

PCILO Method for Excited States

II. 2nd Order Corrected Transition Energies

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The zeroth order excitonic wave-function built previously is considered as a zeroth order wave-function for the excited state. The interaction with other singly, doubly and triply excited determinants is taken into account through a 2nd order perturbation process. A proper definition of the unperturbed Hamiltonian allows cancellation between the ground state and excited state series, and thus the direct calculation of transition energies. The complete localization of MO's in the CNDO approximation makes the calculation very rapid. The method is applied to the series of linear polyenes $H-(CH=CH)_N-H$ ($2 \leq N \leq 7$) with the CNDO/2 parametrization. The evolution of the excitonic wave-function is analyzed.

Die zuvor konstruierte excitonische Wellenfunktion nullter Ordnung wird als Wellenfunktion nullter Ordnung für den angeregten Zustand verwendet. Die Wechselwirkung mit anderen einfach, doppelt und dreifach angeregten Determinanten wird mittels Störungsrechnung 2. Ordnung berücksichtigt. Bei geeigneter Wahl des ungestörten Hamiltonoperators hebt sich der Grundzustand bei Berechnung der Übergangsenergien heraus, was auf ihre direkte Bestimmung hinausläuft. Die vollständige Lokalisierung der MO's hat zur Folge, daß bei Anwendung des CNDO-Verfahrens die Berechnung sehr schnell vonstatten geht. Die Methode wird auf die Reihe linearer Polyene des Typs $H-(CH=CH)_N-H$ ($2 \leq N \leq 7$) angewendet (CNDO/2-Parametrisierung). Die excitonische Wellenfunktion wird bezüglich der Zellenpopulation und deren Schwankungen untersucht.

On prend la fonction d'onde excitonique déjà construite comme fonction d'onde d'ordre zéro pour l'état excité. L'interaction avec les autres déterminants monoexcités, les déterminants di- et tri-excités est prise en considération par une perturbation au 2^e ordre. Un choix judicieux de l'Hamiltonien non perturbé met en évidence d'importantes suppressions entre les séries de l'état excité et de l'état fondamental, et par conséquent le calcul direct des énergies de transition. Malgré le caractère multiconfigurationnel de Ψ_0 , la localisation complète des OM rend le calcul extrêmement rapide dans les hypothèses CNDO. La méthode est appliquée à la série des polyènes linéaires $H-(CH=CH)_N-H$ ($N = 2$ à 7). Analyse de la fonction d'onde excitonique en terme de populations de loge et de leur fluctuations.

The use of fully localized Molecular Orbitals (MO's) for the ground state energy calculation appeared to be very interesting from both computational and interpretative points of view [1]. The PCILO (Perturbative Configuration Interaction from Localized Orbitals) method [2] built along this scheme has been widely used for conformational studies. This method, at least with the CNDO [3] approximations on the atomic integrals, is much more rapid than the usual variational methods. The use of localized MO's for the excited states representations generally requires multiconfigurational wave functions. The well-known excitonic methods [4] use fully localized MO's and represent the excited

state as a linear combination of local single excitations. The linear combination results from the solution of the Configuration Interaction (CI) problem between the singly excited determinants. In the preceding paper of this series [5], the construction of such wave-functions have been analyzed for conjugated systems, and it has been proved that the $\pi\pi^*$ transitions might be treated as linear combinations of $\pi\pi^*$ local single excitations, the $(\sigma - \pi)$ coupling which mixes the $\pi\pi^*$ and $\sigma\sigma^*$ excitations being treated by perturbational methods with a sufficient accuracy.

But such excitonic wave functions may only be considered as zeroth-order wave-functions. When one treats the ground state problem one takes into account all the singly and doubly excited determinants which interact with the zeroth-order ground state determinant, and which introduce respectively delocalization and correlation effects [2]. The linear combination of singly excited determinants will interact with the ground state determinant, and with numerous doubly and triply excited determinants. In order to calculate a reasonable transition energy, one must take into account in a coherent way both the interactions with the ground state determinant and with the excited state zeroth order wave-function. The present paper proposes a method which calculates second order corrected transition energies; the second order energy corrections are calculated from both the fully localized single determinant for the ground state and the excitonic multiconfigurational wave-function for the excited state. A convenient definition of the unperturbed Hamiltonian H^0 allows important cancellations between the two series. Due to these cancellations, the computational time of the transition energy is analogous to that of the ground state energy calculations, despite the multiconfigurational character of the excited state and the very great number of doubly and triply excited configurations included in the process.

1. Method

The zeroth order wave-function Ψ_m^0 is a linear combination of certain number of determinants, defining a subspace S

$$\Psi_m^0 = \sum_{I \in S} c_{mI} \Phi_I, \quad (1)$$

For the $\pi\pi^*$ transitions, the states Φ_I will be the singly excited $\pi\pi^*$ determinants

$$\Phi \binom{j^*}{i} = a_{j^*}^\dagger a_i \Phi_0 \quad \Psi_m^0 = \sum_i \sum_{\substack{j \\ \in \{\pi\}}} c_{mij^*} \Phi \binom{j^*}{i}. \quad (2)$$

The coefficients c_{mij^*} are obtained from the diagonalization of the CI matrix restricted to the S subspace, i.e. the π excitonic matrix. Therefore the interaction matrix elements between the zeroth wave functions of two $\pi\pi^*$ excited states Ψ_m^0 and Ψ_n^0 are zero.

$$\langle \Psi_m^0 | H | \Psi_n^0 \rangle = 0.$$

The CI matrix restricted to subspace S is diagonal in the basis of the function Ψ_m^0 .

Now one performs a change of the basis set of the CI in the subspace S ; the determinants outside of S are kept unchanged. Therefore the new basis is now

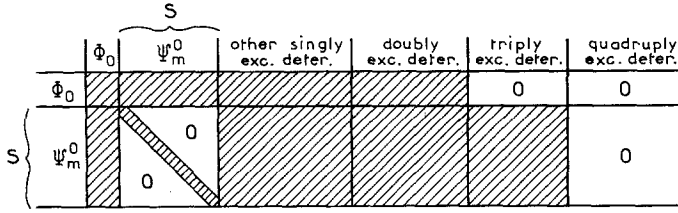


Fig. 1. Structure of the interactions between the excitonic wave-functions Ψ_m^0 with the various functions of the new basis set of the CI matrix. Φ_0 is the ground state single determinant

- i) the multiconfigurational wave functions Ψ_m^0 in the subspace S ,
- ii) the single determinants Φ_j outside of S_0 .

Since the singly excited determinants $\Phi_i^{(j*)}$ belonging to S interact with other singly excited determinants outside of S and some doubly and triply excited determinants, the states Ψ_m^0 also interact with these determinants, as illustrated in Fig. 1.

We shall take into account through a second order perturbation process the interactions of the excitonic wave-function Ψ_m^0 for the state m with the ground state determinant on one hand and with the various excited determinants outside of S on the other hand.

In the second order energy, the summation is restricted to the determinants outside of S :

$$\varepsilon_m^2 = \sum_{I \notin S} \frac{\langle \Psi_m^0 | \mathbf{H} | \Phi_I \rangle^2}{E_m^0 - E_I^0} \quad (3)$$

where E_m^0 and E_I^0 are the zeroth order energies associated with the state m and the determinant Φ_I

$$\mathbf{H}^0 \Psi_m^0 = E_m^0 \Psi_m^0 \quad (4)$$

$$\mathbf{H}^0 \Phi_I = E_I^0 \Phi_I; \quad \text{for } I \notin S. \quad (5)$$

\mathbf{H}^0 will be defined by these relations, and by a proper choice of E_m^0 and E_I^0 .

E_I^0 will be taken as the mean value of the exact Hamiltonian for the state Φ_I , according the Epstein-Nesbet partition of the total Hamiltonian [6].

$$E_I^0 = \langle \Phi_I | \mathbf{H} | \Phi_I \rangle. \quad (6)$$

E_m^0 will not be taken according to the same definition which would lead to absurd dependencies of the transitions energies to the number of particles [7]. We use a "barycentric" definition of \mathbf{H}^0 for the state m

$$E_m^0 = \sum_{I \in S} c_{mI}^2 \langle \Phi_I | \mathbf{H} | \Phi_I \rangle \quad (7)$$

E_m^0 differs from the eigenvalue E'_m of the excitonic matrix. If P_s is the projector on the subspace S ,

$$P_s \mathbf{H} P_s \Psi_m^0 = E'_m \Psi_m^0 \quad (8)$$

$$E'_m = \langle \Psi_m | \mathbf{H} | \Psi_m \rangle = \sum_I \sum_{J \in S} c_{mI} c_{mJ} \langle \Phi_I | \mathbf{H} | \Phi_J \rangle. \quad (9)$$

As will be shown further on, this definition of E_m^0 will lead to important cancellations in the calculation of the transition energy.

The second order energy may be developed.

$$\begin{aligned} \varepsilon_m^2 = & \sum_{I \notin S} \sum_{J \in S} c_{mJ}^2 \frac{\langle \Phi_J | \mathbf{H} | \Phi_I \rangle^2}{E_m^0 - E_I^0} \\ & + \sum_{I \notin S} \sum_{\substack{J \neq K \\ \in S}} c_{mJ} c_{mK} \frac{\langle \Phi_J | \mathbf{H} | \Phi_I \rangle \langle \Phi_I | \mathbf{H} | \Phi_K \rangle}{E_m^0 - E_I^0} \end{aligned} \quad (10)$$

In this expression, the first terms will be called diagonal terms, and the second ones will be called cross-terms. Since one is supposed to work on a given excited state, the subscript m will be omitted here after.

Among the configurations I outside of S , one finds first the ground state configuration, which leads to the correction

$$a = \sum_i \sum_j \sum_k \sum_l \underbrace{2c_{ij^*} c_{kl^*}}_{\in \pi} \frac{F_{ij^*} F_{kl^*}}{E' - E_0^0} \quad (11)$$

where in $F_{ij^*} = \langle i | \mathbf{F} | j^* \rangle$, \mathbf{F} is the Fock operator. This Fock operator reduces to its monoelectric part if i and j are different when the MO's are fully localized in the CNDO hypotheses.

The subspace outside of S also includes singly excited configurations.

If S is built of singly excited $\begin{pmatrix} \pi^* \\ \pi \end{pmatrix}$ configurations, the singly excited configurations outside of S belong to two groups:

– the $\begin{pmatrix} \sigma^* \\ \sigma' \end{pmatrix}$ singly excited configurations, which reduce to the “polarization” $\begin{pmatrix} \sigma^* \\ \sigma \end{pmatrix}$ configurations in the PCILO-CNDO hypotheses.

– the $\begin{pmatrix} \pi^* \\ \sigma \end{pmatrix}$ and $\begin{pmatrix} \sigma^* \\ \pi \end{pmatrix}$ configurations, which only play a role in non-planar systems. The second order effect of the singly-excited configurations is given in Appendix.

According to the Slater's rules, a singly excited configuration $\Phi \begin{pmatrix} j^* \\ i \end{pmatrix}$ only interacts with the doubly excited determinants which involve either i or j^* in their excitation process, i.e. $\Phi \begin{pmatrix} t^* & q^* \\ i & p \end{pmatrix}$ or $\Phi \begin{pmatrix} j^* & q^* \\ i & p \end{pmatrix}$. But in the CNDO hypotheses, the full localization implies

$$t^* = j^* \quad \text{to get a non zero } \left\langle \Phi \begin{pmatrix} j^* \\ i \end{pmatrix} \middle| \mathbf{H} \middle| \Phi \begin{pmatrix} t^* & q^* \\ i & p \end{pmatrix} \right\rangle \text{ matrix element,}$$

or

$$t = i \quad \text{to get a non zero } \left\langle \Phi \begin{pmatrix} j^* \\ i \end{pmatrix} \middle| \mathbf{H} \middle| \Phi \begin{pmatrix} j^* & q^* \\ t & p \end{pmatrix} \right\rangle \text{ matrix element.}$$

The doubly excited determinants which belong to the summation over I in Eq. (3), actually involve one $\binom{\pi^*}{\pi}$ excitation and one $\binom{q^*}{p}$ excitation, where p and q may be σ or π MO's. If n_π is the number of π bonds, and n the total number of bonds, the number of doubly excited determinants involved in the 2nd order correction of the excited state is proportional to $n_\pi^2 \times n^2$.

The triply excited determinants which interact with a given $\Phi \binom{j^*}{i}$ singly excited determinant may be written as $\Phi \binom{j^* \ q^* \ s^*}{i \ p \ r}$ according to the Slater's rules.

But the CNDO hypotheses and the full localization of the MO's implicate

$$p = q \quad \text{and} \quad r = s \quad (\text{or } p = s \text{ and } r = q)$$

since

$$\left\langle \Phi \binom{j^* \ q^* \ s^*}{i \ p \ r} \middle| \mathbf{H} \middle| \Phi \binom{j^*}{i} \right\rangle = \langle pr | q^* s^* \rangle - \langle pr | s^* q^* \rangle.$$

Once more the number of triply excited determinants interacting with the zeroth order description of the excited state is proportional to $n_\pi^2 \times n^2$.

One may already notice at this stage the benefit of the localized model; in a delocalized framework, there would be n^4 triply excited configurations $\Phi \binom{j^* \ q^* \ s^*}{i \ p \ r}$ interacting with a given singly excited determinant $\Phi \binom{j^*}{i}$, even in the CNDO hypotheses. This feature already balance the disadvantage of having a multiconfigurational zeroth order wave-function for the excited state.

2. Cancellations between the Ground State and Excited States 2nd Order Corrections

One knows that if one uses the same set of MO's for the ground state the excited state, and if the excited state zeroth order wave-function is a single configuration, important cancellations occur between the perturbation series of the ground state and of the excited state [8]; for instance in the second order energies, the effect of most of the triply excited determinants upon the excited configuration are equal to the effect of most of the doubly excited determinants upon the ground state determinant.

We shall demonstrate that this phenomenon, which may be called "cancellation of common diagrams in transition energies", also occurs in the excitonic treatment as long as a correct definition of \mathbf{H}^0 has been chosen.

Let us consider for instance the effect of the delocalization single excitations $p \rightarrow q^*$ ($p \neq q$) on the ground and excited states. On the ground state these excitations lead to the so called delocalization 2nd order energy [2]

$$e_0^2 \text{ del} = \sum_{p \neq q} \sum_{q^*} 2F_{pq^*}^2 \left/ \left(E_0^0 - E^0 \binom{q^*}{p} \right) \right.$$

On the excited state, such excitations are also possible. They will lead to some cross terms which will be analyzed in the Appendix and diagonal terms

$$\varepsilon_1^2 \text{ del} = \sum_i \sum_j c_{ij^*}^2 \sum_{p \neq q} \sum 2 \left\langle \Phi \begin{pmatrix} j^* \\ i \end{pmatrix} \middle| \mathbf{H} \middle| \Phi \begin{pmatrix} j^* & q^* \\ i & p \end{pmatrix} \right\rangle^2 / \left(E' - E^0 \begin{pmatrix} j^* & q^* \\ i & p \end{pmatrix} \right) - R \quad (12)$$

where R is a remainder triple summations where p or $q = i$ or j ; this term occurs because when p or q is equal to i or j , there is only one excitation instead of two.

$$\varepsilon_1^2 \text{ del} + R = \sum_i \sum_j c_{ij^*}^2 \sum_{p \neq q} \sum 2 F_{pq^*}^2 / \left(E' - E^0 \begin{pmatrix} j^* & q^* \\ i & p \end{pmatrix} \right)$$

Let us assume

$$E^0 \begin{pmatrix} j^* & q^* \\ i & p \end{pmatrix} - E_0^0 = E^0 \begin{pmatrix} j^* \\ i \end{pmatrix} - E_0^0 + E \begin{pmatrix} q^* \\ p \end{pmatrix} - E_0^0. \quad (13)$$

Then

$$\begin{aligned} E' - E^0 \begin{pmatrix} j^* & q^* \\ i & p \end{pmatrix} &= E' - E^0 \begin{pmatrix} j^* \\ i \end{pmatrix} - E^0 \begin{pmatrix} q^* \\ p \end{pmatrix} + E_0^0 \\ &= \left[E_0^0 - E^0 \begin{pmatrix} q^* \\ p \end{pmatrix} \right] \left[1 - \frac{E' - E^0 \begin{pmatrix} j^* \\ i \end{pmatrix}}{E_0^0 - E^0 \begin{pmatrix} q^* \\ p \end{pmatrix}} \right]. \end{aligned} \quad (14)$$

Since E' is the barycenter of the $\begin{pmatrix} \pi^* \\ \pi \end{pmatrix}$ single excitations, the quantity $E' - E^0 \begin{pmatrix} j^* \\ i \end{pmatrix}$ is small with respect to the denominator $E_0^0 - E^0 \begin{pmatrix} q^* \\ p \end{pmatrix}$ which represents a single excitation energy. Therefore, a limited development gives

$$\left[E' - E^0 \begin{pmatrix} j^* & q^* \\ i & p \end{pmatrix} \right]^{-1} \simeq \left[E_0^0 - E^0 \begin{pmatrix} q^* \\ p \end{pmatrix} \right]^{-1} \left[1 + \frac{E' - E^0 \begin{pmatrix} j^* \\ i \end{pmatrix}}{E_0^0 - E^0 \begin{pmatrix} q^* \\ p \end{pmatrix}} \right] \quad (15)$$

Thus

$$\varepsilon_1^2 \text{ del} + R = \sum_i \sum_j c_{ij^*}^2 \sum_{p \neq q} \sum \frac{2 F_{pq^*}^2}{E_0^0 - E^0 \begin{pmatrix} q^* \\ p \end{pmatrix}} \left[1 - \frac{E' - E^0 \begin{pmatrix} j^* \\ i \end{pmatrix}}{E_0^0 - E^0 \begin{pmatrix} q^* \\ p \end{pmatrix}} \right] \quad (16)$$

$$\begin{aligned} &= \sum_{p \neq q} \sum \frac{2 F_{pq^*}^2}{E_0^0 - E^0 \begin{pmatrix} q^* \\ p \end{pmatrix}} \sum_i \sum_j c_{ij^*}^2 \\ &+ \sum_{p \neq q} \sum \frac{2 F_{pq^*}^2}{E_0^0 - E^0 \begin{pmatrix} q^* \\ p \end{pmatrix}} \sum_i \sum_j c_{ij^*}^2 \left[E' - E^0 \begin{pmatrix} j^* \\ i \end{pmatrix} \right]. \end{aligned} \quad (17)$$

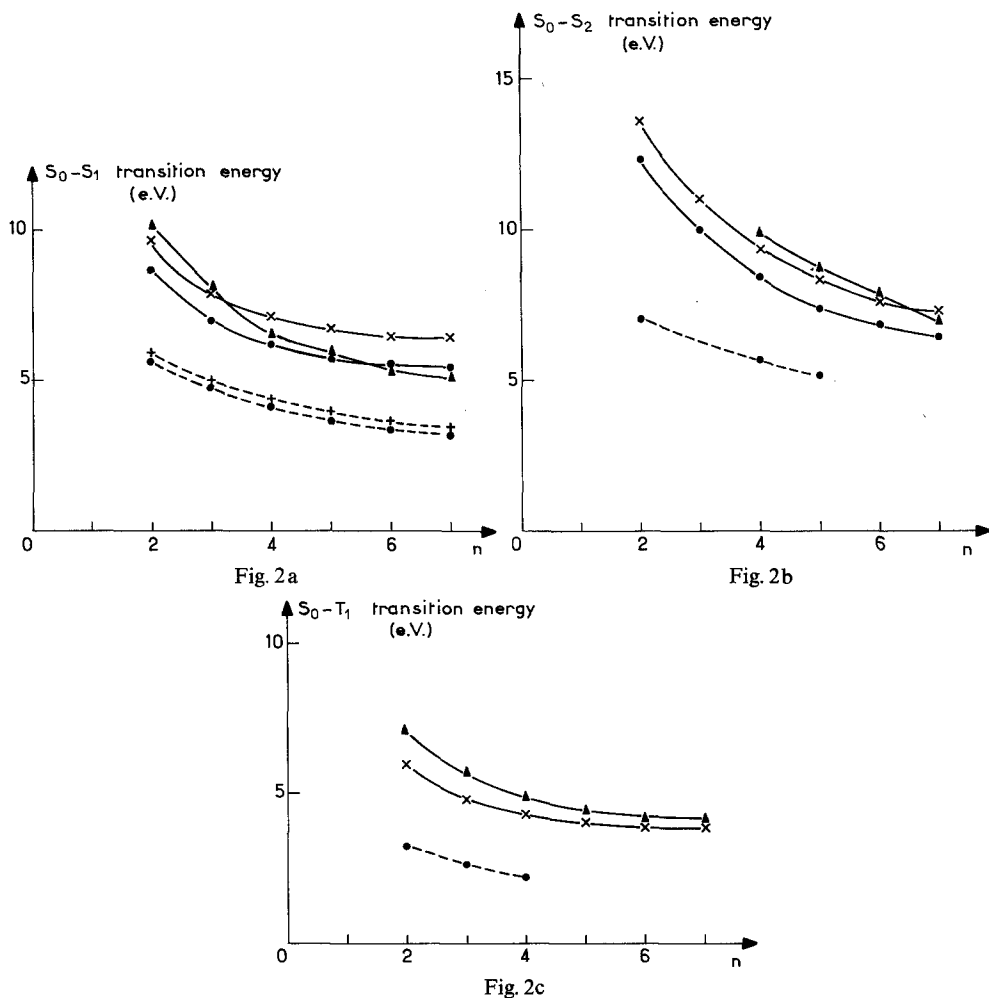


Fig. 2. Evolution of the experimental and calculated transition energies S_0-S_1 towards the first singlet excited state (2a), S_0-S_2 towards the second singlet excited state (2b), S_0-T_1 towards the first triplet excited state (2c). + ··· + experimental values in vapor state, ····· experimental values in solution, × — × E_i^0 zeroth order transition energies, ○ — ○ E_i^m zeroth order transition energies corrected by the $\binom{\sigma^*}{\sigma}$ singly excited determinants, Δ — ΔE_i^2 calculated transition energies after the full second order correction

The normalization condition and the definition of E' [Eq. (8)] imply $\sum_i \sum_j c_{ij}^2 = 1$ and $E' = \sum_i \sum_j c_{ij}^2 E^0 \binom{j^*}{i}$. Therefore $\epsilon_1^2 \text{ del} + R = \epsilon_0^2 \text{ del}$.

This demonstration requires Eq. (13) to be valid. This is verified if H^0 for the ground state is the sum of mono-electronic hamiltonians, for instance in the Moller-Plesset definition of H^0 [9]; with such a definition the transition energies are simply differences between mono-electronic energies, and are therefore additive. With the Epstein-Nesbet definition of H^0 [6], Eq. (13) is only approximate.

The practical consequence of this cancellation is that if ε_0^2 del has been already calculated for the second order ground state energy, through an n^2 summation, the calculation of the delocalization effects on the transition energy only requires the calculation of R , through a $n_\pi^2 \times n$ summation and of the cross terms. The number of cross terms contributions is demonstrated in the Appendix to increase like $n_\pi^3 \times n$ at most. The cancellation of common diagrams reduces the computation time from $n_\pi^2 n^2$ to $n_\pi^3 n$. The same considerations might be developed for the 2nd order correlation effects on ground state, resulting from the interaction with the doubly excited determinants, and on the excited state, resulting from its interaction with the triply excited determinants.

3. Calculated Transition Energies

We have studied the all-trans linear polyenes $C_{2N}H_{2N+2}$ from $N = 2$ to $N = 7$. Most of experimental spectra have been obtained in liquid phase in solvents such as hexane or isooctane [10]. But for butadiene, hexatriene and octatetraene, spectra in gaseous phase have been given [11] showing a bathochromic solvent effect of 0.2–0.3 eV.

In our calculations, all bond angles are taken equal to 120° and the bond lengths are those calculated by Julg [12].

a) $S_0 - S_1$ Transitions Energies

Table 1 gives the zeroth order transition energies E_t^0 , i.e. the transition energies calculated after the diagonalization of the (π) excitonic matrix, $E_t^{2,m}$ the transition energies including the second order correction of the σ monoexcited configurations $\Phi \begin{pmatrix} \sigma^* \\ \sigma \end{pmatrix}$ on the excited state, E_t^2 the transition energies obtained after the full second order correction on both states, and E_t the experimental transition energies ($E_{t,v}, E_{t,s}$ are obtained respectively in vapor phase and in solution).

Figure 2a shows the evolutions of E_t^0 , $E_t^{2,m}$, E_t^2 and the experimental ($E_{t,v}$ and $E_{t,s}$) transition energies with N , the number of double bonds.

The curve E_t^0 parallels the experimental one, but lies several electronvolts too high.

The curve $E_t^{2,m}$ runs also quite parallel to the experimental curves, the calculated transition energies are always lower than the calculated (π) excitonic transition energies E_t^0 , due to the negative effect of the (σ) singly excited configurations.

The effect of the singly excited configurations $\begin{pmatrix} \sigma^* \\ \sigma \end{pmatrix}$ is rather important in small polyenes as noticed by Herzberg *et al.* [12], Dunning and Mc Koy [14] and Giessner and Pullman [15]. Denis and Malrieu [16] had demonstrated that this effect decreases as N^{-1} when using the usual delocalized description. In our model, one notices only a small decrease of this correction (1.05–0.95) when N varies from 2–7 (Table 1). The value of this correction tends towards a *non-zero* constant. This difference between the delocalized and excitonic models is due to

Table 1. Experimental and calculated transition energies for H-(CH=CH)_N-H polyenes from N = 2 to N = 7

| N | State | Experimental values | E _t ⁰ | E _t ^{2,m} | E _t ² | s1 | s2 | d1 | d2 | cs | cd |
|---|-------|---------------------|-----------------------------|-------------------------------|-----------------------------|-------|-------|-------|-------|-------|-------|
| 2 | S1 | 5.9 (5.7) | 9.69 | 8.65 | 10.09 | +0.39 | -1.38 | +0.40 | +0.57 | +1.23 | +0.23 |
| | S2 | | 13.69 | 12.34 | | | | | | | |
| | T1 | 3.20 | 5.99 | 5.99 | 6.98 | +0.66 | -0.65 | +0.96 | +0.48 | -0.47 | 0 |
| 3 | S1 | 5 (4.75) | 7.94 | 6.96 | 7.95 | +0.75 | -1.76 | +0.49 | +0.60 | +0.64 | +0.27 |
| | S2 | | 10.99 | 9.99 | | | | | | | |
| | T1 | 2.60 | 4.81 | 4.81 | 5.65 | +1.12 | -0.97 | +1.05 | +0.52 | -0.97 | 0 |
| 4 | S1 | 4.45 (4.20) | 7.15 | 6.18 | 6.59 | +0.92 | -2.05 | +0.54 | +0.62 | +0.12 | +0.29 |
| | S2 | (5.84) | 9.38 | 8.36 | 9.86 | +0.70 | -2.07 | +0.55 | +0.62 | +1.48 | +0.10 |
| | T1 | 2.20 | 4.30 | 4.30 | 4.84 | +1.27 | -1.20 | +1.09 | +0.53 | -1.16 | 0 |
| 5 | S1 | (3.75) | 6.75 | 5.80 | 5.83 | +0.99 | -2.22 | +0.57 | +0.63 | -0.25 | +0.31 |
| | S2 | (5.27) | 8.39 | 7.40 | 8.72 | +0.84 | -2.15 | +0.56 | +0.63 | +1.20 | +0.17 |
| | T1 | | 4.06 | 4.06 | 4.40 | +1.33 | -1.31 | +1.10 | -1.54 | -1.32 | 0 |
| 6 | S1 | (3.45) | 6.63 | 5.58 | 5.36 | +1.03 | -2.29 | +0.58 | +0.63 | -0.49 | +0.31 |
| | S2 | | 7.77 | 6.81 | 7.79 | +0.92 | -2.24 | +0.57 | +0.63 | +0.85 | +0.22 |
| | T1 | | 3.93 | 3.93 | 4.15 | +1.35 | -1.37 | +1.11 | +0.55 | -1.42 | 0 |
| 7 | S1 | (3.18) | 6.40 | 5.45 | 5.04 | +1.05 | -2.33 | +0.59 | +0.63 | -0.66 | +0.31 |
| | S2 | | 7.35 | 6.40 | 7.08 | +0.97 | -2.30 | +0.59 | +0.63 | +0.52 | +0.25 |
| | T1 | | 3.86 | 3.86 | 4.00 | +1.37 | -1.41 | +1.11 | +0.56 | -1.48 | 0 |

The experimental transition energies as those obtained in solution (values between brackets) and in vapor phase.

E_t⁰ = Zeroth order transition energies.

E_t^{2,m} = Zeroth order transition energies corrected to the 2nd order by the $\begin{pmatrix} \sigma^* \\ \sigma \end{pmatrix}$ singly excited configurations.

E_t² = 2nd order corrected transition energies.

s1 = diagonal 2nd order correction due to the a_q⁺a_p delocalization single excitations.

s2 = diagonal 2nd order correction due to the a_p⁺a_p polarization single excitations.

d1 = diagonal 2nd order correction due to the a_q⁺a_q a_p⁺a_p double excitations.

d2 = diagonal 2nd order correction due to the a_p⁺a_p a_p⁺a_p double excitations.

cs and cd are the cross terms for the single and double excitations.

the non vanishing weight of the polarization local excitation $\begin{pmatrix} \pi_i^* \\ \pi_i \end{pmatrix}$ in the excitonic model and will be discussed in details in a further publication [17].

Figure 3 gives the evolution of the second order correction due to the single excitations, the double excitations and the full second order correction.

The effect of the single excitations on the transition energies decreases from a positive value for N = 2 (+0.23) to a negative value which tends to a constant for N > 7. This effect can be analyzed as follows:

- The delocalization excitations a_q⁺a_p (p ≠ q) are all possible on the ground state determinant, while some of them are impossible when acting on the excited determinants. Since in the CNDO-PCILO hypotheses, the matrix elements are the same, the final diagonal correction is positive (see 1st term of B 1/a and B 3/a of the Appendix). This correction tends to a nearly constant value for N > 5 (see Table 1).

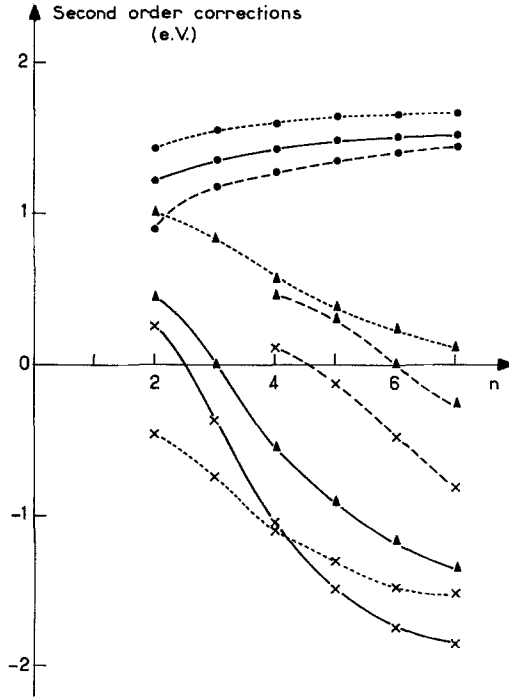


Fig. 3. Evolution with N of the various second order corrections upon the transition energy. Correction due to the single excitations upon the first singlet S_1 \times — \times , the second singlet S_2 \times --- \times , the first triplet T_1 \times ... \times . Correction due to the double excitations upon the first singlet S_1 \bullet — \bullet , the second singlet S_2 \bullet --- \bullet , the first triplet T_1 \bullet ... \bullet . Total second order correction upon the first singlet \blacktriangle — \blacktriangle , the second singlet \blacktriangle --- \blacktriangle , the first triplet \blacktriangle ... \blacktriangle

The polarization excitations $a_{p^*}^+ a_p$ give stronger interactions with the excited determinants $\binom{q^*}{q}$ than with the ground-state determinant (2^{nd} term of the contribution B 3/a of Appendix) and their diagonal element is therefore negative. The variation of this correction is rather important but tends to a constant.

The non-diagonal corrections (due to the interaction of the same doubly excited determinants with *two* singly excited determinants) are more difficult to analyze, and depend on the sign changes of the excitonic wave function.

The double excitations increase the transition energy by a quantity (curve C) which increases slightly from $N=2$ to $N=4$, and remains constant for $N \geq 4$. This effect is mainly due to impossibility of making an excitation $a_{q^*}^+ a_q a_{p^*}^+ a_p$ on a determinant $\Phi \binom{j^*}{i}$ if p or q are equal to i or j .

The final full second order effect is positive for $N < 3$ then it becomes negative and tends to a constant value which is not yet obtained for $N = 7$. This correction

decreases the parallelism of the calculated and experimental transition energies curves, at least for the small values of N ¹.

One may compare E_t^2 , including the full 2nd order correction, with $E_t^{2,m}$ which represents the usual CI of singly excited states. One notices on Fig. 2a that for $N=2$ to $N=4$, $E_t^2 > E_t^{2,m}$, while for $N > 5$, $E_t^2 < E_t^{2,m}$. In the region $3 < N < 6$ (usual conjugated systems) the difference between the full 2nd order corrected transition energy and the usual singly excited states CI is rather small, which may explain the success of this approximation.

b) $S_0 - S_2$ Transition Energy

The transition $S_0 - S_2$ toward the 2nd singlet state is reported in Fig. 2b and Table 1. The results E_t^2 are not reported for $N=2$ and 3 since a near degeneracy occurs between the excitonic wave function Ψ_m^0 and the doubly excited determinants of the type $\begin{pmatrix} j^* & i^* \\ i & j \end{pmatrix}$. For larger polyenes the degeneracy occurs with higher excited states.

The calculated transition energies are too high, worse than for the $S_0 - S_1$ transition, but the various effects are rather similar, except that the fully 2nd order corrected transition energy E_t^2 is always close to E_t^0 , the excitonic transition energy, and larger than $E_t^{2,m}$, the singly excited CI result.

As concerns the effect of the singly excited determinants $\begin{pmatrix} \sigma^* \\ \sigma \end{pmatrix}$, two factors compete: the second excited state is more polar than the first one, and thus interacts less with the $\begin{pmatrix} \sigma^* \\ \sigma \end{pmatrix}$ determinants, but it lies higher in energy, and the denominator energies are smaller.

The single excitations lower more the $S_0 - S_1$ transition energy than the $S_0 - S_2$ transition energy. A detailed analysis shows that this is predominantly due to the cross terms and is difficult to analyze. The double excitations have a very small (~ 0.1 eV) and decreasing effect on the spacing between the two lowest singlet excited states. The full 2nd order correction increases the spacing between these excited states.

c) $S_1 - T_1$ Energy Difference

Figure 2c gives to evolution with N of the zeroth order and the second order transition energy is $S_0 - T_1$.

The singlet-triplet spacing is known experimentally for $N=2$ to 4. The π excitonic treatment gives too large a spacing. This spacing is diminished under the influence of the $\begin{pmatrix} \sigma^* \\ \sigma \end{pmatrix}$ monoexcited states by an almost constant quantity

¹ All the results given here take into account the cancellation of common diagrams demonstrated in Section 2. This cancellation is only approximate (especially in the Epstein-Nesbet definition of H^0). Calculations performed without taking benefit of these cancellations show that they are well satisfied for double excitations, but the "common" single excitations may introduce a correction up to 0.5 eV.

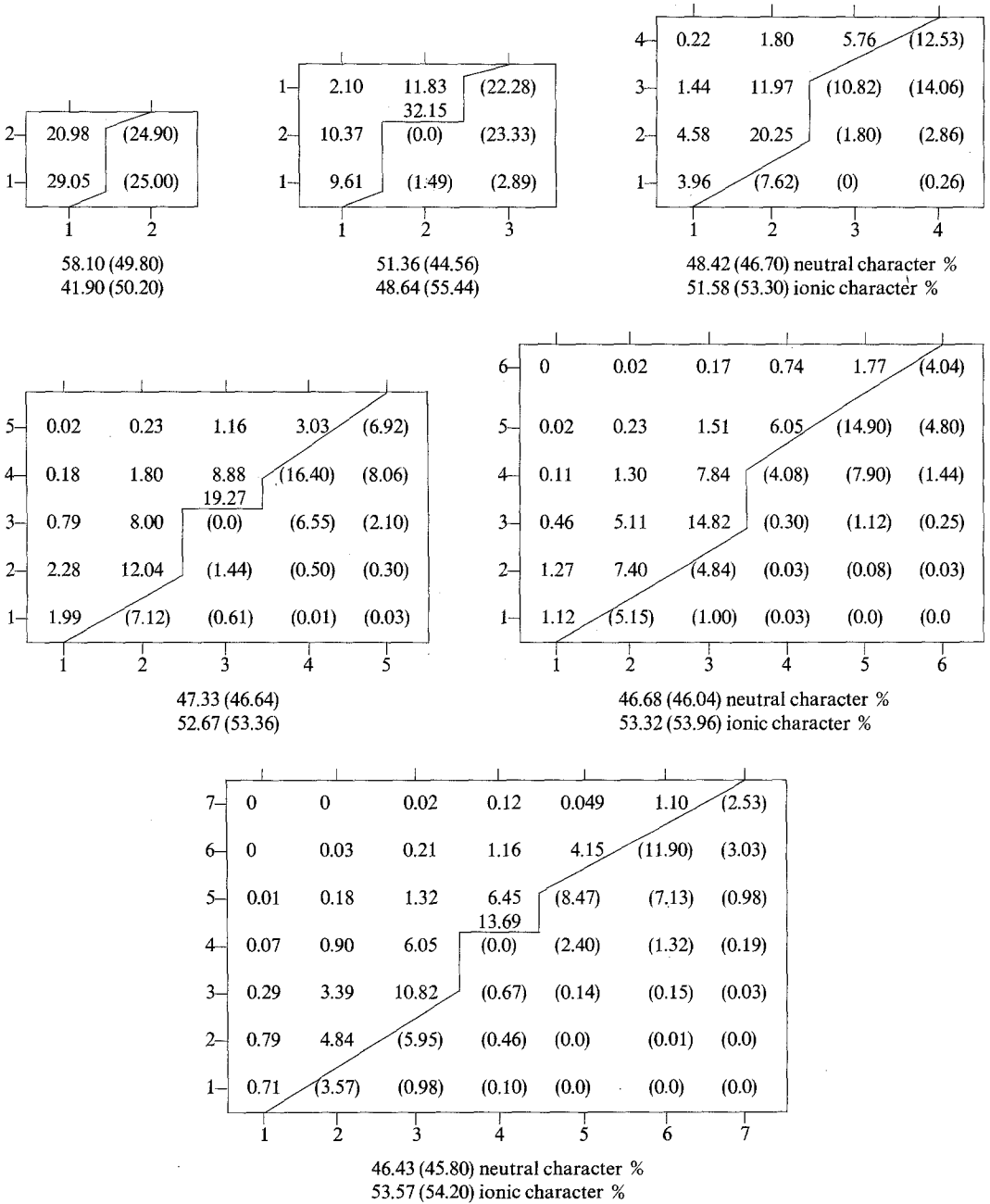


Fig. 4. Weights of the excitonic wave-function on the local excitations (in per cent). The number on line i and column j gives the weight on the $i \rightarrow j^*$ process. The upper part concerns the S_1 singlet excited state, the lower part concerns (numbers between parenthesis) the second singlet excited state S_2 . The symmetry of the problem implies (i, j) to be equal to $(N - i + 1, N - j + 1)$

Table 2. Mean π population, (\bar{n}) and π charges fluctuations (σ) in the double bonds loges for the excitonic description of the two first singlet excited states

| N | State | Loge 1 | | Loge 2 | | Loge 3 | | Loge 4 | |
|---|-------|-----------|----------|-----------|----------|-----------|----------|-----------|----------|
| | | \bar{n} | σ | \bar{n} | σ | \bar{n} | σ | \bar{n} | σ |
| 2 | S_1 | 2 | 0.65 | | | | | | |
| | S_2 | 2 | 0.71 | | | | | | |
| 3 | S_1 | 1.99 | 0.51 | 2.02 | 0.67 | | | | |
| | S_2 | 2.22 | 0.51 | 1.57 | 0.51 | | | | |
| 4 | S_1 | 1.98 | 0.38 | 2.01 | 0.61 | | | | |
| | S_2 | 2.10 | 0.49 | 1.90 | 0.52 | | | | |
| 5 | S_1 | 1.99 | 0.19 | 2 | 0.50 | 2.02 | 0.60 | | |
| | S_2 | 2.03 | 0.43 | 2.04 | 0.49 | 1.87 | 0.44 | | |
| 6 | S_1 | 1.99 | 0.21 | 1.99 | 0.42 | 2.02 | 0.56 | | |
| | S_2 | 2.01 | 0.36 | 2.04 | 0.49 | 1.95 | 0.41 | | |
| 7 | S_1 | 1.99 | 0.17 | 1.99 | 0.34 | 2.00 | 0.30 | 2.05 | 0.54 |
| | S_2 | 2.00 | 0.21 | 2.02 | 0.45 | 2.00 | 0.43 | 1.95 | 0.32 |

(~ 1 eV) since in the CNDO approximations, the triplet π and triplet σ configurations do not interact [16]. The single excitations stabilize more the triplet excited state T_1 than the ground state S^0 , but this stabilization varies more slowly than the corresponding stabilization for the singlet excited state S_1 , so that the $S_1 - T_1$ distance is reduced. The double excitations only give a small decrease (≈ 0.2 eV) in the $S_1 - T_1$ spacing.

4. Analysis of the Wave Functions

a) Ionic versus Neutral Structures

One may analyse the evolution of the relative weight of ionic (delocalization) versus neutral (polarization) structures in the zeroth-order excitonic wavefunction. It appears from Fig. 4 that the first singlet is more neutral than the second one, but the difference decreases when N increases. One may notice that the weight of neutral structures in the first singlet excited state tends towards a constant about 46%. This fact is very important because it introduces a qualitative difference with the usual delocalized MO descriptions of excited states and will be demonstrated and discussed in detail elsewhere [17].

In the triplet states, the neutral structures have larger weight. This is mainly due to the fact that the triplet $\binom{3}{i}^{i^*}$ polarization configurations have lower energies than the singlet $\binom{1}{i}^{i^*}$ polarization configurations, while the $\binom{3}{i}^{j^*}$ and $\binom{1}{i}^{j^*}$ have the same energy in the CNDO approximations.

b) Localization of the Excitation on the Nuclear Skeleton

Qualitatively, from Fig. 4, the first singlet excitations appears to be located on the center of the molecule (bond $N/2$ and $N/2 + 1$ if N is even $(N + 1)/2$ if N is

odd), the second excitations being more probable on the neighbour bonds (bonds number $N/2 - 1$ and $N/2 + 2$ when N is even ($N - 1)/2$ and $(N + 3)/2$ when N is odd).

c) The Populations in the Bond-Loges and their Fluctuations

Table 2 gives the π bond charges, i.e. the mean π populations or mean numbers of π electrons per double bond in the two lowest singlet excited states. The lowest singlet state appears to be almost neutral, in agreement with the pairing theorem in the delocalized description. The fact that the mean population is almost 2.0 does not mean that the polar charge transfer structures play no role. It simply means that the $i \rightarrow j^*$ and $j \rightarrow i^*$ excitations have almost equal weights.

On the contrary the second singlet state implies significant displacement of the mean charges. The central bond(s) is (are) positive, the other bonds are negative.

We also have reported in Table 2 the fluctuations of the number of π electrons per double-bond. For a wave-function

$$\Psi = \sum_{ij^*} c_{ij^*} \Phi \left(\begin{matrix} j^* \\ i \end{matrix} \right)$$

one may define the number of electrons in bond k for $\Phi \left(\begin{matrix} j^* \\ i \end{matrix} \right)$

$$n_{ij^*}^k = \left\langle \Phi \left(\begin{matrix} j^* \\ i \end{matrix} \right) \left| \mathbf{n}^k \right| \Phi \left(\begin{matrix} j^* \\ i \end{matrix} \right) \right\rangle$$

using the operator \mathbf{n}^k , number of particles in loge k [19].

Then if \bar{n}^k is the mean number of electrons in bond k

$$\bar{n}^k = \sum_{ij^*} c_{ij^*}^2 n_{ij^*}^k$$

The fluctuation of the number of electrons in bond k is given by

$$\sigma_k = \sqrt{\sum_{ij^*} (n_{ij^*}^k - \bar{n}^k)^2 c_{ij^*}^2}$$

Since the $n_{ij^*}^k$ differs from 2 only when i or $j^* = k$, this fluctuation decreases for this type of wave function, as may be seen from Table 2 but they are larger than for the ground state.

Conclusions

We have considered the classical π excitonic wave function

$$\Psi = \sum_{ij^*} c_{ij^*} \Phi \left(\begin{matrix} j^* \\ i \end{matrix} \right)$$

as a multiconfigurational zeroth order wave-function. This wave function has been perturbed under the influence of i) the other singly excited determinants (the ${}^1(\sigma^*)$ configurations coupled with the ${}^1(\pi^*)$ configurations through dipole-

dipole interactions), ii) the doubly excited determinants, which introduce polarization effects on the excited state, iii) the triply excited determinants, which introduce bond and interbond correlation effects on the excited state.

A correct definition of H^0 allows, through an algebraic derivation of the various 2nd order corrections, to calculate only the *changes* of polarization, delocalization and correlation energies in the excited state with respect to the ground state, despite the multiconfigurational form of the zeroth order wave-function for the excited state, we have been able therefore to get the "cancellation of common diagrams in excitation energies" well established when the zeroth order wave-function for the excited state is the single determinantal Virtual Orbital approximation. Although a very large number of determinants are taken into account, the calculation of 2nd order corrected transition energies is very short, much shorter than when one perturbs a single configuration using delocalized MO's. For instance the calculation of 10 transition energies in $C_{14}H_{16}$ requires 6m 3 seconds on an IBM 360-75 computer. This speed is obtained through both the complete localization of the MO's reducing the number and calculation time of non zero molecular integrals, and a careful choice of the perturbation procedure. It appears therefore that the use of localized MO's is very useful not only for the ground state energy and ground state properties calculation, but also for the excited states and excitation properties, for which the canonical delocalized MO's are often presented as necessary.

This PCILO method for excited states will be applied to some conceptual and numerical problems. In further publications [17], it will be shown that the single determinantal description of the excited state overestimates the delocalization of the excitation with respect to the excitonic treatment. The method will be applied to some conformational problems involving the excited states.

Appendix

Detailed 2nd order energy corrections on the excited state.

This Appendix gives the various types of interactions which appear in the 2nd order energy correction on the excitonic wave-function

$$\Psi^0 = \sum_i \sum_{\substack{j \\ \in (\pi)}} c_{ij^*} \Phi \begin{pmatrix} j^* \\ i \end{pmatrix}$$

We report successively the 2nd order effects of the triply, doubly, singly, excited determinants and of the ground state determinant Φ_0^0 . The following notations are used

$a_{pq^*} = (pp^*, q^*q^*)$, $a_{pq} = (pp^*, qq)$ are charge-dipole interaction matrix elements.

$b_{pq} = (pp^*, qq^*)$, is a dipole-dipole interaction matrix element

$\Delta \begin{pmatrix} q^* \dots \\ p \dots \end{pmatrix} = E' - E^0 \begin{pmatrix} q^* \dots \\ p \dots \end{pmatrix}$ is a typical energy denominator.

i, j, k and l belong to the subspace $\{\pi\}$ of the π MO's,

σ belong to the complementary subspace,

p and q are any MO's, belonging to $\{\pi\}$ or not.

$s=0$ or 1 according to the singlet or triplet character of the excited state.

In the typical 2nd order energy correction [Eq. (3)] we shall distinguish the cases where Φ_I and Φ_J are 1) both ionic, 2) ionic and neutral and 3) both neutral. In the following paragraphs we give in Table form the various non-zero interactions which occur under the CNDO-hypotheses when the MO's are fully localized, and the corresponding energy corrections, in a form which makes the programming straightforward. In the Tables the doubly bordered columns represent diagonal interactions.

A) Effect of the Triply Excited Determinants

1) Φ_I and Φ_J both ionic

| | | | | | |
|--|----------|--|--|--|--|
| | Φ_J | $\begin{pmatrix} j^* \\ k \end{pmatrix}$ | | | |
| | | $\begin{pmatrix} j^* \\ i \end{pmatrix}$ | $\begin{pmatrix} k^* \\ i \end{pmatrix}$ | $\begin{pmatrix} j^* \\ k \end{pmatrix}$ | $\begin{pmatrix} k^* \\ l \end{pmatrix}$ |
| $\begin{pmatrix} j^* \\ i \end{pmatrix}$ | | $\boxed{\begin{pmatrix} j^* & p^* & q^* \\ i & p & q \end{pmatrix}_a}$ | 0 | 0 | 0 |

Due to the CNDO-PCILO hypothesis we only have diagonal terms:

$$a = \sum_i \sum_j' c_{ij}^2 \left[\sum_{p \neq q} b_{pq}^2 (2 - \delta_{pi} - \delta_{pj} - \delta_{qi} - \delta_{qj} + \delta_{pi} \delta_{qj}) / \Delta \begin{pmatrix} j^* & p^* & q^* \\ i & p & q \end{pmatrix} \right. \\ \left. + \sum_p b_{pp}^2 (1 - \delta_{ip} - \delta_{jp}) / \Delta \begin{pmatrix} j^* & p^* & \bar{p}^* \\ i & p & \bar{p} \end{pmatrix} \right]$$

The δ 's take into account the possible spin restrictions.

2) Φ_I ionic and Φ_J neutral

No triply excited determinant interact with Φ_I and Φ_J in a such a case, due to the CNDO-PCILO hypothesis.

3) Φ_I and Φ_J both neutral

| | | | |
|--|----------|--|--|
| | Φ_J | $\begin{pmatrix} j^* \\ j \end{pmatrix}$ | |
| | | $\begin{pmatrix} i^* \\ i \end{pmatrix}$ | $\begin{pmatrix} j^* \\ j \end{pmatrix}_{j \neq i}$ |
| $\begin{pmatrix} i^* \\ i \end{pmatrix}$ | | $\boxed{\begin{pmatrix} i^* & p^* & q^* \\ i & p & q \end{pmatrix}_a}$ | $\begin{pmatrix} i^* & j^* & p^* \\ i & j & p \end{pmatrix}_b$ |

$$a = \sum_i c_{ii^*}^2 \left[\sum_p \left(\sum_q' 2b_{pq}^2 / \Delta \begin{pmatrix} i^* & p^* & q^* \\ i & p & q \end{pmatrix} + 4(1-s) b_{ip}^2 / \Delta \begin{pmatrix} i^* & i^* & p^* \\ i & i & p \end{pmatrix} + b_{pp}^2 / \Delta \begin{pmatrix} i^* & p^* & p^* \\ i & p & p \end{pmatrix} \right) \right],$$

$$b = \sum_i \sum_j' c_{ij^*} c_{jj^*} \sum_p'' (2 - \delta_{pi} - \delta_{pj}) (1-s) b_{ip} b_{pj} / \Delta \begin{pmatrix} i^* & j^* & p^* \\ i & j & p \end{pmatrix}.$$

Combining the corrections 1a and 3a, and using the demonstration given in Part II, one might introduce explicitly the 2nd order correlation effects on the ground state minus some specific terms.

B) Effect of the Doubly Excited Determinants

1) Φ_I and Φ_J both ionic

| | |
|----------|---|
| Φ_J | $\begin{pmatrix} l^* \\ k \end{pmatrix} k \neq l$ |
| | $\begin{pmatrix} j^* \\ i \end{pmatrix} \quad \begin{pmatrix} k^* \\ i \end{pmatrix} k \neq j \quad \begin{pmatrix} j^* \\ k \end{pmatrix} k \neq i \quad \begin{pmatrix} l^* \\ k \end{pmatrix} l \neq j$ |
| Φ_I | $\begin{pmatrix} j^* \\ i \end{pmatrix} i \neq j$ |
| | $\boxed{\begin{pmatrix} j^* & q^* \\ i & p \end{pmatrix}}_a \quad \begin{pmatrix} j^* & k^* \\ i & p \end{pmatrix}_b \quad \begin{pmatrix} j^* & p^* \\ i & k \end{pmatrix}_c \quad \begin{pmatrix} j^* & l^* \\ i & k \end{pmatrix}_d$ |

$$a = \sum_i \sum_j' c_{ij^*}^2 \left[\sum_{p \neq q} (2 - \delta_{pi} - \delta_{qj} + 2\delta_{pi} \delta_{qj} (1-s)) F_{pq^*}^2 / \Delta \begin{pmatrix} j^* & q^* \\ i & p \end{pmatrix} + \sum_p (2 - \delta_{pi} - \delta_{pj}) (F_{pp^*} + a_{pj^*} - a_{pi})^2 / \Delta \begin{pmatrix} j^* & p^* \\ i & p \end{pmatrix} \right],$$

$$b = \sum_i \sum_j' \sum_k'' c_{ij^*} c_{ik^*} \left[\sum_{p \neq q, j} (-1)^{(1 + \delta_{pj}(1-s))} F_{pk^*} F_{pj^*} / \Delta \begin{pmatrix} j^* & k^* \\ i & p \end{pmatrix} - (F_{kk^*} + a_{kj^*} - a_{ki}) F_{kj^*} / \Delta \begin{pmatrix} j^* & k^* \\ i & k \end{pmatrix} - (F_{jj^*} + a_{jk^*} - a_{ji}) F_{jk^*} / \Delta \begin{pmatrix} j^* & k^* \\ i & j \end{pmatrix} \right],$$

$$c = \sum_i \sum_j' \sum_k'' c_{ij^*} c_{kj^*} \left[\sum_{p \neq i, k} (-1)^{(1 + \delta_{pj}(1-s))} F_{kp^*} F_{ip^*} / \Delta \begin{pmatrix} j^* & p^* \\ i & k \end{pmatrix} + F_{ki^*} (F_{ii^*} + a_{ij^*} - a_{ik}) / \Delta \begin{pmatrix} j^* & l^* \\ i & k \end{pmatrix} + F_{ik^*} (F_{kk^*} + a_{kj^*} - a_{ki}) / \Delta \begin{pmatrix} j^* & k^* \\ i & k \end{pmatrix} \right],$$

$$d = \sum_i \sum_j' \sum_k'' \sum_l''' c_{ij^*} c_{kl^*} 2(1-s) F_{ij^*} F_{kl^*} / \Delta \begin{pmatrix} j^* & l^* \\ i & k \end{pmatrix}.$$

2) Φ_I ionic, Φ_J neutral

| | | | | |
|----------|---|--|--|--|
| | | Φ_J | | |
| | | $\begin{pmatrix} k^* \\ k \end{pmatrix}$ | | |
| Φ_I | | $\begin{pmatrix} i^* \\ i \end{pmatrix}$ | $\begin{pmatrix} j^* \\ j \end{pmatrix}$ | $\begin{pmatrix} k^* \\ k \end{pmatrix} \quad k \neq i, j$ |
| | $\begin{pmatrix} j^* \\ i \end{pmatrix} \quad i \neq j$ | $\begin{pmatrix} j^* & i^* \\ i & p \end{pmatrix}_b$ | $\begin{pmatrix} j^* & p^* \\ i & j \end{pmatrix}_c$ | $\begin{pmatrix} j^* & k^* \\ i & k \end{pmatrix}_d$ |

$$b = \sum_i \sum_j' c_{ij^*} c_{ii^*} \left[\sum_p'' -2F_{pi^*} F_{pj^*} / \Delta \begin{pmatrix} j^* & i^* \\ i & p \end{pmatrix} + (-1)^s F_{ij^*} (F_{ii^*} + a_{ij^*} - a_{ii}) / \Delta \begin{pmatrix} j^* & i^* \\ i & i \end{pmatrix} - F_{ji^*} (F_{jj^*} + a_{ji^*} - a_{ji}) / \Delta \begin{pmatrix} i^* & j^* \\ j & i \end{pmatrix} \right],$$

$$c = \sum_i \sum_j' c_{ij^*} c_{jj^*} \left[\sum_p'' -2F_{jp^*} F_{ip^*} / \Delta \begin{pmatrix} j^* & p^* \\ i & j \end{pmatrix} + (-1)^s F_{ij^*} (F_{jj^*} + a_{jj^*} - a_{ji}) / \Delta \begin{pmatrix} j^* & j^* \\ i & j \end{pmatrix} - F_{ji^*} (F_{ii^*} + a_{ij^*} - a_{ij}) / \Delta \begin{pmatrix} j^* & i^* \\ i & j \end{pmatrix} \right],$$

$$d = \sum_i \sum_j' \sum_k'' c_{ij^*} c_{kk^*} 2(1-s) F_{ij^*} (F_{kk^*} + a_{kj^*} - a_{ki}) / \Delta \begin{pmatrix} j^* & k^* \\ i & k \end{pmatrix}.$$

3) Φ_I and Φ_J both neutral

| | | | |
|----------|--|--|---|
| | | Φ_J | |
| | | $\begin{pmatrix} j^* \\ j \end{pmatrix}$ | |
| Φ_I | | $\begin{pmatrix} i^* \\ i \end{pmatrix}$ | $\begin{pmatrix} j^* \\ j \end{pmatrix} \quad j \neq i$ |
| | $\begin{pmatrix} i^* \\ i \end{pmatrix}$ | $\begin{pmatrix} i^* & q^* \\ i & p \end{pmatrix}_a$ | $\begin{pmatrix} i^* & j^* \\ i & j \end{pmatrix}_b$ |

$$a = \sum_i c_{ii^*}^2 \left[\sum_{p \neq q} \sum (2 - \delta_{pi} - \delta_{qi}) F_{pq^*}^2 / \Delta \begin{pmatrix} i^* & q^* \\ i & p \end{pmatrix} + \sum_p 2(1-s) \delta_{pi} (F_{pp^*} + a_{pi^*} - a_{pi})^2 / \Delta \begin{pmatrix} i^* & p^* \\ i & p \end{pmatrix} \right],$$

$$b = \sum_i \sum_j' c_{ii^*} c_{jj^*} 2(1-s) (F_{ii^*} + a_{ij^*} - a_{ij}) (F_{jj^*} + a_{ji^*} - a_{ji}) / \Delta \begin{pmatrix} i^* & j^* \\ i & j \end{pmatrix}.$$

C) Effect of the Singly Excited Determinants which do Not Belong to S

1) Φ_I and Φ_J both ionic

| | | | | | |
|----------|---|--|---|---|--------------|
| Φ_I | Φ_J | $\begin{pmatrix} l^* \\ k \end{pmatrix} k \neq l$ | | | |
| | | $\begin{pmatrix} j^* \\ i \end{pmatrix}$ | $\begin{pmatrix} k^* \\ i \end{pmatrix} k \neq j$ | $\begin{pmatrix} j^* \\ k \end{pmatrix} k \neq i$ | l^* k |
| | $\begin{pmatrix} j^* \\ i \end{pmatrix} i \neq j$ | $\begin{pmatrix} j^* \\ \sigma \\ i \end{pmatrix} a$ | $\begin{pmatrix} \sigma^* \\ i \end{pmatrix} b$ | $\begin{pmatrix} j^* \\ \sigma \end{pmatrix} c$ | 0 |

$$a = \sum_i \sum_j' c_{ij}^2 \sum_\sigma \left(F_{i\sigma}^2 / \Delta \begin{pmatrix} j^* \\ \sigma \end{pmatrix} + F_{j^*\sigma}^2 / \Delta \begin{pmatrix} \sigma^* \\ i \end{pmatrix} \right),$$

$$b = \sum_i \sum_j' \sum_k'' \sum_\sigma \left(c_{ij} c_{ik} F_{j^*\sigma} F_{\sigma^*k} / \Delta \begin{pmatrix} \sigma^* \\ i \end{pmatrix} + c_{ij} c_{kj} F_{i\sigma} F_{k\sigma} / \Delta \begin{pmatrix} j^* \\ \sigma \end{pmatrix} \right).$$

2) Φ_I ionic, Φ_J neutral

| | | | | |
|----------|---|---|---|--|
| Φ_I | Φ_J | $\begin{pmatrix} k^* \\ k \end{pmatrix}$ | | |
| | | $\begin{pmatrix} i^* \\ i \end{pmatrix}$ | $\begin{pmatrix} j^* \\ j \end{pmatrix}$ | $\begin{pmatrix} k^* \\ k \end{pmatrix} k \neq i, j$ |
| | $\begin{pmatrix} j^* \\ i \end{pmatrix} i \neq j$ | $\begin{pmatrix} \sigma^* \\ i \end{pmatrix} a$ | $\begin{pmatrix} j^* \\ \sigma \end{pmatrix} b$ | 0 |

$$a = \sum_i \sum_j' 2c_{ij} c_{ii^*} \sum_\sigma F_{j^*\sigma} F_{\sigma^*i} / \Delta \begin{pmatrix} \sigma^* \\ i \end{pmatrix}$$

$$b = \sum_i \sum_j' 2c_{ij} c_{jj^*} \sum_\sigma F_{i\sigma} F_{\sigma j} / \Delta \begin{pmatrix} j^* \\ \sigma \end{pmatrix}$$

3) Φ_I and Φ_J both neutral

| | | | | |
|----------|--|--|--|--|
| Φ_I | Φ_J | j^* j^* | | |
| | | $\begin{pmatrix} i^* \\ i \end{pmatrix}$ | $\begin{pmatrix} j^* \\ j \end{pmatrix} j \neq i$ | |
| | $\begin{pmatrix} i^* \\ i \end{pmatrix}$ | $\begin{pmatrix} i^* \\ \sigma \\ i \end{pmatrix} a$ | $\begin{pmatrix} \sigma^* \\ \sigma \end{pmatrix} b$ | |

$$a = \sum_i c_{ii}^2 \sum_{\sigma} F_{i\sigma}^2 / \Delta \left(\begin{matrix} i^* \\ \sigma \end{matrix} \right) + F_{\sigma^* i^*}^2 / \Delta \left(\begin{matrix} \sigma^* \\ i \end{matrix} \right) + 4(1-s) b_{i\sigma} / \Delta \left(\begin{matrix} \sigma^* \\ \sigma \end{matrix} \right),$$

$$b = \sum_i \sum_j c_{ii^*} c_{jj^*} \sum_{\sigma} 4(1-s) b_{i\sigma} b_{j\sigma} / \Delta_{\sigma\sigma^*}.$$

D) Effect of the Ground State Determinant

$$a = \sum_i \sum_j \sum_k \sum_l c_{ij^*} c_{kl^*} F_{ij^*} F_{kl^*} / \Delta(0).$$

One may see from these formulae that

i) the diagonal corrections a should imply two summations over the π MO's and two summations over all MO's (i.e. a time proportional to $n_{\pi}^2 n^2$), but the introduction of the ground state corrections reduce them to summations of the type $\sum_i \sum_j \sum_k \sum_p$ involving $n_{\pi}^3 n$ elements.

ii) The cross-terms ($\Phi_I \neq \Phi_J$) b, c, d only involve $\sum_i \sum_j \sum_k \sum_p$ summations of the type $\sum_i \sum_j \sum_k \sum_p$ involving $n_{\pi}^3 n$ matrix elements.

The total computation time of a 2nd order corrected transition energy is therefore proportional to $n_{\pi}^3 n$, while the 2nd order corrected ground-state energy required a time proportional to n^2 . One may distinguish two cases;

i) The conjugated system involved in the zeroth order description of the excitation is kept constant (n_{π} constant), n increasing with the number of substituents. Then the computation time of the transition energy only increases like n .

ii) The dimension of the conjugated system increases like n ($n_{\pi} = n/5$ in conjugated hydrocarbons), and the computation time of the transition energy varies as $n^4/(5)^3$.

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