

## Simultaneous presence of two charges or two spins in a linear polyene

Multi-electron populations in octatetraene from a PPP+(quasi-total) C.I. wave function

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**Summary.** In this work we examine the ease of finding simultaneously two charges or two spins in various AO positions of a linear neutral polyene such as octatetraene. By applying the general multi-electron population analysis on a correlated wave function we calculate contributions from various ionic and covalent (in a probabilistic sense) resonance structures as well as electron-pair distributions with parallel and anti-parallel spins; the initial wave function used is a PPP+(quasi-total) CI wave function. Based on the second and fourth order anticommutation relations (and independently of the level of the MO wave function used) we show existing relationships between the quantities considered, as well as their constant behaviour. Covalent structures depend strongly on the parity and distance between the AO positions, while ionic ones are *quasi-constant* along the polyene. It is also shown that when the AO positions considered are non-vicinal, (+) and (–) charges appear *mutually independent* and the  $\pi$ -electron conjugation has, rather surprisingly, no effect on them.

**Key words:** Linear polyene – Population analysis – Density operators

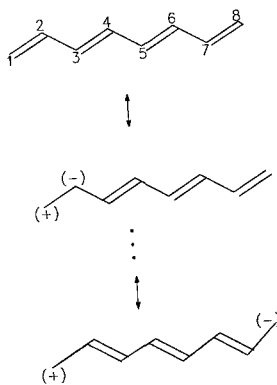
### 1 Introduction

The well-known investigation of the one-electron density matrices provides the probability of finding one electron in an Atomic Orbital (AO). Likewise multi-electron density matrices provide the probability of *simultaneously* finding two or more electrons and/or holes in some AOs; such an investigation leads to a multi-electron population analysis [1–3] which has the general purpose of examining various types of cooperative electronic events, including the simultaneous presence of two charges or two spins in some target AOs of a molecular system.

One of the purposes of the present work is to examine the ease of finding simultaneously (+) and (–) charges as a function of their distance inside of a long linear polyene. Since  $\pi$ -electrons of a polyenic system are considered as “delocalized” or “mobile” electrons (in comparison with  $\sigma$ -electrons), it is also interesting to investigate the effect of  $\pi$ -conjugation in the correlation of the two charges,

and examine how the parity (even or odd) of the AO positions (where the two charges are assumed to be located) affects their mutual dependence. The interest for the study of  $\pi$ -conjugated systems has been recently stimulated by the fact that a wide range of molecular devices destined for Molecular Electronics [4], as for example molecular wires [5], involve as principal element of their structure long (but not infinite)  $\pi$ -systems; in the present work as model  $\pi$ -system for our investigations we choose the all trans octatetraene.

Suppose, for instance, we have a positive charge at one end of the polyene; the associated negative charge, in the globally neutral system, can be transmitted through the  $\pi$ -bonds of the polyene by means of the resonance structures presented in scheme 1. The contributions of such structures are calculated [2, 3] as probabilities of finding negative charges at positions 2, ..., 8 (that is, electron-pairs in the corresponding  $p_z$  AOs,  $\varphi_2, \dots, \varphi_8$ ) when *simultaneously* a positive charge is present at position 1 (that is two electron-holes in  $p_z$  AO,  $\varphi_1$ ), while the remaining electrons of the system can reside elsewhere. The calculation of such probabilities require going beyond the two-electron density matrices [6, 7] and introducing the required restrictions [2] in the usual two-electron density operators.



Scheme 1

Apart from the presence of two charges, the simultaneous presence of two electron-spins,  $(\alpha, \alpha)$  or  $(\alpha, \beta)$ , in a polyene is also of interest. Such a type of two-electron  $(\alpha, \beta)$  spin-correlation analysis, performed from totally covalent Valence-Bond (VB) wave functions, allowed Malrieu et al. to “look at Chemistry as spin-ordering problem” [7]. Furthermore, the knowledge of two-electron cooperative effects can help us in understanding the mechanism of the through-bond interaction of two radical centres [8], and in general the (anti)-ferromagnetism of non-classical polymers [9] or other planar polyenes [10–12]; two-electron correlation structures calculated from PPP+CI wave functions allowed other authors [13] to measure the degree of ionicity and/or covalence of numerous low-lying excited states of polyenes.

## 2 Method

The contributions from the various resonance structures involving two charges or spins are calculated by means of a methodology [1–3] with two steps: in the first we decompose [14] usual Molecular Orbital (MO) wave functions in totally local ones

using Moffitt's theorem [15], and then we calculate expectation values of multi-electron density operators [2, 3].

In this methodology there is no restriction on the initial MO wave function, but in the present work a PPP + (quasi) total CI wave function will be used as starting material. PPP wave functions have been also used frequently by other authors [11, 13, 16] for the study of  $\pi$ -systems in cases where an extensive CI is presumed to be necessary or when the  $\pi$ -systems are very large.

The adopted parameterization for the SCF part is the standard one presented in basic textbooks [17]. The CI space is selected by using the mixed variational-perturbational process of the CIPSI method [18]: the reference space of MO-Slater determinants is iteratively increased until no variation in the ground state energy, smaller than a threshold, is observed; the final CI eigenfunction is then obtained by diagonalisation of the final multireference space increased by those MO determinants which are selected by perturbations. Since the threshold on the last iteration is chosen very low ( $10^{-5}$  a.u.) our CI can be considered as (quasi) total. An idealised geometry for octatetraene is adopted: 1.46 Å for simple bonds, 1.34 Å for double bonds, and  $120^\circ$  for all the angles. The relationships found between the quantities considered and their constant behaviour are based on the second and fourth order anticommutation relations [2, 3a] which, of course, are independent of the parameterization of the SCF part.

### 3 Results and discussion

#### 3.1 Simultaneous presence of two charges or spins of a different type: (+, -) or ( $\alpha$ , $\beta$ )

In this section we present the results concerning contributions from resonance structures involving two charges or spins of a different type: (+, -) or ( $\alpha$ ,  $\beta$ ).

First, the charges or spins have been considered located in AO positions,  $\varphi_1$  and  $\varphi_t$  (with  $t = 2, 3, \dots, 8$ ); the following quantities are then calculated:

–  $P_{2;2}(\varphi_t\varphi_{\bar{t}}; \varphi_1\varphi_{\bar{1}})$ : expectation values of the density operators

$$\varphi_t^+ \varphi_{\bar{t}}^+ \varphi_1 \varphi_{\bar{1}} \varphi_1^+ \varphi_{\bar{1}}^+ \varphi_t \varphi_{\bar{t}},$$

which measure contributions from the *ionic resonance structures* [2, 3a] involving a positive charge in AO,  $\varphi_1$ , and a negative in  $\varphi_t$  (see Introduction); they are noted as [(+), (-)].

–  $P_{2;0}(\varphi_1\varphi_{\bar{t}};)$ : expectation values of the density operators

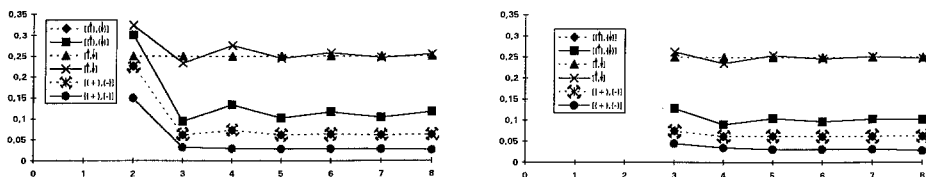
$$\varphi_1^+ \varphi_{\bar{t}}^+ \varphi_{\bar{t}} \varphi_1,$$

which provides probabilities of finding one electron with  $\alpha$ -spin in AO  $\varphi_1$ , and simultaneously another with  $\beta$ - in  $\varphi_t$  (without any further restriction); this is the *electron-pair* ( $\alpha$ ,  $\beta$ ) *distribution* in AO space, and is noted as [ $\uparrow$ ,  $\downarrow$ ].

–  $P_{2;2}(\varphi_1\varphi_{\bar{t}}; \varphi_{\bar{1}}\varphi_t)$ : expectation values of the density operators

$$\varphi_1^+ \varphi_{\bar{t}}^+ \varphi_{\bar{1}} \varphi_t \varphi_{\bar{1}}^+ \varphi_t^+ \varphi_{\bar{t}} \varphi_1,$$

which provide the same probabilities as  $P_{2;0}(\varphi_1\varphi_{\bar{t}};)$  by imposing the supplementary restrictions that Atomic Spin Orbitals – ASOs –  $\varphi_t$  and  $\varphi_{\bar{1}}$  be simultaneously unoccupied; these probabilities can be considered as the contributions of the



**Fig. 1.** Contributions (in ordinate) of resonance structures with two spins or charges of a different type,  $[(\uparrow), (\downarrow)]$  or  $[(+), (-)]$ , and electron-pair distributions  $[\uparrow, \downarrow]$ , for the couples of AO positions  $\varphi_1, \varphi_t$ , where  $t = 2, 3, \dots, 8$  (in abscissa). Broken lines refer to results obtained from the decomposition of the HF wave function and full ones from HF+CI

**Fig. 2.** Contributions (in ordinate) of resonance structures with two spins or charges of a different type,  $[(\uparrow), (\downarrow)]$  or  $[(+), (-)]$ , and electron-pair distributions  $[\uparrow, \downarrow]$ , for the couples of AO positions  $\varphi_2, \varphi_t$ , where  $t = 3, 4, \dots, 8$  (in abscissa). Broken lines refer to results obtained from the decomposition of the HF wave function and full ones from HF+CI

covalent ( $\alpha, \beta$ ) structures [2, 3a] and are symbolised as  $[(\uparrow), (\downarrow)]$ . The term “covalent structure” is adopted in order to emphasise the different ( $\alpha, \beta$  spin-alternant) nature of such probabilities with respect to the ionic ones, and must not be confused with the same term used in V.B. wave functions: in V.B. language this term is associated to a wave function (or its weight) of the type  $1/\sqrt{2}[\|\dots\varphi_i\varphi_{\bar{j}}\dots\| + \|\dots\varphi_j\varphi_{\bar{i}}\dots\|]$ , which is a spin-eigenfunction, and not to a probability. In this work the term, “covalent structure” will be exclusively used in a probabilistic ( $\alpha, \beta$  spin-alternant) sense.

Our calculations have been performed for both the uncorrelated MO wave function (single determinant HF wave function) and the correlated one. The results are presented in Fig. 1.

The contribution from an ionic structure,  $[(+), (-)]$ , has a non-negligible value of 0.15 only when the negative charge is located at the AO  $\varphi_2$  with the two charges in  $\alpha$ -position. When the negative charge is located elsewhere the contribution from  $[(+), (-)]$  reduces drastically to a mean value of ca. 0.029; it is worth noticing that:

- (i) the value of 0.029 is achieved even for  $t = 3$ , that is for  $\beta$ -position of the charges, and
- (ii) this value is *quasi-constant* for all the AO positions ( $t \geq 3$ ) where the negative charge is located, that is it is independent from the relative distance of the positive and negative charges.

The values of the electron-pair distributions,  $[\uparrow, \downarrow]$ , and the contributions of the covalent structures  $[(\uparrow), (\downarrow)]$ , are very close ( $\approx 0.32$  and  $\approx 0.30$  respectively) only when the two electrons are located in the vicinal AO positions  $\varphi_1$  and  $\varphi_2$ . This can be rationalised as follows: based on the second order anticommutation relation one can write out the relationship between the multi-electron density operators considered [4], or their expectation values:

$$P_{2,0}(\varphi_1\varphi_{\bar{i}}) - P_{2,2}(\varphi_1\varphi_{\bar{i}}; \varphi_{\bar{1}}\varphi_i) = P_{4,0}(\varphi_1\varphi_{\bar{1}}\varphi_{\bar{i}}\varphi_i) + P_{3,1}(\varphi_1\varphi_{\bar{1}}\varphi_{\bar{i}}; \varphi_i) + P_{3,1}(\varphi_1\varphi_i\varphi_{\bar{i}}; \varphi_{\bar{1}}) \quad (1a)$$

or

$$[\uparrow, \downarrow] - [(\uparrow), (\downarrow)] = [\uparrow\downarrow, \uparrow\downarrow] + [\uparrow\downarrow, (\downarrow)] + [(\uparrow), \uparrow\downarrow]. \quad (1b)$$

Since the right-hand side of the above relation involves four- or three-electron ionic structures, these structures are very unfavourable when  $t=2$ , that is for vicinal AO positions, in which case a formal double bond exists between them; their contributions is, therefore, near zero explaining the very close value of  $[\uparrow, \downarrow]$  and  $[(\uparrow), (\downarrow)]$  for  $\varphi_1$  and  $\varphi_2$ .

For other target couples of AO positions,  $\varphi_1$  and  $\varphi_t$ , where  $t \geq 3$ , the values of  $[\uparrow, \downarrow]$  fluctuate below and above a mean value,  $M_1$ :

$$M_1 = 0.252 \quad (t \geq 3).$$

The local minima correspond for  $t=3, 5, 7$ , and the local maxima for  $t=2, 4, 6, 8$  (see also Ref. [7] and discussion); it is worth noticing that the mean value of 0.252 is very close with the constant value of  $0.5 * 0.5 = 0.25$  for the uncorrelated  $[\uparrow, \downarrow]$ . All these trends are also valid for the contributions of the covalent structures  $[(\uparrow), (\downarrow)]$  which for  $t \geq 3$  fluctuate, below and above a mean value,  $M'_1$ :

$$M'_1 = 0.111 \quad (t \geq 3).$$

The contributions of  $[(\uparrow), (\downarrow)]$  are, as expected, much smaller (about half) from the values of  $[\uparrow, \downarrow]$ , because in the former case there are two more conditions that must be fulfilled. For  $t \geq 3$ , one must notice:

(i) the remarkable similarity of the curves of  $[\uparrow, \downarrow]$  with  $[(\uparrow), (\downarrow)]$ ; in fact the difference  $D_1 = P_{2;0}(\varphi_1\varphi_{\bar{i}}) - P_{2;2}(\varphi_1\varphi_{\bar{i}}; \varphi_{\bar{1}}\varphi_t)$ , is quasi-constant:

$$D_1 = [\uparrow, \downarrow] - [(\uparrow), (\downarrow)] \approx \text{constant} \quad (t \geq 3).$$

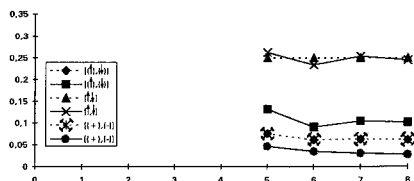
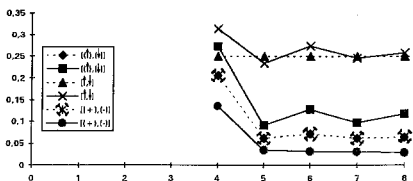
This result can be rationalised by referring also in relation (1) for  $t \geq 3$ . The constant behaviour of the contributions of ionic structures for  $t \geq 3$  holds not only for  $[(+), (-)]$  but also shown in Sect. 3.2 (Figs. 5–9), for other ionic structures as e.g.  $[\uparrow\downarrow, \uparrow\downarrow]$ ; therefore, the fact that the right-hand side of relation (1) is almost the same for  $t \geq 3$ , explains the constant behaviour of the difference  $D_1$ . The numerical value of  $D_1$  issued from actual calculations is  $D_1 \approx 0.141$  ( $t \geq 3$ )

(ii) our calculations show furthermore that  $D_1$  is essentially the same with the difference of the mean values,  $M_1 - M'_1$ :

$$D_1 = M_1 - M'_1 \quad (t \geq 3).$$

The contributions of structures such as  $[(+), (-)]$ ,  $[(\uparrow), (\downarrow)]$  and  $[\uparrow, \downarrow]$  are also calculated for the AO positions  $\varphi_2$  and  $\varphi_t$ , where  $t=3, 4, \dots, 8$ , for both the uncorrelated and correlated MO wave functions. The results are presented in Fig. 2. The main differences between Figs. 1 and 2 are

(i) in Fig. 2 the fluctuations of the curves of  $[\uparrow, \downarrow]$  and  $[(\uparrow), (\downarrow)]$  are smoother; (ii) the values of all the quantities studied for the vicinal AO positions  $\varphi_2$  and  $\varphi_3$ , for which no formal double bond can be written, are significantly smaller than those for the vicinal  $\varphi_1$  and  $\varphi_2$ . Apart from these differences, the general aspect of the curves of Fig. 2 is close to Fig. 1. The main similarities are that: i) the curve of the ionic situations  $[(+), (-)]$ , as well as those issued from the uncorrelated wave function are flat; ii) the mean distances between the curves are essentially the same; iii) the mean values of the quantities considered are very close in both Figs. 1 and 2. While in Fig. 1 local maxima for the structures  $[(\uparrow), (\downarrow)]$  and  $[\uparrow, \downarrow]$  exist for the couples of  $\varphi_1, \varphi_t$  with  $t=3, 5, 7$ , in Fig. 2 they appear for the couples of  $\varphi_2, \varphi_t$  with  $t=4, 6, 8$ ; consequently one can generalise as follows: *local maxima (resp. minima) for the contributions  $[(\uparrow), (\downarrow)]$  and  $[\uparrow, \downarrow]$  appear presented for AO positions separated by an even (resp. odd) number of carbon atoms.*



**Fig. 3.** Contributions (in ordinate) of resonance structures with two spins or charges of a different type,  $[(\uparrow), (\downarrow)]$  or  $[(+), (-)]$ , and electron-pair distributions  $[\uparrow, \downarrow]$ , for the couples of AO positions  $\varphi_3, \varphi_t$ , where  $t=4, 5, \dots, 8$  (in abscissa). Broken lines refer to results obtained from the decomposition of the HF wave function and full ones from HF+CI

**Fig. 4.** Contributions (in ordinate) of resonance structures with two spins or charges of a different type,  $[(\uparrow), (\downarrow)]$  or  $[(+), (-)]$ , and electron-pair distributions  $[\uparrow, \downarrow]$ , for the couples of AO positions  $\varphi_4, \varphi_t$ , where  $t=5, 6, 7, 8$  (in abscissa). Broken lines refer to results obtained from the decomposition of the HF wave function and full ones from HF+CI

As shown in Fig. 2, the effect of electron correlation is much less important for the vicinal AO positions  $\varphi_2$  and  $\varphi_3$  in comparison with figure 1; this holds for all the quantities considered  $[\uparrow, \downarrow]$ ,  $[(\uparrow), (\downarrow)]$  and  $[(+), (-)]$ . The ionic curve is presently lowered uniformly for all the AO positions.

Figure 3 shows results from calculations performed for the AO positions  $\varphi_3$  and  $\varphi_t$ , where  $t=4, 5, \dots, 8$ , while Fig. 4 for the AO positions  $\varphi_4$  and  $\varphi_t$ , where  $t=5, 6, \dots, 8$ . All the calculated quantities for the AO positions  $\varphi_3$  and  $\varphi_t$ , from both the uncorrelated and the correlated MO wave functions, *present a remarkable transferability* to those for the AO positions  $\varphi_1$  and  $\varphi_t$ . The transferability concerns the values of the local maxima or minima (whenever existing), the mean distances of the curves, as well as the mean values of all the curves: the curves in Fig. 3 are superposable with part of the curves in Fig. 1. The same *remarkable transferability* holds if we compare the results showed in Figs. 2 and 4. Comparing Figs. 3 and 4 one can find the same similarities and differences which are previously observed in Figs. 1 and 2.

### 3.2 Simultaneous presence of two charges or spins of the same type:

$(-, -)$  or  $(\alpha, \alpha)$ .

We present in this section the results concerning the contributions of resonance structures involving two charges or spins of the same type  $\{(-, -)$  or  $(\alpha, \alpha)\}$ .

Figure 5 shows the results issued from both the uncorrelated and correlated MO wave function when the two charges or spins are located in the AO positions  $\varphi_1$  and  $\varphi_t$  (where  $t=2, 3, \dots, 8$ ); the following quantities are calculated:

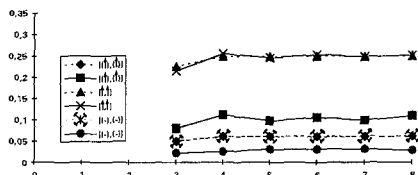
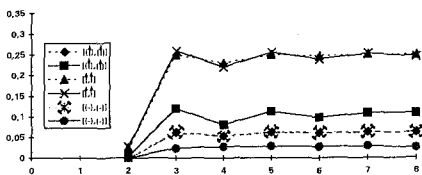
–  $P_{4,0}(\varphi_1\varphi_{\bar{1}}\varphi_t\varphi_{\bar{t}})$ : expectation values of the density operators

$$\varphi_1^+ \varphi_{\bar{1}}^+ \varphi_t^+ \varphi_{\bar{t}}^+ \varphi_{\bar{t}} \varphi_t \varphi_{\bar{1}} \varphi_1,$$

which provide probabilities of finding two electron pairs simultaneously in the AO positions  $\varphi_1$  and  $\varphi_t$ ; they are represented as  $[(+), (+)]$  or  $[\uparrow\downarrow, \uparrow\downarrow]$ .

–  $P_{2,0}(\varphi_1\varphi_t)$ : expectation values of the density operators

$$\varphi_1^+ \varphi_t^+ \varphi_t \varphi_1,$$



**Fig. 5.** Contributions (in ordinate) of resonance structures with two spins or charges of the same type,  $[(\uparrow), (\uparrow)]$  or  $[(-), (-)]$ , and electron-pair distributions  $[\uparrow, \uparrow]$ , for the couples of AO positions  $\varphi_1, \varphi_t$ , where  $t = 2, 3, \dots, 8$  (in abscissa). Broken lines refer to results obtained from the decomposition of the HF wave function and full ones from HF + CI

**Fig. 6.** Contributions (in ordinate) of resonance structures with two spins or charges of the same type,  $[(\uparrow), (\uparrow)]$  or  $[(-), (-)]$ , and electron-pair distributions  $[\uparrow, \uparrow]$ , for the couples of AO positions  $\varphi_2, \varphi_t$ , where  $t = 3, 4, \dots, 8$  (in abscissa). Broken lines refer to results obtained from the decomposition of the HF wave function and full ones from HF + CI

which provide probabilities of finding two electrons of  $\alpha$ -spin simultaneously in the AO positions  $\varphi_1$  and  $\varphi_t$  (without any further restriction); they are represented as  $[\uparrow, \uparrow]$ .

–  $P_{2,2}(\varphi_1\varphi_t; \varphi_{\bar{1}}\varphi_{\bar{t}})$ : expectation values of the density operators

$$\varphi_1^+ \varphi_t^+ \varphi_{\bar{1}} \varphi_{\bar{t}} \varphi_{\bar{1}}^+ \varphi_{\bar{t}}^+ \varphi_1 \varphi_t,$$

which provide same probabilities as  $P_{2,0}(\varphi_1\varphi_t)$ , concerning the location of two  $\alpha$ -spin electrons, by imposing the supplementary restrictions that no electrons of  $\beta$ -spin can be located in the AOs  $\varphi_1$  and  $\varphi_t$ ; they are represented as  $[(\uparrow), (\uparrow)]$ .

For the vicinal AO positions  $\varphi_1$  and  $\varphi_2$ , all the quantities considered are very small; this holds for the contribution of  $[\uparrow, \uparrow]$  while the contribution of  $[(\uparrow), (\uparrow)]$  and  $[(-), (-)]$  are almost zero. For the other AO positions  $\varphi_1$  and  $\varphi_t$ , where  $t \geq 3$ , the contribution of  $[\uparrow, \uparrow]$  shows a very important increment, and fluctuate above and below a mean value  $M_2$ :

$$M_2 = 0.245 \quad (t \geq 3);$$

the corresponding increment of  $[(\uparrow), (\uparrow)]$  is more moderate, fluctuating around a mean value,  $M'_2$ :

$$M'_2 = 0.103 \quad (t \geq 3).$$

Contrarily, the contribution of  $[(-), (-)]$  structures increase by a small amount to a mean value of  $\approx 0.027$ , which becomes *quasi-constant* even for  $t \geq 3$ .

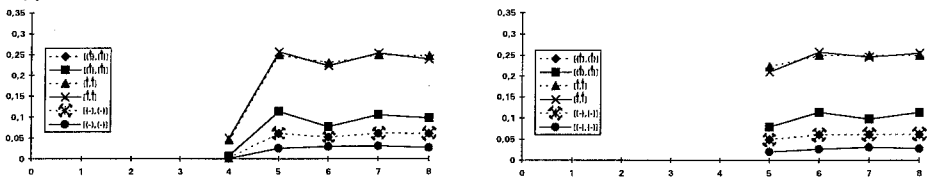
Both the  $[\uparrow, \uparrow]$  and  $[(\uparrow), (\uparrow)]$  present their *local minima (resp. maxima) for AO positions separated by an odd (resp. even) number of carbon atoms*.

The curves of  $[\uparrow, \uparrow]$  and  $[(\uparrow), (\uparrow)]$  present a remarkable similarity: the difference  $D_2 = P_{2,0}(\varphi_1\varphi_t) - P_{2,2}(\varphi_1\varphi_t; \varphi_{\bar{1}}\varphi_{\bar{t}})$  is considered quasi-constant:

$$D_2 = [\uparrow, \uparrow] - [(\uparrow), (\uparrow)] \approx \text{constant} \quad (t \geq 3).$$

In order to understand the constant behaviour of  $D_2$ , obtained from our numerical results, we proceed as follows: in the 2nd order general anticommutation relation, referring to two spin-orbitals  $k_1$  and  $k_2$  [2],

$$k_1^+ k_2^+ k_2 k_1 + k_1^+ k_2 k_2^+ k_1 + k_1 k_2^+ k_2 k_1^+ + k_1 k_2 k_2^+ k_1^+ = 1,$$



**Fig. 7.** Contributions (in ordinate) of resonance structures with two spins or charges of the same type,  $[(\uparrow), (\uparrow)]$  or  $[(-), (-)]$ , and electron-pair distributions  $[\uparrow, \uparrow]$ , for the couples of AO positions  $\varphi_3, \varphi_t$ , where  $t = 4, 5, \dots, 8$  (in abscissa). Broken lines refer to results obtained from the decomposition of the HF wave function and full ones from HF + CI

**Fig. 8.** Contributions (in ordinate) of resonance structures with two spins or charges of the same type,  $[(\uparrow), (\uparrow)]$  or  $[(-), (-)]$ , and electron-pair distributions  $[\uparrow, \uparrow]$ , for the couples of AO positions  $\varphi_4, \varphi_t$ , where  $t = 5, 6, 7, 8$  (in abscissa). Broken lines refer to results obtained from the decomposition of the HF wave function and full ones from HF + CI

we choose  $k_1 = \varphi_{\bar{1}}$  and  $k_2 = \varphi_{\bar{t}}$ , and then we multiply from both sides with the density operator  $\varphi_1^+ \varphi_t^+ \varphi_t \varphi_1$ ; after performing some convenient commutations we obtain

$$\begin{aligned} \varphi_{\bar{1}}^+ \varphi_t^+ \varphi_t \varphi_1 &= \varphi_1^+ \varphi_t^+ \varphi_{\bar{1}}^+ \varphi_{\bar{t}}^+ \varphi_{\bar{t}} \varphi_{\bar{1}} \varphi_t \varphi_1 + \varphi_1^+ \varphi_t^+ \varphi_{\bar{1}}^+ \varphi_{\bar{t}}^+ \varphi_{\bar{t}} \varphi_{\bar{1}} \varphi_t \varphi_1 \\ &\quad + \varphi_1^+ \varphi_t^+ \varphi_{\bar{1}} \varphi_{\bar{t}}^+ \varphi_{\bar{t}} \varphi_{\bar{1}}^+ \varphi_t \varphi_1 + \varphi_1^+ \varphi_t^+ \varphi_{\bar{1}} \varphi_{\bar{t}} \varphi_{\bar{1}}^+ \varphi_{\bar{t}}^+ \varphi_t \varphi_1. \end{aligned}$$

From this expression we obtain the following relationship for the expectation values of the density operators appearing above:

$$\begin{aligned} D_2 = P_{2;0}(\varphi_1 \varphi_t) - P_{2;2}(\varphi_1 \varphi_t; \varphi_{\bar{1}} \varphi_{\bar{t}}) &= P_{4;0}(\varphi_1 \varphi_{\bar{1}} \varphi_t \varphi_{\bar{t}}) + P_{3;1}(\varphi_1 \varphi_{\bar{1}} \varphi_t; \varphi_{\bar{t}}) \\ &\quad + P_{3;1}(\varphi_1 \varphi_t \varphi_{\bar{t}}; \varphi_{\bar{1}}) \end{aligned} \quad (2a)$$

or

$$D_2 = [\uparrow, \uparrow] - [(\uparrow), (\uparrow)] = [\uparrow\downarrow, \uparrow\downarrow] + [\uparrow\downarrow, (\uparrow)] + [(\uparrow), \uparrow\downarrow] \quad (2b)$$

The difference  $D_2$  is therefore quasi-constant, due to the fact that the contributions of ionic structures are almost the same for  $t \geq 3$  (see also Sect. 3.1).

Since the system considered is a closed shell there is no privilege for electrons of  $\alpha$  or  $\beta$  spins; therefore the term  $P_{3;1}(\varphi_1 \varphi_{\bar{1}} \varphi_t; \varphi_{\bar{t}})$  of relation (2a) is equal to  $P_{3;1}(\varphi_1 \varphi_{\bar{1}} \varphi_{\bar{t}} \varphi_t)$  of Eq. (1a) and then

$$D_2 = D_1. \quad (3)$$

The numerical value of  $D_2$  issued from our calculations is  $D_2 \approx 0.141$  ( $t \geq 3$ ).

Figure 6 shows the results from the contributions of  $[(-), (-)]$ ,  $[\uparrow, \uparrow]$  and  $[(\uparrow), (\uparrow)]$  for the case when the target AO positions are the  $\varphi_2$  and  $\varphi_t$ , where  $t = 3, 4, \dots, 8$ . In the present case there is no near zero values for the vicinal AO positions  $\varphi_2$  and  $\varphi_3$  (for which no formal double bond can be written), as previously for  $\varphi_1$  and  $\varphi_2$ . The fluctuations (wherever existing) are also smoother, in comparison with Fig. 5. The other trends for the results presented in Figs. 5 and 6 are in general similar; especially the mean values of all the quantities considered are very close.

Figures 7 and 8 show the results for the cases when the target AOs are the  $\varphi_3$  and  $\varphi_t$  where  $t = 4, \dots, 8$ , and  $\varphi_4$  and  $\varphi_t$  where  $t = 5, \dots, 8$  respectively. Comparing these results with those of Figs. 5 and 6, one can find a *remarkable*



transferability for Figs. 5 and 7 as well as for Figs. 6 and 8. When the results of Figs. 7 and 8 are compared, we find the same features presented above for Figs. 5 and 6.

3.3 Comparison of the simultaneous presence of two charges or spins of a different type with those of the same type

Comparing the curves of Fig. 1 (concerning charges or spins of a different type) with those of Fig. 5 (charges or spins of the same type) one finds that:

- (i) the mean values  $M_1$  and  $M'_1$  of Fig. 1 are very close to the mean values  $M_2$  and  $M'_2$  of Fig. 5.
- (ii) the ionic curves are in both cases very flat, and their quasi-constant value persists even for  $t = 3, 8$  (two charges distant from one carbon atom).
- (iii) the fluctuations of the neutral curves are in opposite directions for parallel and anti-parallel spins: the local minima (resp. maxima) of Fig. 1 correspond to the local maxima (resp. minima) of Fig. 5. Furthermore, our numerical results show that the sums  $C = P_{2,0}(\varphi_1\varphi_{\bar{t}}) + P_{2,0}(\varphi_1\varphi_t)$  and  $C' = P_{2,2}(\varphi_1\varphi_{\bar{t}};\varphi_{\bar{1}}\varphi_t) + P_{2,2}(\varphi_1\varphi_t;\varphi_{\bar{1}}\varphi_{\bar{t}})$  are nearly constant for  $t \geq 3$ :

$$C = [\uparrow, \downarrow] + [\uparrow, \uparrow] \approx 0.498 \quad (t \geq 3),$$

$$C' = [(\uparrow), (\downarrow)] + [(\uparrow), (\uparrow)] \approx 0.216 \quad (t \geq 3).$$

In order to understand this constant behaviour issued from our numerical results, we utilise 4th order anticommutation relations [2, 3a] for fermion creation ( $k_i^+$ ) and annihilation ( $k_i^-$ ) operators. These are

$$\sum_{\rho\sigma\tau\omega} k_1^\rho k_2^\sigma k_3^\tau k_4^\omega k_4^{\bar{\omega}} k_3^{\bar{\tau}} k_2^{\bar{\sigma}} k_1^{\bar{\rho}} = 1,$$

where, e.g.,  $\rho$  and  $\bar{\rho}$  denote opposed signs. (This result is readily seen since  $\sum_{\omega} k_4^\omega k_4^{\bar{\omega}} = 1$  reduces the left-hand side to a "3rd order anticommutation" which can similarly be further reduced finally to 1; for explicit development of such relations see Ref. [2] and [3a].)

Since the system considered is a closed shell there is no privilege for electrons of  $\alpha$  or  $\beta$  spins; therefore the expectation values of some density operators involved in the 4th order anticommutation relation are equal. Taking into account such equalities and by choosing  $k_1 = \varphi_1$ ,  $k_2 = \varphi_{\bar{1}}$ ,  $k_3 = \varphi_t$  and  $k_4 = \varphi_{\bar{t}}$  we obtain the following expression for  $C'$

$$\begin{aligned} 2C' &= 2P_{2,2}(\varphi_1\varphi_{\bar{t}};\varphi_{\bar{1}}\varphi_t) + 2P_{2,2}(\varphi_1\varphi_t;\varphi_{\bar{1}}\varphi_{\bar{t}}) \\ &= 1 - \{P_{4,0}(\varphi_1\varphi_{\bar{1}}\varphi_t\varphi_{\bar{t}}) + 2P_{3,1}(\varphi_1\varphi_{\bar{1}}\varphi_t;\varphi_{\bar{t}}) \\ &\quad + 2P_{3,1}(\varphi_1\varphi_t\varphi_{\bar{t}};\varphi_{\bar{1}}) + P_{2,2}(\varphi_1\varphi_{\bar{1}};\varphi_t\varphi_{\bar{t}}) \\ &\quad + P_{2,2}(\varphi_t\varphi_{\bar{t}};\varphi_1\varphi_{\bar{1}}) + 2P_{1,3}(\varphi_1;\varphi_{\bar{1}}\varphi_t\varphi_{\bar{t}}) \\ &\quad + 2P_{1,3}(\varphi_t;\varphi_1\varphi_{\bar{1}}\varphi_{\bar{t}}) + P_{0,4}(\varphi_1\varphi_{\bar{1}}\varphi_t\varphi_{\bar{t}})\} \end{aligned} \tag{4a}$$

or

$$2C' = 2[(\uparrow), (\downarrow)] + 2[(\uparrow), (\uparrow)] = 1 - \{\text{various ionic}\}. \tag{4b}$$

Since the contributions of the various ionic structures are quasi-constant for the AO positions  $\varphi_1$  and  $\varphi_t$ , when  $t \geq 3$ , the  $C'$  must be the same for these AO positions.

As far as the sum  $C$  is concerned, using relations (1a) and (2a) in Eq. (4a) we obtain also a similar relation

$$2C = 2[\uparrow, \downarrow] + 2[\uparrow, \uparrow] = 1 - [\text{various ionic}]. \quad (5)$$

Even though in Eq. (5) the expression of "various ionic" structures is slightly different from Eq. (4), the constant behaviour for these expressions remains valid. Taking into consideration relation (3), one can obtain straightforwardly the following very simple relation, which ties up the constant quantities of Figs. 1 and 5:

$$D = \frac{C - C'}{2} \quad (6)$$

where  $D$  is defined as  $D = D_1 = D_2$ .

The curve of  $[\uparrow, \uparrow]$  issued from the uncorrelated MO wave function (Fig. 5) is no more flat than the one for  $[\uparrow, \downarrow]$  (Fig. 1); the former follows that the fluctuations of the curve are obtained from the correlated MO wave function. This is because electrons of parallel spins are partially correlated, due to the Pauli principle which is used in the construction of the ground state MO Slater determinant.

### 3.4 Correlation effects

The adopted method of calculating the expectation values of various types of multi-electron density operators, which pass through the decomposition of usual MO wave functions in the framework of Moffitt's theorem, offers the possibility to investigate spin and charge correlation effects. As shown in Figs. 1–4, in the HF level contributions of the ionic and covalent structures are (incorrectly) the same, and in the HF + CI level, as expected [1b, 3a, 14a, 19], the former diminish while the latter increase; the effect of the CI in non-vicinal AO positions is uniform for the (+), (–) charges regardless of their distance inside the polyene, while for the  $\alpha$ ,  $\beta$  electrons provoke oscillations along the polyene.

#### 3.4.1 Correlation effects in two electron spins

In order to study the correlation effects in two electron spins we have considered the correlation differences,  $d$ , that is the differences in the contributions of various covalent structures obtained in HF and HF + CI levels; the correlation differences referred to electrons with antiparallel spins,  $d[(\uparrow), (\downarrow)]$ , and parallel ones,  $d[(\uparrow), (\uparrow)]$ , are calculated as

$$d[(\uparrow), (\downarrow)] = [P_{2,0}(\varphi_i \varphi_{\bar{i}}; \varphi_{\bar{i}} \varphi_i)]_{\text{HF+CI}} - [P_{2,0}(\varphi_i \varphi_{\bar{i}}; \varphi_{\bar{i}} \varphi_i)]_{\text{HF}},$$

$$d[(\uparrow), (\uparrow)] = [P_{2,0}(\varphi_i \varphi_i; \varphi_{\bar{i}} \varphi_{\bar{i}})]_{\text{HF+CI}} - [P_{2,0}(\varphi_i \varphi_i; \varphi_{\bar{i}} \varphi_{\bar{i}})]_{\text{HF}}.$$

The magnitudes and signs of various correlation differences depend not only on the parallel or anti-parallel behaviour of electron spins, but also on

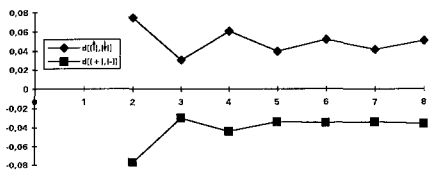


Fig. 9. Correlation differences (in ordinate) for two spins or charges of a different type,  $d[(\uparrow), (\downarrow)]$  or  $d[(+), (-)]$ , for the couples of AO positions  $\varphi_1, \varphi_t$ , where  $t=2, 3, \dots, 8$  (in abscissa)

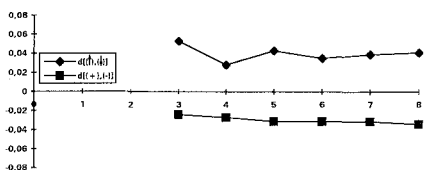


Fig. 10. Correlation differences (in ordinate) for two spins or charges of a different type,  $d[(\uparrow), (\downarrow)]$  or  $d[(+), (-)]$ , for the couples of AO positions  $\varphi_2, \varphi_t$ , where  $t=3, 4, \dots, 8$  (in abscissa)

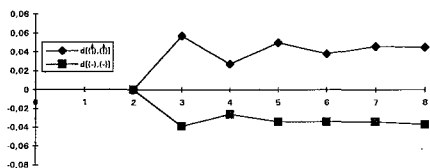


Fig. 11. Correlation differences (in ordinate) for two spins or charges of the same type,  $d[(\uparrow), (\uparrow)]$  or  $d[(−), (−)]$ , for the couples of AO positions  $\varphi_1, \varphi_t$ , where  $t=2, 3, \dots, 8$  (in abscissa)

the relative AO positions of the polyene  $\varphi_i$  and  $\varphi_t$ . Positive values of  $d$  mean that when we take into account, in the CI level, the relative positions of the two electrons, this makes the electron to be more “repulsive” in the target AOs  $\varphi_i$  and  $\varphi_t$ ; in other words, positive values of  $d$  express a tendency of electrons to avoid each other when located in  $\varphi_i$  and  $\varphi_t$ . Negative values of  $d$  mean that electron correlation diminishes the repulsion of electrons when located in  $\varphi_i$  and  $\varphi_t$ .

The  $d[(\uparrow), (\downarrow)]$  are given in Fig. 9 for the AO positions  $\varphi_1, \varphi_t$ , where  $t=2, \dots, 8$ , and in Fig. 10 for  $\varphi_2, \varphi_t$ , where  $t=3, 4, \dots, 8$ . Both fluctuate in positive values, but the fluctuations in  $\varphi_2, \varphi_t$  are smoother than those of  $\varphi_3, \varphi_t$ . A common characteristic of these curves is that the local maxima appear in AO positions separated by an even number of carbon atoms; this means that correlation makes two anti-parallel spins more repulsive in AO positions separated by an even than an odd number of carbon atoms.

The  $d[(\uparrow), (\uparrow)]$  are given in Fig. 11 for the AO positions  $\varphi_1, \varphi_t$  and in Fig. 12 for  $\varphi_2, \varphi_t$ , where  $t$  takes the same values as above. The minimum correlation appears for vicinal  $\varphi_1, \varphi_2$  and  $\varphi_2, \varphi_3$ . As for the anti-parallel spins, both curves fluctuate in positive values and the fluctuations in  $\varphi_2, \varphi_t$  are also smoother. However, local maxima for the correlation of parallel spins appear in AO positions separated by an odd number of carbons. This means that *the effect of correlation in electrons with parallel spins is always the opposite from that in anti-parallel spins*: correlation makes two parallel spin electrons more repulsive in these AO positions in which the anti-parallel spin electrons are less repulsive.

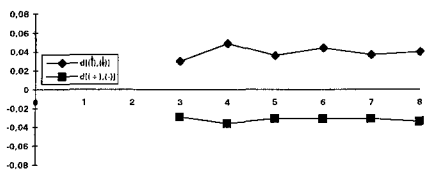


Fig. 12. Correlation differences (in ordinate) for two spins or charges of a different type,  $d[(\uparrow), (\downarrow)]$  or  $d[(+), (-)]$ , for the couples of AO positions  $\varphi_2, \varphi_t$ , where  $t = 3, 4, \dots, 8$  (in abscissa)

### 3.4.2 Correlation effects in two charges

The charge correlation differences,  $d[+, -]$  and  $d[-, -]$ , defined as

$$d[+, -] = [P_{2;2}(\varphi_i\varphi_{\bar{i}}; \varphi_i\varphi_{\bar{i}})]_{\text{HF+CI}} - [P_{2;2}(\varphi_i\varphi_{\bar{i}}; \varphi_i\varphi_{\bar{i}})]_{\text{HF}},$$

$$d[-, -] = [P_{4;0}(\varphi_i\varphi_{\bar{i}}\varphi_i\varphi_{\bar{i}})]_{\text{HF+CI}} - [P_{4;0}(\varphi_i\varphi_{\bar{i}}\varphi_i\varphi_{\bar{i}})]_{\text{HF}},$$

for various AO positions are given in Figs. 9–11. As expected, they are negative for all AO positions. The local maxima, whenever existing, appear for AO positions separated by an even number of carbon atoms in the case of two charges of a different type (+, -) and by an odd number of carbon atoms in the case of the same type (-, -). The fluctuations in charge correlation differences, when existing, are always in opposite direction with those of electron spin correlation differences.

The main common characteristic of charge correlation differences is the almost flat aspect of the corresponding curves in Figs. 9–11 for non-neighbouring AO positions; this means that *the effect of correlation is almost the same regardless the distance or the parity of the AO positions considered.*

#### *An a posteriori examination of charge correlation*

The above correlation differences  $d[+, -]$  concern the electronic correlation issued from the comparison of the HF and HF + CI levels; our multi-electron population analysis methodology allows us to go beyond this traditional comparison and examine the mutual dependence of (+) and (-) charges inside a given molecular system as the octatetraene.

If (+) and (-) charges were totally independent one from another then the contribution of an ionic resonance structure, that is the probability of finding a (+) in AO positions  $\varphi_1$ , and simultaneously a (-) in  $\varphi_t$ , should be given by a simple product,

$$P_{0;2}(\varphi_1\varphi_{\bar{1}}) * P_{2;0}(\varphi_t\varphi_{\bar{t}}),$$

of the probabilities of finding these two (assumed) independent events: here  $P_{0;2}(\varphi_1\varphi_{\bar{1}})$  is the expectation value of the operator  $\varphi_1\varphi_{\bar{1}}\varphi_1^+\varphi_{\bar{1}}^+$  (giving the probability of finding a (+) charge in  $\varphi_1$ ), and  $P_{2;0}(\varphi_t\varphi_{\bar{t}})$  is this of the operator  $\varphi_t^+\varphi_{\bar{t}}^+\varphi_{\bar{t}}\varphi_t$  (giving the probability of finding a (-) charge in  $\varphi_t$ ). Since the existing (real) probability of finding simultaneously (+) and (-) charges is given by  $P_{2;2}(\varphi_t\varphi_{\bar{t}}; \varphi_1\varphi_{\bar{1}})$  (see Sect. 3.1), then the difference

$$\text{CF}[+, -] = P_{2;2}(\varphi_t\varphi_{\bar{t}}; \varphi_1\varphi_{\bar{1}}) - P_{0;2}(\varphi_1\varphi_{\bar{1}}) * P_{2;0}(\varphi_t\varphi_{\bar{t}})$$

is the correlation function (CF) for the (+) and (-) charges in AO-space. Defined as above,  $\text{CF}[+, -]$  is an a posteriori measure of the correlation of (+) and (-)

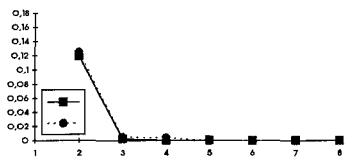


Fig. 13. Correlation function,  $CF[(+), (-)]$ , for two charges in AO positions  $\varphi_1, \varphi_t$ , where  $t=2, 3, \dots, 8$ . Broken line refers to equal C-C bond lengths and full line to alternating ones; both correspond to the HF + CI level

charges; very small values of  $CF[+, -]$  in a molecular system, means that the (+) and (-) charges are quasi-independent one from another.

The calculated  $CF[+, -]$ s for the AO positions  $\varphi_1, \varphi_t$ , where  $t=2, 3, \dots, 8$ , are given in Fig. 13. For vicinal positions  $\varphi_1, \varphi_2$   $CF[+, -]$  is  $\approx 0.12$ , but very small  $\approx 0.002$ , for  $\varphi_1, \varphi_3$ ; for other  $\varphi_1, \varphi_t$  ( $t=4, \dots, 8$ ) is almost the same, near zero ( $\approx 10^{-4}$ ). This result means that, except for vicinal AO positions defining a formal double bond, the (+) and (-) charges are practically *independent one from another* inside the octatetraene with alternating carbon-carbon bond lengths.

Closing our investigation we tentatively ask about the role of the difference of the carbon-carbon bond lengths to the mutual dependence of (+) and (-) charges inside the linear polyene. For this purpose similar calculations are performed in the all trans octatetraene topology in which all the carbon-carbon bond lengths are equal to 1.40 Å. The PPP+(quasi) total CI ground state eigenfunction of this system is decomposed according to Moffitt's theorem, and then the expectation values of the ionic density operators as well as those of  $\varphi_1 \varphi_{\bar{1}} \varphi_1^{\dagger} \varphi_{\bar{1}}^{\dagger}$  and  $\varphi_t^{\dagger} \varphi_{\bar{t}} \varphi_t^{\dagger} \varphi_{\bar{t}}^{\dagger}$  (whose physical meaning is previously given) are calculated as usually. The results for the correlation functions  $CF[+, -]$  are given in fig. 13. In the present case of equal carbon-carbon bond length the  $CF[+, -] \approx 0.13$  for vicinal AO positions defining a formal double bond,  $\varphi_1 \varphi_2$ , and remains also very small, of the order of  $10^{-3}-10^{-4}$ , for other positions. The general trend issued from these calculations is that the correlation function is essentially of the *same magnitude* with the case of octatetraene with alternating carbon-carbon bond lengths. One can therefore conclude that the correlation of (+) and (-) charges is controlled from the linear topology of the all trans (neutral) octatetraene system, and not from the carbon-carbon bond lengths.

The probability of finding simultaneously (+) and (-) charges in two totally isolated  $\pi$ -systems, as for instance two isolated ethylene, is, obviously, equal to the simple product of the probabilities of finding a (+) or (-) charge independently one from another in one ethylene, and therefore:

$$CF[+, -] = 0.$$

A similar effect ( $CF[+, -] \approx 10^{-3}-10^{-4}$ ) occurs precisely at the two ends of octatetraene, regardless of the difference of the carbon-carbon bond lengths, showing rather surprisingly that the  $\pi$ -conjugation has no effect on the correlation of (+) and (-) charges.

#### 4 Conclusion

The probabilities of finding simultaneously two charges along the unsubstituted neutral polyene, that is the contributions of various ionic resonance structures, as a function of the distance are quasi-constant for nonvicinal AO positions.

Contrarily, the probabilities of finding simultaneously two electron spins, that is the contributions of the covalent resonance structures, (in a probabilistic sense), as well as the electron-pair distributions for various couples of AO positions,

$$(p_x, p_t) \quad \text{where } x=1, 2, 3, 4 \text{ and } t > x,$$

depend on whether:

(i)  $x$  is an odd (Figs. 1, 3, 5, 7) or an even (Figs. 2, 4, 6, 8) AO position, that is if  $x$  labels the beginning or the end of a formal double bond in a given direction of the linear polyene

(ii) the considered electron spins are anti-parallel (Figs. 1–4) or parallel (Figs. 5–8). For a given parity of  $x$  (even or odd), the results for anti-parallel spins exhibit exactly the opposite trends than for parallel spins: the local minima of the former correspond to the local maxima of the latter, and the opposite. For a given type of electron-spin pairs (anti-parallel or parallel) the oscillations of the various curves are smoother for  $x$  even than for  $x$  odd.

The fact that the contributions of the ionic structures are quasi-constant for non vicinal atoms can also explain why the complete neglect of ionic Slater determinants in the reference space of the Effective (Heisenberg) Valence-Bond (EVB) method [20, 7] is a very good approach and the EVB hamiltonian had an important success [21]. It is also worth noticing that the curve of  $N_{2,0}(\varphi_1\varphi_{\bar{t}})$  (and not this of  $N_{2,0}(\varphi_1\varphi_{\bar{t}}; \varphi_{\bar{1}}\varphi_t)$  as one should expected) is in very good agreement with the results of Ref. [7].

For a given type of a pair of charges  $\{(+, -) \text{ or } (-, -)\}$  or spins (antiparallel or parallel) all the curves representing contributions of the various two-charge or two-spin resonance structures along the polyene, exhibit a *remarkable transferability*, provided of course, that  $x$  is of the same parity.

Based on the 4th order anticommutation relation, we have shown that the electron-pair distributions for parallel and antiparallel spins follow a law stating that their sum for non vicinal AO positions is quasi-constant with the distance; the same law holds also for the contributions of the covalent resonance structures:

$$C = [\uparrow, \downarrow] + [\uparrow, \uparrow] \approx \text{constant},$$

$$C' = [(\uparrow), (\downarrow)] + [(\uparrow), (\uparrow)] \approx \text{constant}.$$

Based on the 2nd order anticommutation relation, we have shown that the difference between electron-pair distributions and covalent structures is the same for both parallel and anti-parallel spins; this difference is also quasi-constant for non vicinal AO positions:

$$D = [\uparrow, \downarrow] - [(\uparrow), (\downarrow)] = [\uparrow, \uparrow] - [(\uparrow), (\uparrow)] \approx \text{constant}.$$

(The actual values of  $C$ ,  $C'$  and  $D$  issued from our numerical results are  $C=0.498$ ,  $C'=0.216$  and  $D=0.141$ .)

The effect of electron correlation is *uniform for ionic structures* and quasi-independent from the parity and the distance of the AOs, provided that these AOs are not vicinal. Contrarily, correlation effects for the  $\alpha, \beta$  electron-pair distributions as well as for the covalent structures depend strongly from both the parity and the distance of the two AOs. The oscillating aspect of curves for pair distributions and covalent structures of electrons with anti-parallel spins is *due exclusively to electron correlation*, since when the uncorrelated HF wave function is analysed the corresponding curves are flat; on the contrary, electrons with parallel spins are partially correlated even in the HF wave function, due to the Pauli principle.

Finally, an a posteriori examination of the correlation of (+) and (−) charges inside the unsubstituted neutral octatetraene, show that these charges are in practice independent one from another for all the AO positions (except, of course, for vicinal positions defining a formal double bond). In octatetraene, the (+) and (−) charges in the ends of this polyene behave as being in two isolated  $\pi$ -systems; this holds true for both the real octatetraene having alternating carbon–carbon bond lengths, as well as the similar “octatetraene” system with equal carbon–carbon bond lengths. Therefore, the correlation of (+) and (−) charges is controlled from the linear topology of the all trans polyenic system, and rather surprisingly the  $\pi$ -electron conjugation has no effect on it.

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