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PCILO Method for Excited States

I. Construction of the Zeroth Order Wave-Function for Planar Conjugated Systems

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In the scope of building a PCILO method for excited states, one builds and tests excitonic zeroth order wave-functions. For $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ transitions, the $(\sigma+\pi)$ excitonic and purely (π) excitonic wave functions are compared, showing that the $\sigma-\pi$ coupling between $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ and $\begin{pmatrix}\sigma^*\\ \sigma\end{pmatrix}$ single excitations may be considered as a perturbation. The excited state wave-functions are analyzed in terms of neutral and ionic structures, and the fluctuation of the charges in the two-electrons loges are studied, showing that the $\sigma-\pi$ coupling favours the neutral structures and diminishes the charge-fluctuations.

Im Rahmen der Aufstellung einer PCILO-Methode für angeregte Zustände werden Wellenfunktionen 0. Ordnung mit delokalisierter Anregung konstruiert und getestet. Für $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$-Übergänge werden $(\sigma+\pi)$-angeregte und rein π-angeregte Wellenfunktionen verglichen, wobei gezeigt wird, daß die $\sigma-\pi$-Kopplung zwischen $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$- und $\begin{pmatrix}\sigma^*\\ \sigma\end{pmatrix}$-Einfachanregungen als Störung behandelt werden kann. Die Wellenfunktionen der angeregten Zustände werden nach neutralen und ionischen Strukturen analysiert. Die Ladungsverschiebungen in den Zweielektronen-Elektronendichteanteilen werden untersucht, wobei gezeigt wird, daß die $\sigma-\pi$-Kopplung die neutralen Strukturen begünstigt und die Ladungsverschiebungen verringert.

Introduction

A method hereafter named PCILO has been proposed recently [1] for the study of the ground state of closed shell molecules [1] and of localized radicals [2] in the CNDO hypotheses. This method is much more rapid, even to the third order of perturbation, than the classical variational Hartree-Fock method although it includes correlation effects. This method, which has been widely used for the study of conformational properties of large molecules [3], has the following principles:

a) The bonding and antibonding orbitals localized on bond i may be represented with two hybrids i_1 and i_2 by the linear combination.

$$i=\alpha i_1+\beta i_2\,,$$
$$i^*=\beta' i_1-\alpha' i_2\,.$$

b) The bonding orbitals are used to build a zeroth order wave function as a fully localized determinant.

c) The antibonding orbitals are used to build an excited configurations basis allowing the construction of a CI matrix.

d) The lowest eigenvalue and eigenstate of this matrix are developed according to a Rayleigh-Schrödinger perturbation series.

The use of localized orbitals to represent ground-state wave functions is very successful, because of the existence of a large overlap between the zeroth order fully localized determinant and the SCF one [4]. But even when a satisfactory single determinant representation of an excited state can be found using symmetry (therefore delocalized) Molecular Orbitals, obtained by diagonalization of a symmetrical hamiltonian (Hückel, SCF hamiltonian), one cannot find in general a satisfactory single determinant representation for the excited state using localized MO's.

In fact, when using localized MO's, the singly excited determinants only represent local excitations from the bonding MO φ_i on the bond i towards the antibonding MO φ_{j^*} on the bond j. To get a reasonable representation of the excited state which transforms the excited state according to the symmetry operations of the molecule, one must represent it as a linear combination of several determinants, each of them representing a local excitation. In the excitonic treatment [5], the excited states are represented by localized singly excited determinants

$$\Psi_0^m = \sum_i \sum_{j^*} c_{ij^*}^m \Phi\begin{pmatrix} j^* \\ i \end{pmatrix}.$$

Each bonding MO can be excited towards its antibonding MO; this process leads to a determinant $\Phi\begin{pmatrix} i^* \\ i \end{pmatrix} = a_{i^*}^+ a_i \Phi_0$, which will be called a polarization determinant hereafter.

In the same way, each bonding MO φ_i can be excited towards an antibonding MO φ_{j^*}, and we obtain the delocalization (or charge-transfer) determinant $\Phi_{ij^*} = a_{j^*}^+ a_i \Phi_0$.

At the beginning of the calculation, all these determinants are (nearly) degenerate. When the total hamiltonian including electron repulsion is considered, these single excited determinants interact. According to the perturbation theory for degenerate states [6], the correct first-order energies are solutions of the Configuration Interaction (CI) problem limited to these states.

All excited states obtained after diagonalization of the matrix are linear combination of locally excited states and therefore represent delocalized excitations ("exciton states"). The good symmetry properties result from the $C_{ij^*}^m$ values obtained as the eigenvector m of the CI matrix.

The excitonic treatment has been applied to the $\begin{pmatrix} \pi^* \\ \pi \end{pmatrix}$ transition of unsaturated molecules by Simpson [5], using $\Phi\begin{pmatrix} \pi^* \\ \pi \end{pmatrix}$ polarization configurations only. Other authors [7, 8] have introduced the $\begin{pmatrix} \pi^* \\ \pi \end{pmatrix}$ delocalization configurations.

Our purpose is to build a PCILO method for excited states, i.e. an all-valence electrons method taking correlation effects into account. The inclusion of localized orbitals implies the multiconfigurational character of a correct zeroth-order wave function Ψ_0^m for the excited state, but it is hoped that the simplifications due to the full localization of the MO's (especially in the molecular integrals calculation) will give the same advantages as what does the PCILO method for the ground-state energy.

In the present work we study the correctness of various zeroth order representations of the $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ excited states. In all-valence electrons methods, one may build an excitonic matrix which involves simultaneously the $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ and $\begin{pmatrix}\sigma^*\\ \sigma\end{pmatrix}$ singly excited determinants i.e. the $(\sigma+\pi)$ excitonic treatment. Another possibility consists in building the (π) excitonic matrix of the $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ singly excited determinants, and in treating the interaction between $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ and $\begin{pmatrix}\sigma^*\\ \sigma\end{pmatrix}$ determinants [9, 10, 11] as a perturbation (π excitonic treatment).

As well as in the PCILO method for energy calculation of the groundstate, we have used the CNDO II parametrization [12]. This preliminary study deals with the linear polyenes series.

1. Structure of the $(\sigma+\pi)$ Excitonic Matrix

As said in the introduction, the CI matrix contains all (σ and π) polarization and delocalization configurations.

a) The *diagonal elements* of the CI matrix, which represent the mean values of the energy for local excitations, are given in Table 1. The order of the energies of these local excitations may be summarized as follows,

$$\begin{aligned}&E\begin{pmatrix}\pi_A^*\\ \pi_A\end{pmatrix}\ \text{polarization} < E\begin{pmatrix}\pi_B^*\\ \pi_A\end{pmatrix}\ \text{delocalization} < E\begin{pmatrix}\sigma_{CHB}^*\\ \sigma_{CHA}\end{pmatrix}\ \text{delocalization}\\ &< E\begin{pmatrix}\sigma_{CHA}^*\\ \sigma_{CHA}\end{pmatrix}\ \text{polarization} < E\begin{pmatrix}\sigma_{CC}^*\\ \sigma_{CH}\end{pmatrix}\ \text{delocalization} < E\begin{pmatrix}\sigma_{CH}^*\\ \sigma_{CC}\end{pmatrix}\ \text{delocalization}\\ &< E\begin{pmatrix}\sigma_{CCB}^*\\ \sigma_{CCA}\end{pmatrix}\ \text{delocalization} < E\begin{pmatrix}\sigma_{CCA}^*\\ \sigma_{CCA}\end{pmatrix}\ \text{polarization.}\end{aligned}$$

The $\Phi\begin{pmatrix}\sigma^*\\ \pi\end{pmatrix}$ excited configurations are close in energy to the $\Phi\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ configurations, especially in the CNDO/2 parametrization; The $\Phi\begin{pmatrix}\sigma^*\\ \pi\end{pmatrix}$ configurations which represent an excitation from a bond to the antibonding adjacent CH MO have a lower energy than the $\Phi\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ polarization configuration (13.84 eV against 14.40 eV).

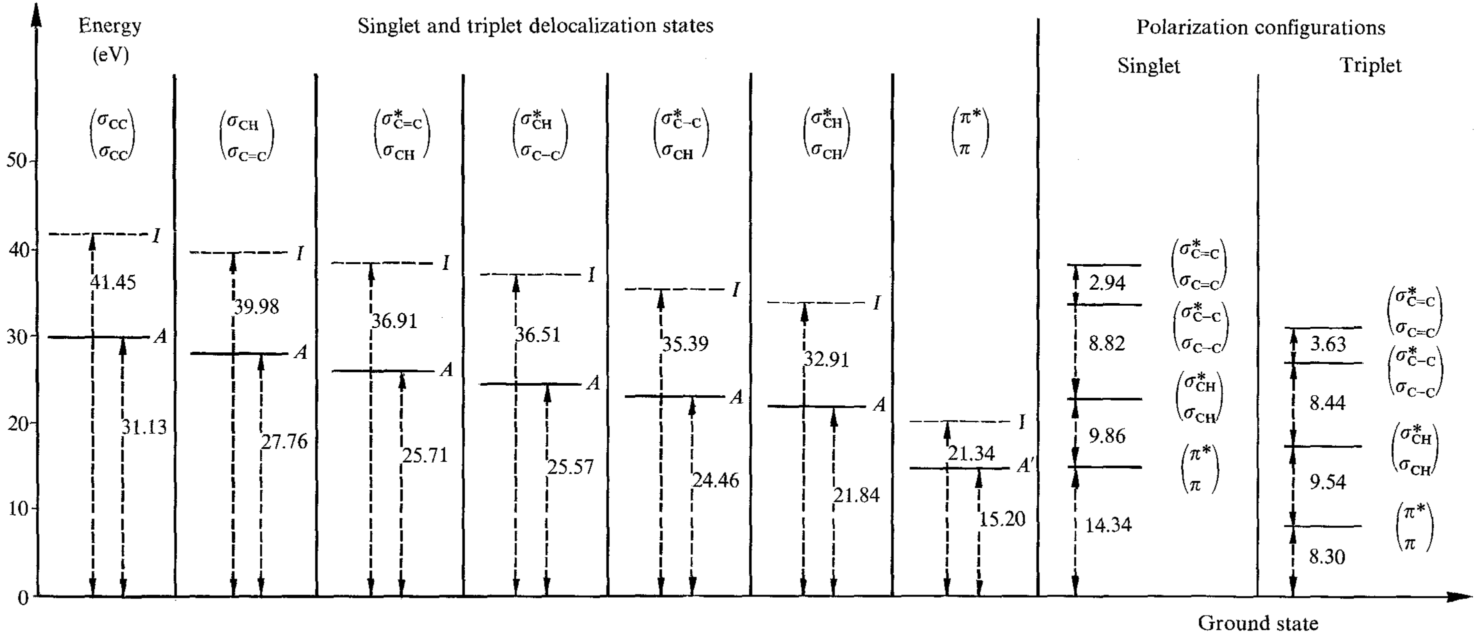
b) *Off Diagonal Elements.* The polarization configurations $\Phi\begin{pmatrix}\pi_A^*\\ \pi_A\end{pmatrix}$ which were supposed to be the most important in the $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ excited states are coupled with

Table 1. Energy (in eV) of the different polarization and delocalization configurations

1) The subscript A means delocalization configuration $\begin{pmatrix}(i+1)^*\\ i\end{pmatrix}$ i.e. from the MO i to the adjacent $i+1$ MO.

2) For the $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ delocalization configurations subscript A' means delocalization configurations $\begin{pmatrix}j^*\\ i\end{pmatrix}$ where i and j are two π MO's separated by a σ MO. For instance in Butadiene i is the first π bond and j the second one.

3) The subscript I mean delocalization configurations $\begin{pmatrix}j^*\\ i\end{pmatrix}$ when the distances between the two MO's i and j is infinite. The energy of these configurations are calculated by : $E_2 = F(j^*, j^*) - F(i, i)$ because when the distance between i and j is infinite, the integral $J_{ij^*} = \langle ij^* | ij^* \rangle = 0$.



$\Phi\binom{\pi_B^*}{\pi_B}$ polarization configurations by dipolar type interactions, and with the $\Phi\binom{\pi_B^*}{\pi_A}$ or the $\Phi\binom{\pi_A^*}{\pi_B}$ delocalization configurations which have the same hole (π_A) or the same particle (π_A^*). These $\Phi\binom{\pi_B^*}{\pi_A}$ delocalization configurations are coupled between themselves, according to the same rule. For planar systems, the singlet $\Phi\binom{\sigma_A^*}{\sigma_A}$ polarization configurations are coupled with all the singlet $\Phi\binom{\pi_B^*}{\pi_B^*}$ polarization configurations, and with themselves by dipolar type interaction. The $\Phi\binom{\sigma_B^*}{\sigma_A}$ delocalization configurations are coupled with some of the $\Phi\binom{\sigma_A^*}{\sigma_A}$ polarization configurations but they are not coupled directly with the $\Phi\binom{\pi^*}{\pi}$ configurations in the CNDO hypotheses. Therefore they should have a less important weight than the $\Phi\binom{\sigma_A^*}{\sigma_A}$ polarization configurations in the $\binom{\pi^*}{\pi}$ excited states. The structure of the CI matrix for a planar molecule is given in Fig. 1. The $\Phi\binom{\pi^*}{\sigma}$ and $\Phi\binom{\sigma^*}{\pi}$ configurations only appear in $\binom{\pi^*}{\pi}$ excited states for non-planar molecules. Two $\Phi\binom{\pi^*}{\pi}$ configurations do not interact very strongly and the dipolar type interaction element between two $\Phi\binom{\pi^*}{\pi}$ configurations decreases as r^{-3} with the distance between the two π bonds. So with Hexatriene we obtain the following values:

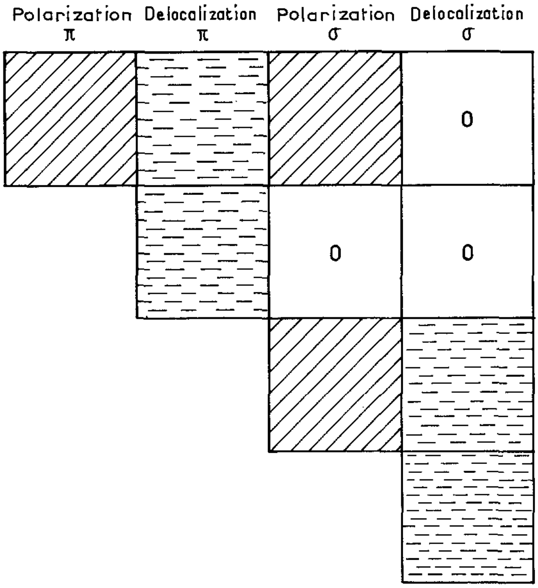


Fig. 1. Structure of the $(\sigma + \pi)$ excitonic matrix

0.753 eV when the two π bonds are separated by a single bond, and 0.131 eV when the two π bonds are separated by 2 single bonds and 1 double bond.

The interaction matrix elements between the $\Phi\begin{pmatrix} i^* \\ i \end{pmatrix}$ configurations and the $\Phi\begin{pmatrix} i^* \\ j \end{pmatrix}$ delocalization configurations are stronger than the interaction matrix elements between the $\Phi\begin{pmatrix} i^* \\ i \end{pmatrix}$ polarization configurations and the $\Phi\begin{pmatrix} j^* \\ i \end{pmatrix}$ delocalization configurations. For instance, when two π MO's are separated by a σ MO we obtain 2.93 eV in the former case and 1.56 eV in the latter case. If $\boldsymbol{F}$ is the Fock operator, $F_{ij} > F_{i^*j^*}$. These interaction matrix elements decrease exponentially with the distance between the two different MO's.

There is a very strong interaction matrix element between the $\Phi\begin{pmatrix} \sigma^*_{\mathrm{CC}} \\ \sigma_{\mathrm{CC}} \end{pmatrix}$ and $\Phi\begin{pmatrix} \pi^* \\ \pi \end{pmatrix}$ polarization configurations: 6.03 eV when the σ and π MO's belong to the same double bond. Then this interaction decreases and becomes 1.28 eV, when the two π and σ MO's are adjacent. This interaction matrix element becomes 0.75 eV, 0.55 eV when the π MO is separated from the σ MO by 1 or 2 other bonds respectively. This agrees with the r^{-3} theoretical decreases. The interaction matrix element between $\Phi\begin{pmatrix} \pi^* \\ \pi \end{pmatrix}$ and $\Phi\begin{pmatrix} \sigma^*_{\mathrm{CH}} \\ \sigma_{\mathrm{CH}} \end{pmatrix}$ polarization configurations is very weak (0.38 eV) when these two bonds are adjacent.

The coupling between $\Phi\begin{pmatrix} \pi^* \\ \pi \end{pmatrix}$ and $\Phi\begin{pmatrix} \sigma^*_{\mathrm{CC}} \\ \sigma_{\mathrm{CC}} \end{pmatrix}$ polarization configurations being stronger than the coupling between the $\Phi\begin{pmatrix} \pi^* \\ \pi \end{pmatrix}$ and $\Phi\begin{pmatrix} \sigma^*_{\mathrm{CH}} \\ \sigma_{\mathrm{CH}} \end{pmatrix}$ polarization configurations, we may expect a more important component of the excited state $\Phi\begin{pmatrix} \pi^* \\ \pi \end{pmatrix}$ on the $\sigma_{\mathrm{C-C}}$ than on the σ_{CH} bonds.

In the triplet excited states, the delocalization configurations have the same mean energies than in the singlet excited states, because in the PCILO method, due to ZDO hypothesis, the exchange integral K_{ij} is zero. But the polarization configurations have lower energies than in the singlet excited states.

For the triplet excited states, in the CNDO hypothesis the transition dipole-transition dipole interactions disappear, and the ${}^3\Phi\begin{pmatrix} \pi\mathrm{A}^* \\ \pi\mathrm{A} \end{pmatrix}$ configurations no longer interact between themselves nor with ${}^3\Phi\begin{pmatrix} \sigma^* \\ \sigma \end{pmatrix}$ excited configurations. The ${}^3\Phi\begin{pmatrix} \pi^*\mathrm{A} \\ \pi\mathrm{A} \end{pmatrix}$ configurations only interact with the ${}^3\Phi\begin{pmatrix} \pi\mathrm{B}^* \\ \pi\mathrm{A} \end{pmatrix}$ delocalization configurations as noticed by several authors [11]. The σ system does not play any role at this stage.

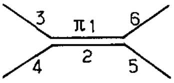
2. Results Obtained with the ($\sigma + \pi$) Excitonic Matrix

The wave function ψ_0^m resulting from the diagonalization of the excitonic matrix will be considered as a zeroth order representation of the excited state m, as does the fully localized determinant Φ_0 for the ground state. Therefore, the zeroth order transition energies are calculated as the difference between the eigenvalue E_m of the excitonic matrix and the energy of the fully localized determinant.

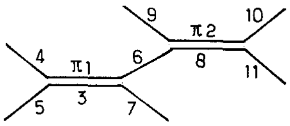
$$\Delta E_m = \langle \Psi_0^m | H | \Psi_0^m \rangle - \langle \Phi_0 | H | \Phi_0 \rangle .$$

We have studied three molecules, ethylene, butadiene and hexatriene.

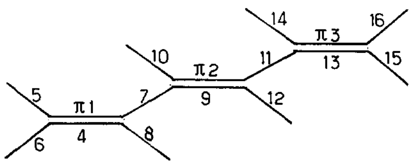
For ethylene and butadiene, the first excited state is a $\begin{pmatrix}\pi^*\\ \sigma\end{pmatrix}$ state, and the second excited state in these two molecules is a $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ state while for Hexatriene, the first excited state becomes the $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ state. In the same way, comparing the ordering of excited states for butadiene and hexatriene, one may notice that two $\begin{pmatrix}\pi^*\\ \sigma\end{pmatrix}$ states and three $\begin{pmatrix}\sigma^*\\ \pi\end{pmatrix}$ states ary lying between the two first $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ states of butadiene, while three $\begin{pmatrix}\pi^*\\ \sigma\end{pmatrix}$ states and zero $\begin{pmatrix}\sigma^*\\ \pi\end{pmatrix}$ states appear between the first two $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ states of hexatriene. These results are in agreement with the INDO calcula-



ethylene



butadiene



hexatriene

Fig. 2. Ethylene II A, butadiene II B, hexatriene II C with the numbering of the bonds (i.e. the MO's)

tions [13] including the CI between all singly excited determinants. But Clark and Ragle [14] using CNDO SCF CI method with spectrum fitted parameters [15] for a calculation of excited states of butadiene, have predicted many $\begin{pmatrix}\pi^*\\ \sigma\end{pmatrix}$ or $\begin{pmatrix}\sigma^*\\ \pi\end{pmatrix}$ states lying before the first $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ state which is obtained as the 7th state.

The assignment of the first band of Ethylene as a Berry band [16] was also found in Clark and Ragle calculations, by C. Giessner-Prettre and A. Pullman with both CNDO II and INDO method, when including in the CI matrix all the singly-excited configurations built from σ and π delocalized MO's [13], and by Kaldor and Shavitt in their non empirical LCAO-SCF with a minimal basis [17]. But theoretical work by Moskowitz [18] and co-workers [19] on the spectrum of ethylene showed that the $\begin{pmatrix}\pi^*\\ \sigma\end{pmatrix}$ excitations were rather close to the $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ excitation $({}^1A_g \rightarrow {}^1B_{1u})$ and might even fall below it in some olefins; Robin and co-workers [20], in their SCF-CI Gaussian orbital calculation on ethylene, claimed that the first band was a $\begin{pmatrix}\sigma^*\\ \pi\end{pmatrix}$ excitation (B_{2u}) where σ^* was interpreted as being composed partly of Rydberg 3*s* orbitals and partly of σ^* CH sigma valence-shell orbitals. Berthod [21] and Polak [22] had also found this first band as being a $\begin{pmatrix}\sigma^*\\ \pi\end{pmatrix}$ band.

From column 7 in Table 2, we notice that $\begin{pmatrix}\pi^*\\ \sigma\end{pmatrix}$ in these three molecules, the first $\begin{pmatrix}\pi^*\\ \sigma\end{pmatrix}$ excitation is a linear combination of the four $\Phi\begin{pmatrix}\pi^*\\ \sigma_{\mathrm{CH}}\end{pmatrix}$ configurations in Ethylene, and of the $\Phi\begin{pmatrix}\pi^*\\ \sigma_{\mathrm{CC}}\end{pmatrix}$ configuration (where σ_{CC} is the single bond adjacent to the π bonds) and of the $\begin{pmatrix}\pi^*\\ \sigma_{\mathrm{CH}}\end{pmatrix}$ configurations where σ_{CH} is adjacent to the

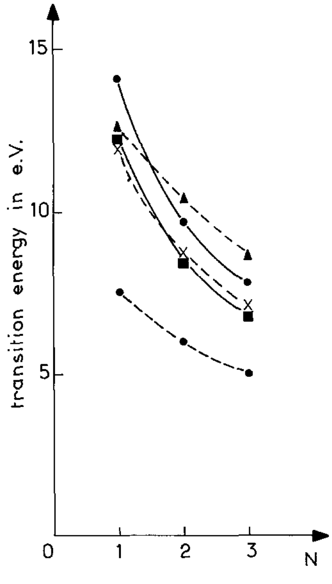


Fig. 3. Transition energy from the ground state to the first ${}^1\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ state. ●---● experimental values. ■——■ values obtained with the (π) excitonic matrix, the σ configurations being introduced by perturbation treatment. ×---× values obtained with the $(\sigma+\pi)$ excitonic matrix, ●——● values obtained with the (π) excitonic matrix, ▲---▲ values obtained with delocalized orbitals using a SCF-CI (with all monoexcited configurations) INDO method by Giessner-Prettre and Pullman [15]

π bond in butadiene and hexatriene. The second $\binom{\pi^*}{\sigma}$ state is predominantly represented by the $\binom{\pi^*}{\sigma_{CC}}$ configurations (where σ_{CC} belongs to the double bond) and the third $\binom{\pi^*}{\sigma}$ state is represented by the $\Phi\binom{\pi^*}{\sigma_{CH}}$ configurations, the three $\binom{\sigma^*}{\pi}$ states are predominantly represented by the $\Phi\binom{\sigma^*_{CH}}{\pi}$ configurations (when σ_{CH} bonds are adjacent to the double bonds).

Analysis of the $\binom{\pi^*}{\pi}$ wave function will be given in paragraph 7.

We have found a ${}^3\binom{\pi^*}{\pi}$ as the first triplet state in the three molecules we have studied so far. In butadiene and hexatriene the second triplet state is another ${}^3\binom{\pi^*}{\pi}$ state which is followed by a ${}^3\binom{\pi^*}{\sigma}$ triplet state (where σ is the single σ bond adjacent to the π bonds).

The calculated transition energies are collected in column 6 of Table 2.

3. $(\sigma-\pi)$ Mixing in the $\binom{\pi^*}{\pi}$ States

Table 2 shows that in the three molecules we have studied for the $\binom{\pi^*}{\pi}$ states, besides the $\binom{\pi^*}{\pi}$ delocalization or polarization configurations, one finds some $\binom{\sigma^*}{\sigma}$ polarization configurations (especially when σ_{CC} belongs to the double bond) with non-negligible weights. *Ab initio* calculations also show that the $\binom{\pi^*}{\pi}$ monoexcited states have important components on $\binom{\sigma^*}{\sigma}$ monoexcited configurations. For instance Dunning and McKoy calculated that in ethylene the $\binom{\sigma^*}{\sigma}$ configuration has a coefficient of 0.206 [10]. Denis and Malrieu on the basis of a second-order perturbation treatment [11] estimated that the effect of $\binom{\sigma^*_{CC}}{\sigma_{CC}}$ configurations is twice larger than the effect of $\binom{\sigma^*_{CH}}{\sigma_{CH}}$ configuration, and demonstrated that both of them decrease as n^{-1}.

We have calculated the $(\sigma-\pi)$ mixing as the difference between 1 and the sum of the square coefficients of all the $\Phi\binom{\pi^*}{\pi}$ configurations. The results obtained for the three molecules we have studied are shown in Table 3: The $(\sigma-\pi)$ mixing in the first $\binom{\pi^*}{\pi}$ decreases rapidly from ethylene (15.50%) to hexatriene (4.63%)

Table 2. Transition energies of singlet and triplet states obtained

1) after diagonalization of the $(\sigma+\pi)$ excitonic matrix, in column 6. $(E^t_{(\sigma+\pi)})$,
2) after diagonalization of the (π) excitonic matrix, in column 8 $(E^t_{(\pi)})$,
3) after diagonalization of the π excitonic matrix plus correction of the $\Phi\begin{pmatrix}\sigma^*\\ \sigma\end{pmatrix}$ configurations obtained by perturbation in column 9.

The values are given in eV, referred to the fully localized zeroth order ground state. In column 7, there are the coefficients (in absolute value) of the most important configurations representing a given excited state. The subscript $C^m_{(\sigma+\pi)}$ represents the coefficients obtained with the $(\sigma+\pi)$ excitonic matrix and the subscript $C^m_{(\pi)}$ represents the coefficient obtained with the (π) excitonic matrix ($C^m_{(\pi)}$ are the values between brackets in column 7).

See Fig. 2 for the numbering of MO's for ethylene, butadiene and hexatriene.

The subscript P_i refers to the polarization configuration $\begin{pmatrix}i^*\\ i\end{pmatrix}$. The subscript D_{ij} refers to the delocalization configuration $\begin{pmatrix}j^*\\ i\end{pmatrix}$ i and j are the numbers of two MO's.

Molecules	States			Experimental transition energies	$E^t_{(\varrho+\pi)}$	$C^m_{(\varrho+\pi)}(C^m_{(\pi)})$	$E^t_{(\pi)}$	$E^{t1}_{(\pi)}$
Ethylene	Singlet	$\begin{pmatrix}\pi^*\\ \sigma\end{pmatrix}$	$^1B_{1g}$		9.99	$D_{3,1}=D_{4,1}=D_{5,1}=D_{6,1}=0.50$		
		$\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$	$^1B_{1u}$	7.6 [17]	12.05	$P_1=0.91\ (1)$ $P_2=0.31$	14.19	12.38
		$\begin{pmatrix}\pi^*\\ \sigma\end{pmatrix}$	$^1B_{2g}$		12.07	$D_{21}=0.70$ $D_{3,1}=D_{4,1}=D_{5,1}=D_{6,1}=0.35$		
		$\begin{pmatrix}\sigma^*\\ \pi\end{pmatrix}$	$^1B_{2g}$		12.33	$D_{1,3}=D_{1,4}=D_{1,5}=D_{1,6}=0.46$ $D_{12}=0.39$		
		$\begin{pmatrix}\sigma^*\\ \pi\end{pmatrix}$	$^1B_{1g}$		12.75	$D_{1,3}=D_{1,4}=D_{1,5}=D_{1,6}=0.50$		
		$\begin{pmatrix}\sigma^*\\ \pi\end{pmatrix}$	$^1B_{3u}$		13.32	$D_{1,3}=D_{1,4}=D_{1,5}=D_{1,6}=0.50$		
	Triplet	$\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$	$^3B_{1g}$	4.6 [22]	8.11	$P_1=1\ (1)$	8.11	8.11
		$\begin{pmatrix}\pi^*\\ \sigma\end{pmatrix}$			9.99	$D_{3,1}=D_{4,1}=D_{5,1}=D_{6,1}=0.50$		
		$\begin{pmatrix}\pi^*\\ \sigma\end{pmatrix}$			12.07	$D_{21}=0.71$ $D_{3,1}=D_{4,1}=D_{5,1}=D_{6,1}=0.35$		

Table 2b

Molecules	States			Experimental transition energies	$E^t_{(\varrho+\pi)}$	$C^m_{(\varrho+\pi)}(C^m_{(\pi)})$	$E^t_{(\pi)}$	$E^{t1}_{(\pi)}$
Butadiene	Singlet I	$\begin{pmatrix}\pi^*\\ \sigma\end{pmatrix}$	^1B_u		8.67	$D_{6,1}=D_{6,2}=0.41$		
	II	$\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$	^1B_u	5.92 [23]	8.72	$P_1=P_2=0.55$ (0.54) $D_{1,2}=D_{2,1}=0.40$ (0.46) $P_3=P_8=0.13$	9.69	8.65
	III	$\begin{pmatrix}\pi^*\\ \sigma\end{pmatrix}$	^1A_u		9.76	$D_{3,1}=D_{8,2}=0.43$ $D_{7,1}=D_{9,2}=0.36$		
	IV	$\begin{pmatrix}\pi^*\\ \sigma\end{pmatrix}$	^1B_g		10.36	$D_{5,1}=D_{10,2}=0.41$		
	V	$\begin{pmatrix}\sigma^*\\ \pi\end{pmatrix}$	^1A_u		10.87	$D_{1,7}=D_{2,9}=0.53$		
	VI	$\begin{pmatrix}\sigma^*\\ \pi\end{pmatrix}$	^1B_g		11.38	$D_{1,4}=D_{2,11}=0.46$ $D_{1,7}=0.37$		
	VII	$\begin{pmatrix}\sigma^*\\ \pi\end{pmatrix}$	^1A_u		11.62	$D_{1,5}=D_{1,10}=0.54$		
	VIII	$\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$	^1A_g	7.20 [23]	11.78	$P_1=P_2=0.59$ (0.50) $D_{1,2}=D_{2,1}=0.25$ (0.50) $P_3=P_8=0.22$	13.69	12.34
	Triplet I	$\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$	^3B_u	3.20 [22]	5.99	$P_1=P_2=0.63$ (0.63) $D_{1,2}=D_{2,1}=0.32$ (0.32)	5.99	5.99
	II	$\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$	^3A_g	3.90 [22]	8.03	$P_1=P_2=0.69$ (0.69) $D_{1,2}=D_{2,1}=0.14$ (0.14)	8.03	8.03
	III	$\begin{pmatrix}\pi^*\\ \sigma\end{pmatrix}$			8.67	$D_{6,1}=D_{6,2}=0.41$ $D_{7,1}=D_{9,2}=0.34$		

Table 2c

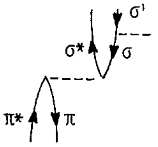
Molecules	States		Experimental transition energies	$E^t_{(\varrho+\pi)}$	$C^m_{(\varrho+\pi)}(C^m_{(\pi)})$	$E^t_{(\pi)}$	$E^{t1}_{(\pi)}$
Hexatriene	Singlet I	$\binom{\pi^*}{\pi}$	5 [25]	7.14	$P_2 = 0.60\ (0.57)$ $P_1 = P_3 = 0.31\ (0.31)$ $D_{1,2} = D_{3,2} = 0.32\ (0.34)$ $D_{2,1} = D_{2,3} = 0.29\ (0.32)$ $D_{1,3} = D_{3,1} = 0.12\ (0.15)$ $P_{13} = 0.14$	7.94	6.96
	II	$\binom{\pi^*}{\sigma}$		7.95	$D_{7,2} = D_{11,2} = 0.42$		
	III	$\binom{\pi^*}{\sigma}$		8.88	$D_{9,2} = 0.46$ $D_{10,2} = D_{12,2} = 0.42$		
	IV	$\binom{\pi^*}{\sigma}$		9.48	$D_{5,1} = D_{16,3} = 0.34$ $D_{7,1} = D_{11,3} = 0.34$		
	V	$\binom{\pi^*}{\pi}$		9.90	$P_1 = 0.53\ (0.47)$ $P_2 = 0\ (0)$ $D_{1,2} = D_{3,2} = 0.14\ (0.12)$ $D_{1,3} = D_{3,1} = 0.11\ (0.17)$ $D_{2,1} = D_{2,3} = 0.38\ (0.48)$ $P_4 = P_{13} = 0.16$	10.99	9.91
	VI	$\binom{\sigma^*}{\pi}$		10.43	$D_{2,10} = D_{2,12} = 0.55$	4.81	4.81
	Triplet I	$\binom{\pi^*}{\pi}$	2.6 [22]	4.81	$P_1 = P_3 = 0.33\ (0.33)$ $P_2 = 0.72\ (0.72)$ $D_{1,2} = 0.28\ (0.28)$ $D_{1,3} = D_{3,1} = 0.08\ (0.08)$ $D_{2,1} = D_{2,3} = 0.27\ (0.27)$		
	II	$\binom{\pi^*}{\pi}$		6.83	$P_1 = P_3 = 0.65\ (0.65)$ $P_2 = 10^{-4}\ (10^{-4})$ $D_{2,1} = D_{2,3} = 0.26\ (0.26)$ $D_{1,2} = D_{3,2} = 0.12\ (0.12)$ $D_{1,3} = D_{3,1} = 0.05\ (0.05)$	6.83	6.83

in conformity with the conclusions reached by Denis and Malrieu [11]; in the second $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ excited state, the $(\sigma-\pi)$ mixing decreases also with n, but it is always higher than in the first $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ excited state $\left(2.8\text{ and }2.4\text{ times larger than in the first }\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}\text{ state, for butadiene and hexatriene respectively}\right)$. The $(\sigma-\pi)$ mixing is predominantly due to the $\begin{pmatrix}\sigma^*_{\mathrm{CC}}\\ \sigma_{\mathrm{CC}}\end{pmatrix}$ polarization configurations (see Table 2) and the $\Phi\begin{pmatrix}\sigma^*_{\mathrm{CH}}\\ \sigma_{\mathrm{CH}}\end{pmatrix}$ polarization configurations have a light weight.

Table 3. $(\sigma\pi)$ mixing and weight of the $\Phi\begin{pmatrix}\sigma^*\\ \sigma\end{pmatrix}$ polarization configurations which interact directly with $\Phi\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ configurations and weight of the $\Phi\begin{pmatrix}\sigma'^*\\ \pi\end{pmatrix}$ delocalization configurations which interact indirectly $\left(\text{through the }\Phi\begin{pmatrix}\sigma^*\\ \pi\end{pmatrix}\text{ polarization configurations}\right)$ with the $\Phi\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ configurations

		State	Ethylene %	Butadiene %	Hexatriene %
	$(\sigma-\pi)$ mixing	Singlet I	15.50	6.00	4.63
		II		17.00	8.10
		Triplet I et II	0	0	0
Weights of configurations which interact directly	$\begin{pmatrix}\sigma^*\\ \sigma\end{pmatrix}$ polarization configurations	Singlet I	9.64	4.04	3.18
		II		9.50	5.42
with $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ configurations	$\begin{pmatrix}\sigma^*_{\mathrm{CH}}\\ \sigma_{\mathrm{CH}}\end{pmatrix}$ polarization configurations	Singlet I	0.64	0.46	0.40
		II		1.00	0.39
Weights of configurations which interact indirectly	$\begin{pmatrix}\sigma^*_{\mathrm{C=H}}\\ \sigma_{\mathrm{CH}}\end{pmatrix}$ delocalization configurations	Singlet I	3.18	0.76	0.40
		II		1.72	1.14
with $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ configurations	$\begin{pmatrix}\sigma^*_{\mathrm{C-C}}\\ \sigma_{\mathrm{CH}}\end{pmatrix}$ delocalization configurations	Singlet I		0.25	0.18
		II		0	0.09
	$\begin{pmatrix}\sigma^*_{\mathrm{CH}}\\ \sigma_{\mathrm{C=C}}\end{pmatrix}$ delocalization configurations	Singlet I	0.31	0.05	0.03
		II		0.46	0.09
	$\begin{pmatrix}\sigma^*_{\mathrm{CH}}\\ \sigma_{\mathrm{C-C}}\end{pmatrix}$ delocalization configurations	Singlet I		0.05	0.03
		II		1.02	0.11
	$\begin{pmatrix}\sigma'^*_{\mathrm{CH}}\\ \sigma_{\mathrm{CH}}\end{pmatrix}$ delocalization configurations with σ_{C} and σ'_{CH} gem bond	Singlet I	1.11	0.07	0.01
		II		0.57	0.07
	$\begin{pmatrix}\sigma'^*_{\mathrm{CC}}\\ \sigma_{\mathrm{CC}}\end{pmatrix}$ delocalization configurations	Singlet I		0.281	0.09
		II		1.57	0.17

So, with the perturbation treatment, the $\Phi\begin{pmatrix}\sigma'^*\\ \sigma\end{pmatrix}$ delocalization configurations would appear in the $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ states at the 2nd order only, and their introduction in the $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ states can be visualized by the following diagrams



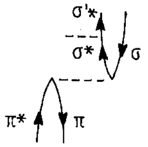


Table 3 shows that the $\Phi\begin{pmatrix}\sigma'^*_{\mathrm{CC}}\\ \sigma_{\mathrm{CH}}\end{pmatrix}$ delocalization configuration where σ_{CC} belongs to the double bond have a more important weight than the $\Phi\begin{pmatrix}\sigma'^*_{\mathrm{CC}}\\ \sigma_{\mathrm{CH}}\end{pmatrix}$ where σ_{CC} belongs to a single bond, and than the $\begin{pmatrix}\sigma^*_{\mathrm{CH}}\\ \sigma_{\mathrm{CC}}\end{pmatrix}$ configurations. This can be easily understood because when σ_{CC} belongs to a double bond, $\begin{pmatrix}\sigma^*_{\mathrm{CH}}\\ \sigma_{\mathrm{CC}}\end{pmatrix}$ interacts with $\Phi\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ configuration through the $\Phi\begin{pmatrix}\sigma^*_{\mathrm{CC}}\\ \sigma_{\mathrm{CC}}\end{pmatrix}$ polarization configuration (with σ_{CC} belonging to a double bond) which has a very strong interaction matrix element with the $\Phi\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ configurations.

4. Possibility of Treatment of the ($\sigma-\pi$) Mixing as a Perturbation

If we consider all the singly excited configurations (σ and π) as degenerate, it becomes impossible to treat the excited states of large molecules because the CI matrix will be too large. For a molecule with N bonds, the matrix involves $N^2 \times N^2$ elements (N polarization configuration $+ (N-1)\,N$ delocalization configurations). For hexatriene the CI matrix already is a 256×256 matrix (neglecting symmetry considerations).

Generally we are much more concerned by the $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ excited states, so it would be interesting to consider a (π) excitonic matrix with only the $\Phi\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ polarization and delocalization configurations. Thus for hexatriene we only have a 9×9 CI matrix. We will now demonstrate that such a thing is possible, and that the interaction of the $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ configurations with the $\begin{pmatrix}\sigma^*\\ \sigma\end{pmatrix}$ configurations may be considered as a perturbation.

Treating by perturbation theory the interaction of a $\Phi\binom{\sigma^*}{\sigma}$ configuration with the $\Phi\binom{\pi^*}{\pi}$ state of ethylene, the coefficient of $\Phi\binom{\sigma^*}{\sigma}$ in the first order perturbed wave function Ψ_1 will be given by

$$\frac{\left\langle \Phi\binom{\sigma^*}{\sigma} |H| \Phi\binom{\pi^*}{\pi} \right\rangle}{E\binom{\pi^*}{\pi^*} - E\binom{\sigma^*}{\sigma}} = 0.28$$

when σ and π bonds belong to the same double bond.

When the σ_{CH} is a single σ bond adjacent to the π bond, the expression is

$$\frac{\left\langle \Phi\binom{\sigma^*_{\mathrm{CH}}}{\sigma_{\mathrm{CH}}} |H| \Phi\binom{\pi^*}{\pi} \right\rangle}{E\binom{\pi^*}{\pi} - E\binom{\sigma^*_{\mathrm{CH}}}{\sigma_{\mathrm{CH}}}} = 0.04\,.$$

When the σ and the π bonds set wider apart, these coefficients become negligible.

So with a polyenic planar molecule, it is correct to consider as degenerate the $\Phi\binom{\pi^*}{\pi}$ polarization configurations and the $\Phi\binom{\pi'^*}{\pi}$ delocalization configurations only, and to treat the influence of the $\Phi\binom{\sigma^*}{\sigma}$ configurations as a perturbation.

5. Results of the π Excitonic Calculation

In Table 2, column 8, gives the transition energies obtained after diagonalization of the excitonic matrix containing the $\Phi\binom{\pi^*}{\pi}$ polarization and $\Phi\binom{\pi'^*}{\pi}$ delocalization configurations only.

The excitations energies obtained for the singlet states are higher than those calculated with the excitonic matrix containing σ and π monoexcited states, which shows the importance of the $\Phi\binom{\sigma^*}{\sigma}$ configurations in lowering the excitation energy from the ground state to a $\binom{\pi^*}{\pi}$ state. But the difference between the excitation energies calculated by diagonalization of these two excitonic matrices is more important for the second $\binom{\pi^*}{\pi}$ excited state than for the first $\binom{\pi^*}{\pi}$ one. We expected this result since the $(\sigma-\pi)$ mixing is stronger in the second $\binom{\pi^*}{\pi}$ excited state than in the first $\binom{\pi^*}{\pi}$ one. The difference ΔE between the excitation energies we obtain after the diagonalization of the two excitonic matrices, decreases while n increases. (For the first singlet state $\Delta E = 2.14$ eV for ethylene and 0.80 eV for hexatriene). For the triplet state the transition energy remains of course unchanged, when one goes from the $(\sigma+\pi)$ to the (π) excitonic treatment.

If we introduce the effect of the σ monoexcited configurations by a Rayleigh Schrödinger perturbation [6] on the multideterminantal Ψ_0^m wave functions resulting from the purely π excitonic treatment, we obtain the transitions energies given in Table 2, column 9. We can see that the interaction of $\Phi\begin{pmatrix}\sigma^*\\ \sigma\end{pmatrix}$ singly excited configurations lowers the transition energies, and comparison with the transition energies obtained after diagonalization of the excitonic matrix containing $(\sigma+\pi)$ monoexcited states, shows that for ethylene, the transition energy obtained after perturbation is only a little higher (0.33 eV) that the one obtained with the $(\sigma+\pi)$ excitonic matrix.

Experimentally, the separation between the lowest triplet and singlet states for ethylene, butadiene and hexatriene is respectively 3 eV, 2.8 eV, 2.6 eV [22]. With the (π) excitonic matrix we obtain 6.08 eV, 3.70 eV, and 3.13 eV, and with the $(\sigma+\pi)$ excitonic matrix we obtain 3.94 eV, 2.73 eV, and 2.33 eV: These last results are better than the first ones, because the $(\sigma-\pi)$ mixing only reduces the singlet energies. The results obtained with the $(\sigma+\pi)$ excitonic matrix are not too far from the experimental ones.

7. Analysis of the Wave Function of the $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ Excited States Obtained after Diagonalization of an Excitonic Matrix

A) Ionic Character of the Excited States

With the two types of excitonic matrices we have used, we show that the $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ states are not purely polarization or delocalization configurations, but a mixing of both excitations. This is in agreement with the introduction by Pople and Walmsley [7] of the delocalization configurations in the excitonic model. As was said by Salem [27], some ionic terms which appear in the molecular orbital wave function – those which give a charge separation within double bonds – can be found in the exciton states of Simpson, whereas others – for charge separation across the single bonds – are found in the charge transfer states only.

For hexatriene, in both first singlet and triplet states, the excitation tends to localize on the central bond but with a non negligible coefficient for the terminal bond polarization configurations while in the second singlet and triplet states, the excitation moves towards the two terminal bonds, with a completly negligible coefficient for the central bond polarization configurations. One may analyse from Table 4 the influence of the σ system on the ionic character of the $\pi\pi^*$ excited states.

a) In both singlet and triplet $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ states, the weight of the delocalization configurations (i.e. their ionic character) increases when the number n of double bonds increases. (From 0% in ethylene to 39.79% in hexatriene for the first singlet for instance).

Table 4. Weight of polarization and delocalization configurations in singlet and triplet states obtained with the ($\sigma+\pi$) excitonic matrix (4A) and with the (π) excitonic matrix (4B)

(4A)

Molecules	State	Ethylene %	Butadiene %	Hexatriene %
Weight of polarization configuration $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$	Singlet I	84.50	61.83	55.58
	II		70.50	57.03
	Triplet I	100	79.38	72.52
	II		95.22	83.72
Weight of delocalization configuration $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$	Singlet I	0	32.17	39.79
	II		12.50	34.87
	Triplet I	0	20.62	27.48
	II		4.78	16.28

(4B)

Molecules	State	Ethylene %	Butadiene %	Hexatriene %
Weight of polarization configuration $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$	Singlet I	100	58.10	51.37
	II		49.80	44.57
	Triplet I	100	73.38	72.52
	II		95.22	83.72
Weight of delocalization	Singlet I	0	41.90	48.63
	II		50.20	55.43
	Triplet I	0	20.62	27.48
	II		4.78	16.28

b) The ionic character is more pronounced for the singlet than for the triplet $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ states. This is due to the fact that the local neutral (polarization) triplet configurations have lower energies than the local polarization singlet configurations (${}^3E_{\text{pol}} = {}^1E_{\text{pol}} - 2K_{ii^*}$) while the local triplet and singlet delocalization configurations have the same energies (K_{ij^*} being zero in the CNDO hypothesis).

c) Except for ethylene, the weight of neutral (polarization) excitations in the $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ excited state is increased by the inclusion of the σ system in the excitonic matrix. This fact may be understood as follows. If the π wave function resulting from the π excitonic matrix diagonalization may be written as follows:

$$\Psi = \alpha \Psi^n + \beta \Psi^i ,$$

where Ψ^n and Ψ^i represent neutral and ionic structures, then the $\sigma-\pi$ interaction lowers the transition energy by an amount which increases when α increases. Therefore the best value of α in the ($\sigma+\pi$) treatment is higher in absolute value than in the purely π treatment. This fact also explains that the ($\sigma-\pi$) mixing is larger on the second $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ excited states (more strongly neutral) than in the first one.

d) One may notice that the inclusion of the $(\sigma-\pi)$ interaction may reverse the relative ionic character of the two first $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ singlet states; for instance in the butadiene molecule the (π) excitonic treatment gives respectively 58 and 50% of neutral character to the two first $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ singlet excited states of butadiene while the $(\sigma+\pi)$ excitonic treatment gives respectively 62 and 70%.

B) Charges and Charge-Fluctuations in the Double-Bonds Loges

In Table 5 the mean populations of each π double bonds (column 3, 4) show that the relatively high ionic character does not lead to significant net charges; The central loge gains 0.03 electrons in the lowest ${}^1\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ excited state, and lose 0.43 (in the π model) or 0.25 (in the $\sigma+\pi$ model) electron in the second ${}^1\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ excited state.

We have analyzed the fluctuations of the number of electrons in the loge. This statistical concept gives an insight on the delocalization of electrons from one volume to another. In the PCILO method for the ground state, this fluctuation is kept to zero in the zeroth order wave function. For the excited states we must introduce a rather important fluctuation of the bond charge in the zeroth order wave function.

It appears from Table 5 that the $(\sigma-\pi)$ coupling diminishes strongly the charge fluctuation in the excited states.

Table 5. Mean population and charge fluctuation in the double-bonds loges for the two first singlet states obtained with the $(\sigma+\pi)$ or (π) excitonic matrix

Molecules	State	Mean population in the first loge	Fluctuation in the first loge[a]	Mean population in the second loge[a]	Fluctuation in the second loge[a]
Butadiene	*First singlet*				
	$(\sigma+\pi)$ excitonic matrix	2	0.57		
	(π) excitonic matrix	2	0.65		
	Second singlet				
	$(\sigma+\pi)$ excitonic matrix	2	0.35		
	(π) excitonic matrix	2	0.71		
Hexatriene	*First singlet*				
	$(\sigma+\pi)$ excitonic matrix	1.98	0.46	2.04	0.61
	(π) excitonic matrix	1.99	0.51	2.03	0.67
	Second singlet				
	$(\sigma+\pi)$ excitonic matrix	2.13	0.41	1.75	0.51
	(π) excitonic matrix	2.22	0.51	1.57	0.51

[a] The first loge is the external one. The second loge is the central one in hexatriene.

Conclusion

At this stage of calculation, the numerical results suffer from three defects: a) the CI is limited to the single excitations, b) the Rydberg AO's are not included, c) the parameters have been fitted on ground state properties. Therefore we do not discuss in details the agreement between our calculated spectra and the experimental ones.

From a methodological point of view, one must notice the agreement between our results and those obtained from the diagonalization of the singly excited CI matrix built using SCF delocalized MO's [15]. If we used SCF localized MO's, the results would be identical, since the space of singly excited configuration is unvariant under the unitary transformations in the spaces of occupied or virtual MO's. We actually used fully localized MO's, and the similarity of our results with those of Giessner and Pullman shows the unimportance of the tails of localized SCF MO's, i.e. of the delocalization in the ground state.

The main purpose of this paper was to build and test a zero-order wave function using localized MO's. For $\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ transitions we had two possibilities; i) a $(\sigma+\pi)$ excitonic wave function, involving a rather large number of determinants; ii) a purely (π) excitonic wave function, which will only consider the $(\pi\to\pi^*, \sigma\to\sigma^*)$ coupling as a perturbation. The analysis of the wave functions shows that the $(\sigma-\pi)$ coupling has strong effects on the wave function (especially on the ionic character and charge fluctuations in the π system) but as concerns the energy it may be actually considered as a perturbation. At this stage the transition energies obtained with the CNDO/2 parameters are too high. But this is only a zeroth order model; the interaction of the ground state determinant with singly and doubly excited configurations and the interaction of the multiconfigurational wave function for the excited state with doubly and triply excited determinants will be taken into account through an appropriate second order perturbation treatment. The PCILO method for excited states so constructed will be developped in a further publication.

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