 123.5°$

Fig. 1. Molecular geometries of the C_5H_7 and C_9H_{11} radicals (a) and of the C_6H_8 and $C_{10}H_{12}$ radical cations (b). The corresponding structures are planar and belong to C_{2v} and C_{2h} point groups, respectively.

charged open-shell systems represent small PA chains bearing a neutral soliton and positively charged polaron defects, respectively. From comparison with the geometry of the corresponding neutral closed-shell systems, the regular polyacetylene chains, the neutral soliton defect is estimated to extend over at least seven carbon atoms whereas the spread of the charged polaron defect is larger. Further assessment of the defect width would however require considering longer chain.

The geometry of the C_6H_8 and $C_{10}H_{12}$ neutral closed-shell PA chains as well as of the charged C_5H_7 and C_9H_{11} compounds mimicking charged solitons was optimized at the MP2/6-311G* level of approximation. The BLA amounts to 0.104 and 0.090 (0.032 and 0.040) Å for the neutral (charged) compounds.

2.2. Polarizabilities and hyperpolarizabilities

The static electronic longitudinal polarizability $[\alpha_L^e(0;0) = \alpha]$ and second hyperpolarizability $[\gamma_L^e(0;0, 0,0) = \gamma]$ have been evaluated using the finite field (FF) approach. In comparison to the other tensor elements, longitudinal components focus most of the interest due to their largest amplitudes and the possibility of enhancing them by π-electron delocalization. The FF approach consists in evaluating the system energy for different amplitudes of the applied external electric field and, subsequently, in differentiating it numerically. In this study, field amplitudes of 0.0, 0.0010, 0.0020, 0.0040 and 0.0080 a.u. are used together with Romberg quadrature in order to reach an accuracy on $\alpha(\gamma)$ of 0.1 (100) a.u. or better. The power series expansion convention (usually called B convention) is chosen for defining γ. More details about the FF procedure can be found in [22]. The calculations are performed by using the Dunning's correlation consistent basis sets with or without diffuse functions [27–29]. Following the basis set investigation of [23], the cc-pvdz basis set is selected for the radical cation whereas for the neutral radical, the basis set is built from the aug-cc-pvdz basis set from which the *s* and *p* diffuse functions on the H atoms as well as the *s* and *d* diffuse functions on the C atoms are removed. Similarly, in the case of the closed-shell compounds, the cc-pvdz basis set is used to determine the linear and non-linear responses of the charged compounds whereas for the regular PA chains, the modified aug-cc-pvdz basis set (obtained by removing the *s* and *p* diffuse functions on the H atoms as well as the *s* and *d* diffuse functions on the C atoms) is chosen. For both types of closed-shell systems, additional calculations not presented here have verified that these basis sets are sufficiently flexible to reproduce the (hyper)polarization phenomena. 6D and 10F Cartesian functions are used.

In the case of the closed-shell systems, the calculations are carried out at the Møller–Plesset (MP) second-order level of approximation, which has been shown to account for most of the electron correlation ef-

fects [30]. For the open shell systems, in addition to reference calculations which are performed using the UHF-based CCSD(T) scheme, i.e., the UHF-coupled-cluster methods with single and double excitations as well as with a perturbative treatment of the triple excitations [UCCSD(T)], the *l*-fold spin-projection scheme due to Löwdin [25] is employed. It consists of removing the successive spin contamination contributions by adopting the UHF method as well as the UHF-based MP perturbation theory schemes limited to fourth order in electron–electron interactions. At the UHF level, $l = 6$ spin projections (up to $S = 13/2$) are carried out exactly whereas at the MPn levels they are done in an approximate way described by Schlegel [31] up to $l = 4$ ($S = 9/2$). All calculations are performed using the GAUSSIAN-03 program [32].

3. Results and discussion

3.1. Spin projection versus UCCSD(T) schemes for small open-shell systems

The evolution of the polarizability and second hyperpolarizability values with the order of the spin projection scheme is sketched in Fig. 2 for the C_5H_7 radical at different levels of electron correlation and in comparison with the reference UCCSD(T) value. Fig. 3 is the analogous of Fig. 2 for the C_6H_8 radical cation. No matter which molecule or which level of approximation, both the polarizability and the second hyperpolarizability converge rapidly with the successive spin contamination removals. Indeed, the first correction is important (its extends from −70% for the MP3 γ value of C_6H_8 to +97% for the HF γ value of C_6H_8), the second contribution is already smaller by one order of magnitude (from −17% for the HF γ value of C_5H_7 to +9% for the HF α value of C_5H_7) and the next corrections are much smaller if not negligible. Thus, most of the spin contamination comes from quartet and sextet determinants. At least for the first dominant contamination, the correction on γ is much larger than the correction on α.

For the neutral compound, including electron correlation effects results in an increase of α while the removal of spin contamination by the spin projection technique leads to a decrease of α. The opposite behavior is obtained for the radical cation. After correcting for spin contaminations, the evolution of α with the inclusion of successive electron correlation corrections tends towards the UCCSD(T) reference value. Indeed, for C_5H_7, the UMP2 and UMP4 α values are 14.0% and 10.0% larger than the UCCSD(T) values whereas accounting for spin contamination at least up to order $l = 2$, these overestimations reduce to 4.2% and 1.6%, respectively. For the radical cation, the UMP2 and
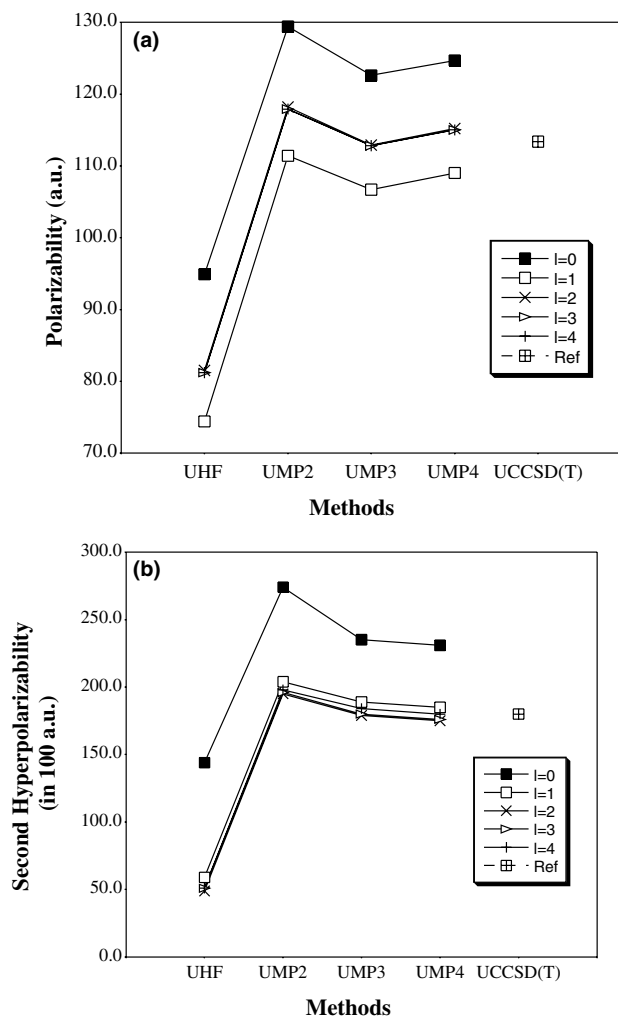
Fig. 2. Evolution with the order of the spin projection scheme of the polarizability (a) and second hyperpolarizability (b) of the C_5H_7 radical at different orders of the Møller–Plesset (MP) treatment. The corresponding UCCSD(T) values are also included.
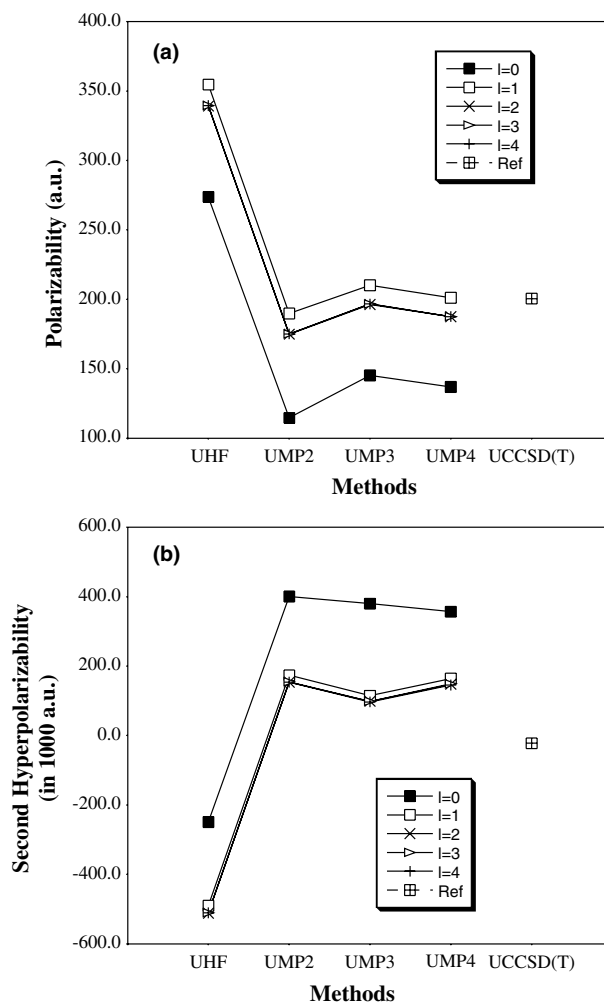

Fig. 3. Evolution with the order of the spin projection scheme of the polarizability (a) and second hyperpolarizability (b) of the C_6H_8 radical cation at different orders of the MP treatment. The corresponding UCCSD(T) values are also included.

UMP4 methods underestimate the α values with respect to UCCSD(T) by 42.8% and 31.8% whereas using spin projection with $l \geqslant 2$, the underestimations go down to 12.8% and 6.5%, respectively.

For γ, the situation is partly different. On the one hand, the behavior of the γ value of C_5H_7 as a function of both the order of the spin projection and the order of the electron correlation treatment with respect to the reference UCCSD(T) result are qualitatively similar to the case of the linear response, though, the electron correlation effects are much larger. At second order, this leads to an increase of γ by about 300% ($l \geqslant 1$). Further inclusions up to third- and fourth-orders have however a much negligible impact. On the other hand, for γ of C_6H_8, the successive inclusions of electron correlation do not lead to a rapid convergence, even when spin contamination is removed. Indeed, for $l = 2$, going from HF to MP2, MP3, and MP4, the γ value increases by 130%,

decreases by 36%, and then increases again by 49%. Moreover, the PUMP4 values differ substantially from the reference UCCSD(T) result (-22×10^3 a.u.).

3.2. Chain length dependence and comparison with closed-shell polyacetylene chains

In a second step, the chain length dependence of the linear and non-linear response properties has been assessed for short chains. Calculations at the PUHF and PUMPn ($4 \geqslant n \geqslant 2$) levels ($l \leqslant 6$) have been performed for the C_9H_{11} radical and $C_{10}H_{12}$ radical cation. Like for the shortest systems, the linear and non-linear responses of both compounds converge nicely with the order of the spin projection. For all compounds and levels of electron correlation, the variations in α and γ between $l = 3$ and 4 are negligible whereas between $l = 2$ and 3, the variations can be as large as 10%.

For C_9H_{11}, the PUHF, PUMP2, PUMP3, and PUMP4 α values ($l = 3$) amount to 164.3, 299.2, 271.8, and 285.7 a.u., respectively while the ROMP2 value attains 350.7 a.u. Since UCCSD(T) calculations on C_9H_{11} require excessive computational needs, the comparison is made with respect to the ROMP2 method, of which the α and γ estimates for C_5H_7 are in close agreement with the UCCSD(T) values [22,23]. The corresponding γ values for C_9H_{11} are -1×10^3, 208×10^3, 164×10^3 and $179 \, 10^3$ a.u. whereas the ROMP2 value is 190×10^3 a.u. Thus, the passage from C_5H_7 to C_9H_{11} is accompanied by increases of α and γ by factors of 2.5 and 10, respectively [PUMP4 ($l = 3$)]. For comparison, the α values of *all-trans* hexatriene and *all-trans* decapentaene, evaluated at the MP2 level using the modified aug-cc-pvdz basis set amount to 144 and 345 a.u., respectively, showing an exaltation of α by a factor of 2.4. Their γ values attain 321×10^2 and 306×10^3 a.u., respectively, also displaying an increase by one order of magnitude when the system grows by two CH=CH units.

For the $C_{10}H_{12}$ radical cation, the PUHF, PUMP2, PUMP3, and PUMP4 α values ($l = 3$) amount to 1614, 223.7, 487.3, and 389.4 a.u. while the UCCSD(T) result is larger and reach 549.0 a.u. The corresponding γ values, listed in the same order, are -529×10^5, 434×10^5, 265×10^5, and 342×10^5 while the UCCSD(T) value is 206×10^5 a.u. Thus, the performance of the spin projection schemes improves for $C_{10}H_{12}$ with respect to C_6H_8. Looking at the chain length dependence, upon going from C_6H_8 to $C_{10}H_{12}$, the polarizability increases by 106% whereas the second hyperpolarizability increases by more than two orders of magnitude [PUMP4, $l = 3$ results]. For comparison, the α values of PA chains bearing a positive soliton defect, C_5H_7 and C_9H_{11}, evaluated at the MP2/cc-pvdz level of approximation are 131.5 and 447.6 a.u., exhibiting an increase by 240% upon adding two CH=CH units. The corresponding γ values amount to -99×10^2 and -170×10^2 a.u.

Fig. 4 compares the linear and non-linear responses of neutral and charged, open- and closed-shell, small π-conjugated systems and provides an indication of the charge and spin pairing effects on the (hyper)polarizability of small π-conjugated systems. To draw Fig. 4, PUMP4 ($l = 3$) values are used for the open-shell systems whereas the responses of the closed-shell systems are obtained at the MP2 level. The neutral closed- and open-shell systems present similar α values whereas for the charged species, the closed-shell systems are shown to exhibit a larger polarizability. Using the coupled Hartree–Fock (CHF) scheme with a Pariser–Parr–Pople (PPP) Hamiltonian, de Melo and Silbey [33] also found that the neutral open-shell and closed-shell systems present similar linear responses. Moreover, in agreement with the present study, [34] already pointed out that charged solitons display larger polarizability than neutral solitons. On the other hand, [33] pointed out
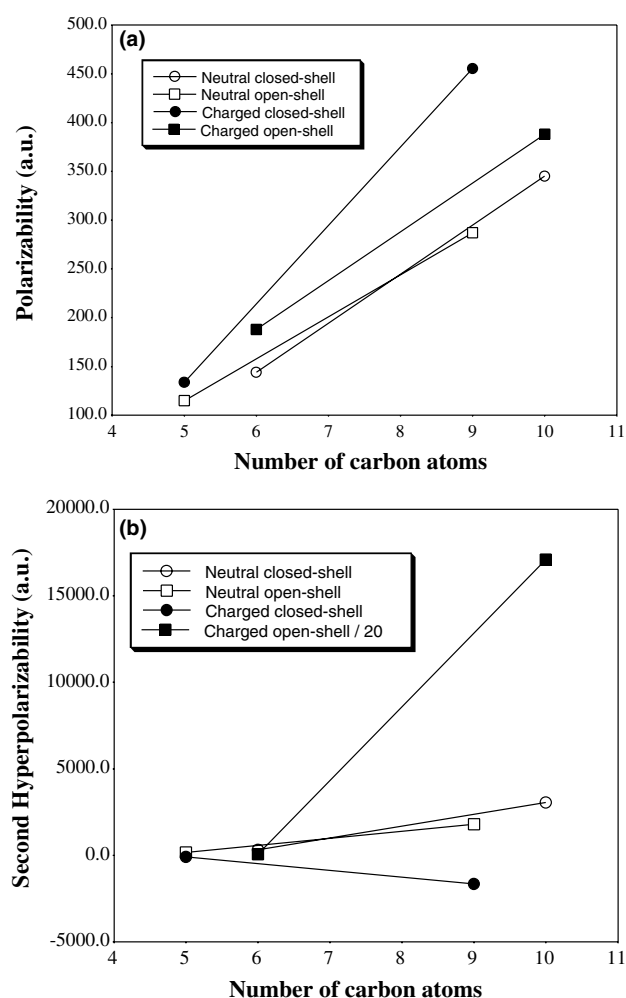

Fig. 4. Polarizability (a) and second hyperpolarizability (b) of neutral and charged, closed- and open-shell, π-conjugated systems. The open-shell results have been evaluated at the PUMP4 ($l = 3$) level whereas the MP2 scheme has been employed for the closed-shell systems (see the text for more details). The lines between the points are guide for the eyes.

that charged polarons (charged open-shell systems) present larger polarizability than the charged solitons whereas the opposite is predicted from our ab initio data on small PA chains. This can be attributed to missing electron correlation effects in the CHF/PPP treatment, which reduce the polarizability of charged polarons (Fig. 3). For both closed- and open-shell species, the charged systems present larger polarizability values than their neutral analog. This is typically attributed to an increase of electron delocalization associated with smaller BLA. Although, as described in Section 2.1, the BLA is reduced by about a factor of two when going from the neutral to the charged systems, the variation of BLA is not sufficient to explain the change in α among the neutral or the charged systems. Indeed, spin pairing effects appear to modulate substantially the BLA impact on α as can be seen from Fig. 4.

Differences between the species are larger in the case of γ. The regular PA chains and those bearing a neutral soliton defect present γ values of similar order of magnitude whereas, when increasing chain length by two CH=CH units, γ becomes much larger in the charged polarons than in the charged solitons. More precisely, when chain length increases, the regular PA chains appear to display a larger γ value than the chain bearing a neutral soliton. This is different from the results of de Melo and Silbey [35] using a PPP Hamiltonian. This inversion can be related to the overestimation of γ of the neutral soliton due to spin contaminations. Finally, in agreement with [34], short PA chains bearing a positively charged polaron defect display substantial γ values. Nevertheless, in these semi-empirical studies, like in the UHF calculations reported in Fig. 3, the γ values are negative whereas the ab initio spin-projected values are positive.

4. Conclusions and outlook

The Löwdin spin projection technique has been applied for the first time to the calculation of the polarizability (α) and second hyperpolarizability (γ) of PA chains bearing neutral soliton or charged polaron defects. For both neutral and positively charged PA chains, the linear and non-linear responses smoothly evolve when successive spin contaminations are removed. In the case of the neutral systems, provided spin contaminations are removed, when including successive electron correlation using the PUMP2, PUMP3, and PUMP4 schemes, the α and γ values nicely converge towards the reference UCCSD(T) results. A similar behavior is noticed for α in charged open-shell species but not for their corresponding γ where the correlated spin-projected results overestimate the reference values. Nevertheless, for these systems, this overestimation decreases when increasing chain length, and the electron correlation effects are substantial, pointing out the interest of adopting multireference methods.

Comparisons between the linear and non-linear responses of these open-shell systems and those of their corresponding closed-shell analogs, i.e. regular PA chains and PA chains bearing a positively charged soliton, have further demonstrated the dual role of spin pairing and charge on the linear and non-linear responses of π-conjugated systems. In the case of short PA chains, for α, the main enhancing effect comes from charging the system whereas for γ, both the charge and the spin pairing effects have substantial impact. Further investigations of the relative impact on α and γ of neutral versus charged defects in PA chains will include the counterion effects [6] and consider longer chains.

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