

# Configuration Mixing Involving $\sigma$ and $\pi$ Orbitals

## III. Diexcited Configurations in the CNDO and Modified CNDO Methods

CLAUDE GIESSNER-PRETTRE and ALBERTE PULLMAN

Institut de Biologie Physico-Chimique, Laboratoire de Biochimie Théorique  
13, rue P. et M. Curie, Paris 5è

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The  $\sigma$  plus  $\pi$  configuration interaction treatment, including doubly excited configurations is extended to the modified version of CNDO/2 proposed by Del Bene and Jaffé. The results are compared to experiment and to those given by the original method. The effect of double excitations on the electronic distribution and on the dipole moment is examined for both parametrizations.

Eine  $\sigma$ - und  $\pi$ -Konfigurationswechselwirkungsrechnung, die zweifach angeregte Konfigurationen einschließt, wird im Rahmen einer modifizierten Version des CNDO/2-Verfahrens, die von Del Bene und Jaffé vorgeschlagen wurde, durchgeführt. Die Resultate werden mit dem Experiment und mit denen der ursprünglichen Methode verglichen. Der Einfluß der Zweifach-Anregungen auf die Elektronenverteilung und das Dipolmoment wird für beide Parametrisationen untersucht.

Des calculs d'interaction de configuration  $\sigma$  plus  $\pi$ , introduisant les doubles excitations, sont effectués sur des fonctions d'onde obtenues par la méthode CNDO dans sa version modifiée par Del Bene et Jaffé. Les résultats sont comparés à ceux obtenus avec la paramétrisation originale et avec l'expérience. L'action des configurations diexcitées sur la distribution électronique et le moment dipolaire est examinée les deux paramétrisations.

### 1. Introduction

In spite of the speedy development of computing facilities, the possibilities of the treatment of large conjugated molecules in a completely non-empirical fashion are still limited, if only for financial reasons. As a substitute for more elaborate calculations, the CNDO procedure has been developed by Pople and his associates [1, 2] on the basis of an SCF treatment of all valence electrons, originally parametrized so as to reproduce as much as possible the results of non-empirical computations on small molecules. The simplifications brought about by the CNDO assumptions makes relatively easy the introduction of configuration mixing on a large scale, treating  $\sigma$  and  $\pi$  excitations simultaneously and we have recently undertaken a systematic study in this field. In the two previous papers of this series [3, 4], we have dealt with the effect of singly and doubly excited configurations on the energy values calculated in the CNDO/2 original parametrization, and shown that not only the singly-excited configurations have a strong effect, in particular by mixing the  $\pi\pi^*$  and  $\sigma\sigma^*$  excitations, but that the double excitations are by no means negligible and bring about an appreciable lowering of the ground state and important modifications in the ordering of the calculated transitions,

with a decrease in the number of parasit low-lying  $\sigma \leftrightarrow \pi$  transitions found either in the SCF approximation or with mixing of singly-excited configurations only. But the numerical agreement with experimental transitions is not improved by this configuration mixing.

Recently, a modified version of the CNDO procedure has been developed by Del Bene and Jaffé [5–8] aiming at the calculation of spectroscopic transitions, the essential modification involving the use of reduced electron-repulsion integrals (instead of theoretical ones) and of different proportionality constants to overlap for  $\sigma$  and  $\pi$  core integrals<sup>1</sup>. Transitions are calculated with inclusion of a small number of singly-excited configurations (thirty) and rather good agreement with experiment is obtained. Some remaining discrepancies [5, 6, 8] and our configuration mixing studies in CNDO/2, raised the question of the rôle that would be played by more extensive configuration mixing, especially with double excitations, inside the new parametrization. The present paper deals essentially with this question.

In a first part we give the calculated energy values of both the ground and excited states in the DBJ parametrization including the same amount of configuration mixing as in our previous CNDO/2 studies. In the second part we show the effect of the doubly-excited configurations on the calculated ground state properties, both in CNDO/2 and in DBJ. The molecules choosen for this study are the four small compounds previously studied [3, 4] ethylene, formaldehyde, formic acid and formamide, in which *all*  $\sigma$  and  $\pi$  *single excitations* can be introduced, and which have a small number of  $\pi \rightarrow \pi^*$  diexcitations.

The geometries adopted and the number of doubly excited configurations introduced are the same as in Ref. [4], namely 305 for  $C_2H_4$ , 279 (all) for  $H_2CO$ , 228 for  $HCOOH$  and 228 for  $HCONH_2$ .

## 2. Results and Discussion

### *Energy Values and Transitions*

Table 1 gives the energy values of the ground state and of the first excited singlets calculated in the virtual orbital approximation (VO), with inclusion of all the singly-excited configurations (CIS) and with doubly-excited configurations (CISD). The  $n \rightarrow \pi^*$  and first  $\pi \rightarrow \pi^*$  transitions for the three carbonyl compounds given in the first two colums are practically identical to the values given by Del Bene and Jaffé [8] in their approximation, the slight differences observed being probably due to differences in the input geometries.

### *Ethylene*

The first calculated transition in  $C_2H_4$  is a  $\pi \rightarrow \pi^*$  transition. Its location at 7.13 eV before configuration mixing is lowered to 6.37 eV by interaction with the singly excited  $\sigma \rightarrow \sigma^*$  configurations, but the introduction of double excitations lower the ground state by 0.64 eV so as to bring the transition back to 7 eV. These effects are *qualitatively* similar to those observed in CNDO, but very

<sup>1</sup> This parametrization will be called DBJ in the following pages.

Table 1. Energies of the ground state and of the first excited singlets before and after configuration mixing in the DBJ approximation (energies in eV referred to the SCF ground state). The type of transition indicated refers to the configuration with the largest weight. VO: virtual orbital approximation; CIS: all singly excited configurations; CISD: the same plus doubly excited configurations. For each molecule are given, under its name: the total number of singly-excited configurations, the total number of doubly excited configurations included, and the number of  $\sigma$  and  $\pi$  orbitals included in CISD. In parenthesis are indicated the coefficient of the lowest  $\pi \rightarrow \pi^*$  configuration in the state considered

	VO		CIS		CISD
	0		0		-0.64
Ethylene	7.13	$\pi \rightarrow \pi^*$	6.37	$\pi \rightarrow \pi^*$ (0.95)	6.37 $\pi \rightarrow \pi^*$
36, 305	8.17	$\sigma \rightarrow \pi^*$	8.17	$\sigma \rightarrow \pi^*$	7.79 $\sigma \rightarrow \pi^*$
	8.44	$\pi \rightarrow \sigma^*$	8.36	$\pi \rightarrow \sigma^*$	7.99 $\pi \rightarrow \sigma^*$
4 $\sigma$ , 1 $\pi$	8.88	$\sigma \rightarrow \pi^*$	8.86	$\sigma \rightarrow \sigma^*$	
4 $\sigma^*$ , 1 $\pi^*$	⋮		⋮		
	13.32	$\sigma \rightarrow \sigma^*$	13.06	$\sigma \rightarrow \sigma^*$	
	0		0		-0.68
Formaldehyde	3.50	$n \rightarrow \pi^*$	3.44	$n \rightarrow \pi^*$	2.89 $n \rightarrow \pi^*$
24, 279	8.92	$\sigma \rightarrow \pi^*$	8.89	$\sigma \rightarrow \pi^*$	7.42 $n \rightarrow \sigma^*$
	9.10	$n \rightarrow \sigma^*$	9.04	$n \rightarrow \sigma^*$	8.45 $\sigma \rightarrow \pi^*$
5 $\sigma$ , 1 $\pi$	9.97	$\pi \rightarrow \pi^*$	9.30	$\pi \rightarrow \pi^*$ (0.91)	8.88 $\pi \rightarrow \pi^*$
3 $\sigma^*$ , 1 $\pi^*$	11.56	$\pi \rightarrow \sigma^*$			10.08 $n \rightarrow C-H^*$
		$n \rightarrow C-H^*$			
	0		0		-0.37
Formic acid	4.28	$n \rightarrow \pi^*$	4.27	$n \rightarrow \pi^*$	3.75 $n \rightarrow \pi^*$
45, 228	8.29	$\pi \rightarrow \pi^*$	7.81	$\pi \rightarrow \pi^*$ (0.963)	7.22 $\pi \rightarrow \pi^*$
	8.75	$\sigma \rightarrow \pi^*$	8.53	$\sigma \rightarrow \pi^*$	8.24 $\sigma \rightarrow \pi^*$
3 $\sigma$ , 2 $\pi$	10.28	$n \rightarrow \sigma^*$	10.17	$\sigma \rightarrow \sigma^*$ (0.020)	8.74 $n \rightarrow \sigma^*$
4 $\sigma^*$ , 1 $\pi^*$	10.89	$\pi \rightarrow \sigma^*$	10.75	$\pi \rightarrow \sigma^*$	10.07 $\pi \rightarrow \sigma^*$
	0		0		-0.30
Formamide	4.22	$n \rightarrow \pi^*$	4.18	$n \rightarrow \pi^*$	3.82 $n \rightarrow \pi^*$
54, 228	7.73	$\pi \rightarrow \pi^*$	7.37	$\pi \rightarrow \pi^*$ (0.964)	6.59 $\pi \rightarrow \pi^*$
	9.43	$\sigma \rightarrow \pi^*$	8.68	$\pi \rightarrow \sigma^*$	8.32 $n \rightarrow \sigma^*$
3 $\sigma$ , 2 $\pi$	9.56	$\pi \rightarrow \sigma^*$	9.19	$\sigma \rightarrow \pi^*$	8.41 $\pi \rightarrow \sigma^*$
4 $\sigma^*$ , 1 $\pi^*$	9.88	$n \rightarrow \sigma^*$	9.58	$\sigma \rightarrow \sigma^*$ (0.046)	8.94 $\sigma \rightarrow \pi^*$

reduced quantitatively so that the transition, already reasonable without CI remains in the range of the experimental value for the  $N \rightarrow V$  transition. It must of course be kept in mind that the first excited singlet of ethylene is most probably twisted and elongated [9] so that a close fit with a calculated value is rather illusory. Whatever the experimental situation is, it is interesting to observe that in the DBJ procedure no  $\sigma \leftrightarrow \pi$  transition is found below the first  $\pi \rightarrow \pi^*$  singlet, before and after configuration mixing.

### Carbonyl Compounds

In paper I we have reviewed the experimental situation for the three compounds considered, in which the first transition is  $n \rightarrow \pi^*$ , the first  $\pi \rightarrow \pi^*$  singlet being located at much higher energies, 9 eV for  $H_2CO$ ; 8,3 eV in  $HCOOH$  and 7.2 eV in  $HCONH_2$ . Moreover, two intermediate  $\sigma \leftrightarrow \pi$  transitions are present in  $H_2CO$  and perhaps in  $HCOOH$  although the discussion on their exact nature is still open [10, 11, 12] as well as that of an unidentified band in formamide [13].

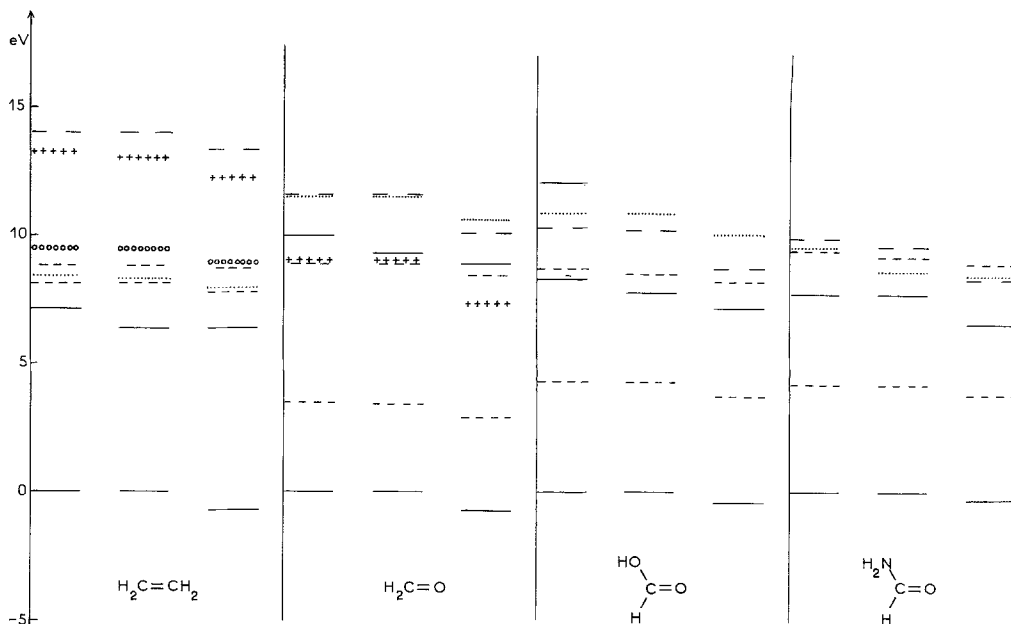


Fig. 1. — Ground state or  $\pi \rightarrow \pi^*$ . - - -  $\sigma \rightarrow \pi^*$  or  $n \rightarrow \pi^*$ . - · -  $\sigma \rightarrow \pi^*$  not interacting with the preceding ones. ·····  $\pi \rightarrow \sigma^*$ . ○○○○○○  $\pi \rightarrow \sigma^*$  not interacting with the preceding ones. — · —  $\sigma \rightarrow \sigma^*$  interacting with the  $\pi \rightarrow \pi^*$ . + + + + +  $\sigma \rightarrow \sigma^*$  not interacting with the  $\pi \rightarrow \pi^*$

The present calculation identifies the first band as  $n\pi^*$ , practically unperturbed by the singly excited configurations, the mixing with doubly excited configurations lowering both the ground state and the  $n \rightarrow \pi^*$  state so that the transitions remain practically unchanged. In CNDO the lowering of the ground state was so strong as to yield too large values of the  $n \rightarrow \pi^*$  transitions, whereas the final DBJ values are rather too small. As to the  $\pi \rightarrow \pi^*$  transitions they appear in a reasonable range even when comparing the three molecules to one another. Although the effect of the doubly excited configurations is small, it does not seem wise to neglect it entirely. This conclusion is still substantiated when one considers the  $\sigma \leftrightarrow \pi$  transitions where an inversion of states can occur ( $n \rightarrow \sigma^*$  of  $\text{H}_2\text{CO}$ ).

The situation in the four molecules is summarized in Fig. 1 in a diagram which can be compared to the corresponding CNDO diagram of paper II. It appears that *qualitatively* all the previously observed effects remain in the DBJ parametrization. But the perturbations are much smaller here than in CNDO and the transition energies even after CISD are close to the experimental values. The perturbation of the ground state is small but clearly non-negligible and this brings us to the next point of this investigation: the effect of the diexcited configurations on the calculated ground state properties.

### Ground State Structure and Dipole Moments

Even though the weight of the SCF ground configuration remains overwhelmingly high in the final ground state after CISD (95% in CNDO; 97–98%

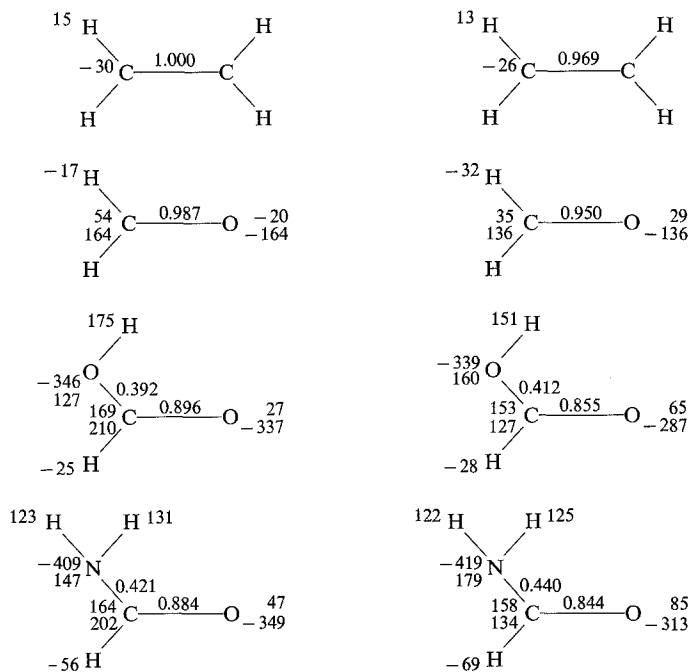


Fig. 2. Electron distribution in CNDO/2; left side: SCF, right side: after introduction of the doubly-excited configurations. Net electronic charges in  $10^{-3}$  electron units; upper number is  $\sigma$  charge, lower number is  $\pi$  charge. The  $\pi$  bond orders are indicated on the bonds

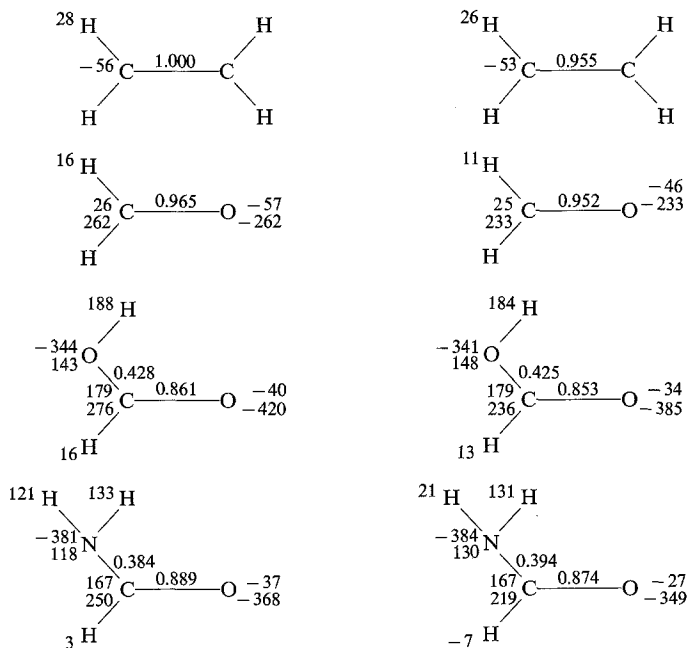


Fig. 3. Same as Fig. 1 in the DBJ parametrization

Table 2. Dipole moments (debye units, before and after configuration mixing) in CNDO/2 (upper value) and DBJ (lower value)

	Experimental [14]	CISD	SCF
H <sub>2</sub> CO	2.34	1.36 2.65	1.90 2.91
HCOOH	1.35–1.7	0.75 1.80	1.09 2.01
HCONH <sub>2</sub>	3.7	3.01 3.69	3.33 3.84

in DBJ), the number of non-negligible configurations suggests that their effect on the electronic charges may well be of importance. We have calculated this effect in both parametrizations, CNDO/2 and DBJ, for the four molecules considered and given them in Fig. 1 and 2 respectively.

A very constant feature observed in both procedures is that the inclusion of doubly-excited configurations increases the *s* character on all atoms (H included) and decreases the *p* character. Thus the hydrogens after configuration mixing retain more electrons than in the SCF result. The double-bond characters of C=C and C=O are decreased while that of CNH<sub>2</sub> and COH is increased; the  $\pi$  polarity of the carbonyl bond decreases but the  $\pi$  electron-pair of NH<sub>2</sub> and OH is more delocalized.

On the whole the general aspect of the electron distribution is not drastically modified by CISD, but the incidence of the changes on the calculated dipole moments is quite interesting. Table 2 summarizes the results for the two parametrizations. The effect is not very large and is a decrease of the moment in both CNDO/2 and DBJ, but since the CNDO values tended to be already too small, the effect of configuration mixing bring them farther from the experimental values. On the contrary the DBJ moments were too large and their decrease brings about a rather satisfactory fit with experiment. The non-empirical calculation of Peyerhimmhoff and Buenker [15] on formic acid also gives a value of the molecular dipole moment which is smaller in the CISD than in the SCF approximation. Thus, the decrease obtained in our calculations is probably not due to the approximations developed in the semi-empirical methods. Of course more studies will be needed so as to assess the generality of these conclusions, but the present work seems to confirm the suggestion [8] that the DBJ parametrization is appropriate not only for the calculation of transition energies.

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Dr. A. Pullman  
Institut de Biologie Physico-Chimique  
Laboratoire de Biochimie Théorique  
13, rue P. et M. Curie  
F-75 Paris 5<sup>e</sup>, France