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# Configuration Mixing Involving σ and π Orbitals

## IV. Introduction of the Neglected Configurations by Second-Order Perturbation Theory

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Second order perturbation theory is used to calculate the energy lowering due to all σ and π double excitations on the ground state, and of all σ and π double and triple excitations on the first excited singlets. The values obtained are compared to previous results coming from configuration interaction calculations including all single and some double excitations. The computations are carried out on CNDO/2 and Del Bene-Jaffé wavefunctions.

Mit Hilfe der Störungstheorie zweiter Ordnung wird die Energieerniedrigung berechnet, die durch Einschluß aller σ- und π-Doppelanregungen auf den Grundzustand, sowie durch Berücksichtigung aller doppelten und dreifachen σ- und π-Anregungen auf die ersten angeregten Singuletzustände bewirkt wird. Die so erhaltenen Werte werden mit Ergebnissen früherer CI-Rechnungen, die unter Berücksichtigung aller einfachen und einiger doppelter Anregungen erhalten wurden, verglichen. Die Berechnungen werden mit CNDO/2- und Del Bene-Jaffé-Wellenfunktionen durchgeführt.

On utilise une méthode de perturbation au deuxième ordre pour calculer l'abaissement d'énergie dû à l'interaction de toutes les configurations diexcitées (σ et π) sur l'état fondamental, et à l'interaction de toutes les configurations di- et triexcitées (σ et π) sur les premiers états excités. Les valeurs obtenues sont comparées aux résultats antérieurs de l'interaction de configuration incluant les états monoexcités et certains diexcités. Les calculs sont effectués sur des fonctions d'onde de type CNDO et Del Bene-Jaffé.

In the previous articles of this series [1–3] we have studied, within the framework of SCF all-valence electron treatments, the importance of singly and doubly excited configurations on the computed energies of the different excited states and on the energy and electron distribution of the ground state. Although our calculations were limited to small and medium-size molecules ranging from formaldehyde to benzene, the size of the matrices to be handled precluded the inclusion of all the double excitations in the treatment except for formaldehyde. Thus, we could not undertake to consider triple excitations, although these are, with respect to singly excited states, equivalent to doubly excited configurations interacting with the ground state.

The existing configuration interaction calculations have, as a rule, shown that triple and higher excitations have a rather small and essentially translationnal effect on most molecular states. However all these computations either have been carried out on small systems [4–7] or take into account a very limited number of molecular orbitals only (generally π orbitals) [8–17]. These studies leave unanswered the question of the role of double excitations of high energy and the role of $\sigma + \pi$ triple excitations in conjugated compounds, the size of which definitely forbids a complete configuration mixing calculation.

To overcome this deficiency, we have turned to second-order perturbation formalism which can introduce, although approximately, all double and triple excitations without the need of solving large matrices.

Several perturbation treatments have been used for the calculation of the ground state correlation [9, 17, 18], in which case comparison with configuration mixing showed that the two methods lead to similar results. For the excited states, Jungen, Labhart and Wagnière [19] found perturbation results very different from configuration mixing or open shell results for the $n \rightarrow \pi^*$ state of formaldehyde. On the contrary Denis and Malrieu [20] and Vischer and Falicov [21] have obtained by second order perturbation on $\pi$ electrons, results which run parallel to those of configuration mixing calculations.

None of these calculations tended to examine the role of extensive $\sigma$ plus $\pi$ configuration mixing on ground and excited states with the exception of the work of Denis and Malrieu [22] on linear polyenes which includes $\sigma$ electrons (supposed to be localized) in the treatment of the two first $\pi \rightarrow \pi^*$ transitions. In the present study we calculate by second-order perturbation theory (hereafter called SOPT) on delocalized SCF orbitals the $\sigma$ plus $\pi$ correlation energy on the ground states and on the first excited singlets of some small conjugated compounds.

## Approximations

The second order perturbation calculations are made according to the procedure developped by Claverie, Diner and Malrieu [23–25]. In this procedure (using an Epstein-Nesbet expansion) one first calculates the second order correction to the ground state energy of the molecule and then directly the same quantity for the SCF transition energy which corresponds to the desired excited state. The corresponding correction on the excited state is easily deduced from these quantities. If the excited state is made of degenerate single excitations *with no common molecular orbital*, it can be handled by the method utilized by Denis and Malrieu [22].

The computations are made within the framework of CNDO/2 with the original parametrization [26] and with Del Bene and Jaffé's parametrization [27] (called respectively CNDO/2 and DBJ hereafter). Thus the present results are strictly comparable to those obtained by configuration mixing on the same molecules in our previous papers.

With DBJ parametrization the calculations were run for the ground state and excited states for ethylene, formaldehyde, formic acid and formamide. The excited states of only the first two molecules could be treated with the CNDO/2 parametrization because of degeneracies we are not able to handle with the available programs.

## Results

We shall examine separately the results for the ground state and the excited singlets.

### *1. Ground State*

The energy lowering of the ground state is reported in Table 1 (column 3) together with the corresponding quantity obtained from configuration mixing of single plus double excitations (CISD) (column 1). In both parametrizations the perturbation calculation give larger energy gain than CISD. In order to separate the effect of the configurations neglected in CISD from the role of higher perturbation order we reran the perturbation taking into account only the double excitations included in CISD. These energy gains (Table 1, columns 2 and 5) are then more similar to (although larger than) those from CISD. Clearly also, stopping at second-order overemphasizes the effect. The proximity of the numerical values given by CISD or SOPT when the same configurations are introduced is in accord with similar results obtained either in *ab initio* calculations [9, 17, 18] or in $\pi$-electrons calculations [21]. It is worth noticing that for ethylene the *ab initio* calculation of Polak and Paldus [9] found by perturbation an energy gain of 2.43 eV whereas CNDO/2 gives 2.63 eV, the two values being very close.

The difference between the limited and the complete perturbation calculation would tend to show that with limited configuration mixing one misses most of the ground state energy lowering in spite of the large number of configurations retained. For ethylene, only the configurations introducing the deepest filled and the highest empty orbitals were neglected and we are anyway missing nearly half of the effect.

A perturbation calculation has the advantage over configuration mixing to evaluate separately the contribution of each double excitation. In the last column of Table 1, we give the energy gain obtained from the most important double excitations, namely those which contribute more than 0.01 eV with the DBJ parametrization. Under the value of the energy we give the number of configurations responsible for this effect. If we compare these values to the corresponding CISD values we see that a small number of properly chosen double

Table 1. *Energy gain* (eV) *of the ground state calculated by configuration interaction including single and double excitations* (CISD) *and by second order perturbation theory* (SOPT)

| | CNDO[a] | | | DBJ[b] | | | |
|---|---|---|---|---|---|---|---|
| | CISD | SOPT | | CISD | SOPT | | |
| | | (1) | (2)[d] | | (1) | (2) | (3) |
| Ethylene | 1.33 | 1.38 | 2.63 | 0.64 (169)[c] | 0.68 | 1.25 | 1.07 (47)[c] |
| Formaldehyde | 2.45 | 3.45 | 3.45 | 0.68 (152)[c] | 0.78 | 0.78 | 0.68 (26)[c] |
| Formic acid | 2.16 | 2.77 | 4.98 | 0.37 (130)[c] | 0.41 | 0.94 | 0.70 (33)[c] |
| Formamide | 1.27 | 1.47 | 4.19 | 0.30 (130)[c] | 0.31 | 0.98 | 0.44 (24)[c] |

(1) Limited to the double excitations included in CISD.
(2) Including all the double excitations.
(3) Including the double excitations which contribute more than 0.01 eV.

[a] With CNDO/2 original parametrization.

[b] With Del Bene and Jaffé's parametrization.

[c] Number of doubly excited configurations included.

[d] The difference between the numbers in this column and those given by Diner, S., Malrieu, J. P., Jordan, F., Gilbert, M.: Theoret. chim. Acta (Berl.) **15**, 100 (1969) is due to different molecular geometries.

excitations can lead to a better energy. For example, for ethylene, 47 "good" double excitations lower the energy by 1.07 eV whereas the 169[1] first doubly excited states yield a gain of only 0.68 eV. This result supports the suggestion made by several authors and based on similar findings [6, 9, 18] to use SOPT as a criterion for the choice of the double excitations to be included in configuration mixing when one is interested in the ground state only.

CISD and SOPT agree to find that double excitations which introduce at least one $\pi \rightarrow \pi^*$ jump are the most important for the energy gain.

## 2. *Excited States*

The energies of the first excited states calculated by SOPT with DBJ wave functions and integrals are collected in Table 2, CISD being given in the first column for comparison. Column 3 give the results of the complete perturbation calculation whereas in column 2 the effect of the triply excited states has been taken out. Thus, we can separate the roles of double and triple excitations. The results obtained for the four molecules have one feature in common: *the introduction of triple excitations is responsible for a simple translation of all the excited states* but does not produce any crossing between the different excited states contrary to double excitations. This is in agreement with previous calculations [7, 11, 15]

Table 2. *Energies of the ground state and of the first excited singlets calculated by configuration mixing* (CISD) *and second-order perturbation* (SOPT) *in* DBJ *parametrization. (Energies in* eV *referred to the* SCF *ground state)*

| | CISD | SOPT | |
|---|---|---|---|
| | | (1) | (2) |
| Ethylene | −0.64 | −1.25 | −1.25 |
| | 6.37 $\pi \rightarrow \pi^*$ | 6.26 $\pi \rightarrow \pi^*$ | 5.30 $\pi \rightarrow \pi^*$ |
| | 7.79 $\mathrm{CH} \rightarrow \pi^*$ | 7.83 $\mathrm{CH} \rightarrow \pi^*$ | 6.89 $\mathrm{CH} \rightarrow \pi^*$ |
| | 7.99 $\pi \rightarrow \mathrm{CH}^*$ | 8.05 $\pi \rightarrow \sigma^*$ | 7.11 $\pi \rightarrow \sigma^*$ |
| Formaldehyde | −0.68 | −0.78 | −0.78 |
| | 2.89 $n \rightarrow \pi^*$ | 3.07 $n \rightarrow \pi^*$ | 2.50 $n \rightarrow \pi^*$ |
| | 7.42 $n \rightarrow \sigma^*$ | 6.78 $n \rightarrow \sigma^*$ | 6.17 $n \rightarrow \sigma^*$ |
| | 8.45 $\sigma \rightarrow \pi^*$ | 8.60 $\sigma \rightarrow \pi^*$ | 8.04 $\sigma \rightarrow \pi^*$ |
| | 8.88 $\pi \rightarrow \pi^*$ | 8.77 $\pi \rightarrow \pi^*$ | 8.17 $\pi \rightarrow \pi^*$ |
| | 10.08 $n \rightarrow \mathrm{CH}^*$ | 9.08 $n \rightarrow \mathrm{CH}^*$ | 8.73 $n \rightarrow \mathrm{CH}^*$ |
| Formic acid | −0.37 | −0.94 | −0.94 |
| | 3.75 $n \rightarrow \pi^*$ | 3.75 $n \rightarrow \pi^*$ | 3.04 $n \rightarrow \pi^*$ |
| | 7.22 $\pi \rightarrow \pi^*$ | 6.78 $\pi \rightarrow \pi^*$ | 6.06 $\pi \rightarrow \pi^*$ |
| | 8.24 $\sigma \rightarrow \pi^*$ | 7.52 $n \rightarrow \sigma^*$ | 6.75 $n \rightarrow \sigma^*$ |
| | 8.74 $n \rightarrow \sigma^*$ | 8.06 $\sigma \rightarrow \pi^*$ | 7.38 $\sigma \rightarrow \pi^*$ |
| Formamide | −0.30 | −0.98 | −0.98 |
| | 3.82 $n \rightarrow \pi^*$ | 3.77 $n \rightarrow \pi^*$ | 3.02 $n \rightarrow \pi^*$ |
| | 6.59 $\pi \rightarrow \pi^*$ | 5.99 $\pi \rightarrow \pi^*$ | 5.25 $\pi \rightarrow \pi^*$ |
| | 8.32 $n \rightarrow \sigma^*$ | 6.90 $n \rightarrow \sigma^*$ | 6.10 $n \rightarrow \sigma^*$ |
| | 8.41 $\pi \rightarrow \sigma^*$ | 7.83 $\pi \rightarrow \sigma^*$ | 7.09 $\pi \rightarrow \sigma^*$ |

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[1] By first we mean those built from highest filled and lowest empty molecular orbitals.

but should no longer be true for high excited states [7, 15]. The lowering of the excited states due to triple excitations is numerically about 75 to 80% of the corresponding effect of double excitations on the ground state.

The perturbation limited to single and double excitations give a different ordering of the excited states of formic acid when compared to the CISD results. Since this molecule is one of the two for which we had to neglect a relatively important number of double excitations, it underlines the importance of double excitations for the spacing of molecular excited states.

In the case of formaldehyde, the CISD calculation introduced all the double excitations so that the differences between column 1 and column 2 are due entirely to orders of perturbation higher than two. It is interesting to notice that these higher orders contributes with a different sign to the excited states according to their $\sigma \leftrightarrow \pi$ or $\sigma \to \sigma^*$ plus $\pi \to \pi^*$ nature.

The perturbation calculation confirms that $\pi \to \pi^*$ and especially $\sigma \to \sigma^*$ transitions are more lowered by interacting with doubly excited configurations than the $\sigma \leftrightarrow \pi$ ones. The very strong effect observed in the CISD results [2, 3] of the $\pi\sigma \to \sigma^*\pi^*$ states on the $\sigma \to \sigma^*$ transitions is still emphasized in the present perturbation calculations. This effect is however probably overestimated when stopping at second order, since in formaldehyde it is for $\sigma \to \sigma^*$ states that the differences between CISD and SOPT calculation are the largest (up to 1.0 eV for $n \to \mathrm{CH}^*$).

This effect is again underlined for formaldehyde and ethylene if the original parametrization of CNDO/2 is used. In Table 3 we see that four high $\mathrm{CH} \to \sigma^*$ transitions are lowered enough to be brought below the $\pi \to \pi^*$ states; in formaldehyde SOPT brings about a crossing of the $n \to \mathrm{CH}^*$ and $\sigma \to \pi^*$ transitions.

Table 3. *Energies of the ground state and of the first excited singlets calculated by configuration mixing* (CISD) *and second order perturbation treatment* (SOPT[a]) *in the* CNDO/2 *original parametrization. (Energies in* eV *referred to the* SCF *ground state)*

| | CISD | SOPT |
|---|---|---|
| Ethylene | −1.33 | −2.63 |
| | 9.70 $\mathrm{CH} \to \pi^*$ | 7.93 $\mathrm{CH} \to \pi^*$ |
| | 11.46 $\pi \to \sigma^*$ | 9.08 $\sigma \to \pi^*$ |
| | 11.80 $\sigma \to \pi^*$ | 9.32 $\mathrm{CH} \to \sigma^*$ |
| | 12.00 $\pi \to \mathrm{CH}^*$ | 9.34 $\mathrm{CH} \to \sigma^*$ |
| | 12.07 $\pi \to \pi^*$ | 9.40 $\pi \to \sigma^*$ |
| | 12.21 $\pi \to \sigma^*$ | 9.85 $\pi \to \pi^*$ |
| | 13.24 $\mathrm{CH} \to \sigma^*$ | 9.88 $\mathrm{CH} \to \mathrm{CH}^*$ |
| | 13.38 $\mathrm{CH} \to \mathrm{CH}^*$ | 10.02 $\pi \to \mathrm{CH}^*$ |
| Formaldehyde | −2.45 | −3.45 |
| | 3.00 $n \to \pi^*$ | 1.03 $n \to \pi^*$ |
| | 7.38 $n \to \sigma^*$ | 3.68 $n \to \sigma^*$ |
| | 8.24 $\sigma \to \pi^*$ | 5.33 $n \to \mathrm{CH}^* (\pi \to \pi^*)$ |
| | 9.18 $n \to \mathrm{CH}^* (\pi \to \pi^*)$ | 6.46 $\sigma \to \pi^*$ |
| | 11.18 $\pi \to \sigma^*$ | 6.64 $\pi \to \pi^*$ |
| | 11.28 $\sigma \to \sigma^* (\pi \to \pi^*)$ | 6.64 $n \to \sigma^*$ |
| | 11.56 $n \to \sigma^*$ | 9.19 $\pi \to \sigma^*$ |

[a] As in case (2) of Tables 1 and 2.

The fact that more extensive configuration interaction has a larger effect in the CNDO parametrization than in the DBJ parametrization parallels the effect observed by Koutecký [28], in $\pi$ Pariser-Parr-Pople calculations with different repulsion integral values.

The examination of the contributions of the different excited configurations to a given transition shows that, like for the ground state, a relatively small number of them give a contribution (of either sign) larger than 0.01 eV to the transition energy. In formaldehyde for example, only 20 different excitations are important for each of the first transitions, but unfortunately only few of them are common to the different excited states. This result seems independent of the molecule and of the parametrization. The comparison of the calculated spectra with DBJ parametrization at the various levels of approximations with the experimental values[2] shows that the introduction of triple excitations lowers too much the energy of the excited singlets. The approximation limited to double excitations either by CISD or by SOPT compares more favorably with experiment. For the two molecules runned in CNDO/2 the calculated values remain too high.

## Conclusion

From this work it appears that high-lying doubly excited configurations cannot be neglected *a priori* in a configuration mixing calculation since they can be responsible for an appreciable fraction of the ground state energy lowering. The same conclusion seems to be valid for excited singlets. This result suggests as a reasonable practical attitude the initial use of perturbation calculations for choosing the excitations which should be retained in an optimized configuration mixing computation.

On the contrary triple excitations do not seem to have a large importance in the ordering or in the spacing of the different excited singlets; their only role seems to be to decrease all the excitation energies.

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[2] For the experimental spectra, the values and references are given in the first article (1) of the series.

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