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Orbital and Excitonic Descriptions of Molecular Excited and Ionized States

I. Delocalization of the Excitation

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The single determinantal Virtual Orbital description of the excited state is compared with the excitonic description for an homogeneous chain of n subunits. The single determinant built from canonical delocalized MO's represents the excited state as a "democratic" mixture of Charge Transfer excitations; the long distances electron jumps are highly probable while the local excitations within the bonds have a vanishing weight when the dimension increases. On the contrary the excitonic treatment (and therefore the Configuration Interaction between singly excited configurations) describes the excited state as mainly built from local excitations and Charge Transfer excitations between adjacent bonds; the long distance electron transfer probability decreases exponentially with the amplitude of the electron jump. Therefore one may say that the Orbital description of the excited state overestimates the electronic delocalization in the excited state. It is shown that the fluctuation of the dipole moment in the excited state varies as n^2 in the Orbital description while in the excitonic model this fluctuation is bounded.

On compare les descriptions excitonique et monodeterminantale (dite Approximation d'Orbitale Virtuelle) des etats excités d'une chaîne homogène de n sous-unités. La représentation à un seul déterminant à l'aide d'orbitales SCF canoniques décrit l'état excité comme un mélange «démocratique» d'«excitations» de transfert de charge: les transferts d'électrons à longue distance y sont très probables, tandis que le poids des excitations locales à l'intérieur des liaisons tend vers zéro quand n augmente. Au contraire le traitement excitonique (et donc l'interaction de configuration des configurations monoexcitées) décrit l'état excité à l'aide d'excitations locales et d'excitations de transfert de charge à courte distance; la probabilité de transferts à longue distance décroît exponentiellement avec l'ampleur du saut. On peut donc dire que la description à un seul déterminant surestime qualitativement la délocalisation électronique dans l'état excité. On montre que la fluctuation quantique du moment dipolaire dans l'état excité croît comme n^2 dans la description orbitale, tandis qu'elle reste bornée dans le modèle excitonique.

Die Beschreibung eines angeregten Zustandes einer homogenen Kette von n Untereinheiten durch eine Determinante mit virtuellen Orbitalen wird mit der excitonischen Beschreibung verglichen. Die einzelne Determinante, die aus kanonischen delokalisierten MO's aufgebaut wird, stellt den angeregten Zustand als eine Mischung von Anregungen mit Ladungsübertragung dar; die Übertragungen von Elektronen über große Entfernungen sind sehr wahrscheinlich, während lokale Anregungen innerhalb der Bindungen ein verschwindendes Gewicht haben, falls die Zahl n ansteigt. Im Gegensatz dazu beschreibt die excitonische Darstellung (und somit die Konfigurationenwechselwirkung mit einfach angeregten Konfigurationen) die angeregten Zustände hauptsächlich durch lokale Anregungen mit Ladungsübertragung zwischen benachbarten Bindungen; die Wahrscheinlichkeit der Übertragung über größere Entfernungen nimmt exponentiell mit der Weite des „Elektronensprungs" ab. Man kann deshalb sagen, daß die Orbitalbeschreibung eines angeregten Zustands die Elektronendelokalisierung überbewertet. Es wird gezeigt, daß die Fluktuation des Dipolmoments im angeregten Zustand wie n^2 in der Orbitalbeschreibung variiert, während sie im excitonischen Modell beschränkt bleibt.

Localized Molecular Orbitals are beginning to be widely used for the study of ground state properties (total ground state energy[1], conformational properties[2], Electron Spin Resonance[3] and Nuclear Magnetic Resonance[4] coupling constants). They have even been used for the study of the stereoselectivity of concerted reactions [7, 8], i.e. outside of the ground state equilibrium region, for nuclear configurations where the bond definition begins to be ambiguous.

The main objection against the localized MO's concerns the representation of excited and ionized states [9]. The idea that the ESCA or ESR experiments show the orbital energy or the orbital repartition as physical features, can only be regarded as naive. But it is clear that the use of symmetry delocalized MO's allows a rather satisfactory single determinantal representation of the excited or ionized states, and the adequacy of the delocalized symmetry MO's for a simple single determinantal representation of the delocalized spectroscopic phenomena certainly explains the complete domination of the delocalized MO's methods over the research and pedagogic works of quantum chemistry [10].

The excited or ionized states may be represented as well from the equivalent sets of localized MO's, using then multideterminantal wave-functions; the excited state appears then as a linear combination of local single excitations, the coefficients of this combination resulting from a partial Configuration Interaction between the local excitations. This is simply the "excitonic" representation of excited states, which has received some applications in molecular physics [11 – 14]. In some sense the situation may be summarized as follows.

– The use of symmetry delocalized MO's, generally implies the variational diagonalization of a one-electron effective hamiltonian (a Hückel type one, or an Hartree-Fock hamiltonian, with possible modifications of the internal field representation in order to get better representations of the excited state). This rather blind procedure allows a single determinantal zeroth order representation of the excited state.

– The excitonic model may use chemically meaningfull localized MO's, atomic core orbitals, bonding and antibonding bond MO's and lone pairs but the description of the excited state requires the diagonalization of a partial CI matrix; the blind procedure is simply displaced from the MO construction to the total WF construction.

In the present paper the two descriptions will be compared on a simple model case, the case of linear homogeneous polymer. It will be shown that the charge-fluctuations (i.e. the probability electron transfers between distant bonds) are overestimated in the single determinantal orbital description of the excited state.

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[1] For single determinantal approximation, see Ref. [1a]; for multiconfigurational perturbative method from SCF localized MO's, *ab initio* calculations, see Ref. [2a], semiempirical calculations, see Ref. [2b]; for multiconfigurational perturbative method from non-SCF bond MO's, one must quote the semi-empirical PCILO method, see Ref. [3], and a few *ab initio* calculations, see first Ref. of [2a] and last Ref. of [3].

[2] *Ab initio* calculations, see Ref. [4]; for semiempirical calculations, the applications of the PCILO method (Ref. [3]) are too numerous to be quoted here.

[3] The fundamental McConnell relationship was already based on the use of localized MO's, [5a]; for some recent *ab initio* calculations see Ref. [5b]; for semiempirical calculations see the PCILO method for localized free radicals [5c].

[4] For *ab initio* calculations, see Ref. [6a]; for semiempirical calculations, see Ref. [6b].

1. Translation of the Single-Determinantal Delocalized Description of the Excitation in Terms of Local Excitations

Let us consider a regular chain of n equivalent bonds. This might be a chain of H_2 molecules, or the π bonds of a linear polyene. Let us consider the (SCF) localized MO's on these bonds, p_i, and the corresponding antibonding (SCF) localized MO's in the valence shell p_{i^*}[5]. One may establish easily the expression of the occupied delocalized (SCF) MO's, by diagonalizing the Fock operator between the bonding localized MO's. Neglecting end effects, and assuming that the Fock operator between non adjacent bonds are negligible in comparison of the Fock operator between adjacent bonds,

$$\begin{aligned} &\langle p_s|F|\,p_s\rangle = E\,\forall\, s \\ &\langle p_s|F|\,p_{s+1}\rangle = \langle p_s|F|\,p_{s-1}\rangle = F\,\forall\, s \\ &\langle p_s|F|\,p_{s+r}\rangle \ll F \qquad\qquad \forall\, s \quad \text{and} \quad |r|>1 \end{aligned} \tag{1}$$

one gets a Fock operator which keeps the form of a Hückel type topological matrix, and the delocalized MO's P_j are given by

$$P_j = \sum_s c_{js} p_s \qquad c_{js} = \sqrt{\frac{2}{n+1}}\sin\frac{j\pi s}{n+1}\,. \tag{2}$$

The corresponding energies increase when j varies from 1 to n. The form of the Fock operator between the virtual orbitals would be the same

$$\begin{aligned} &\langle p_s^*|F|\,p_s^*\rangle = E^*\,\forall\, s \\ &\langle p_s^*|F|\,p_{s+1}^*\rangle = F^*\,\forall\, s \\ &\langle p_s^*|F|\,p_{s+r}^*\rangle = 0 \quad \forall\, s, \qquad r>1 \end{aligned} \tag{3}$$

and the delocalized HF MO's are given by

$$P_j^* = \sum_s c_{js}^* p_s^* \qquad c_{js}^* = \sqrt{\frac{2}{n+1}}\sin\frac{j\pi s}{n+1}\,. \tag{4}$$

The corresponding energies now decrease when n varies from 1 to n, because $FF^*<0$, as may be easily understood by considering the respective phase behaviour of the occupied and virtual localized MO's.

$$\underset{p_i}{\underline{+\quad +}}\qquad \underset{p_{i+1}}{\underline{+\quad +}}\,,$$

$$\underset{p_i^*}{\underline{+\quad -}}\qquad \underset{p_{i+1}^*}{\underline{+\quad -}}\,.$$

Therefore the ordering of the delocalized SCF MO's is given by Fig. 1, which shows the "pairing" of occupied and virtual MO's.

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[5] These SCF localized MO's may be obtained from the usual canonical MO's through any localization process, see Ref. [15].

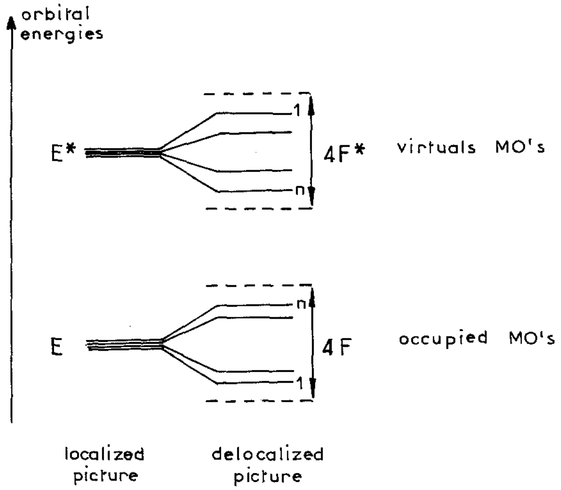

Fig. 1. Ordering of the delocalized MO's obtained from the diagonalization of the Fock operators for the occupied and virtual (HF) localized MO's. The dashed lines represent the limit of the orbital energies when n tends to infinity

The canonical and localized descriptions of the SCF ground state determinant are given by

$$\Phi_0 = \mathscr{A} \prod_{i=1}^{n} P_i = \pm \mathscr{A} \prod_{r=i}^{n} p_r \,. \tag{5}$$

These two descriptions are equivalent since the two sets $\{p_r\}$ and $\{P_i\}$ are obtained from each other through a unitary transformation [16].

N.B. – If the p_i MO's are SCF localized MO's, the Fock operator is zero between occupied and virtual MO's (due to the Brillouin's theorem). This is the reason why we diagonalized separately the two blocks of the Fock operator. If the p_i MO's where fully localized MO's (as in the PCILO method and the usual excitonic treatments), the Fock operator would not split in two blocks, but the diagonalization of the two blocks for occupied and virtual MO's would still give delocalized MO's very close to the SCF ones, since the SCF localized and fully localized MO's are very close [2].

Then the unoptimized single determinantal representation of the excited state (which is frequently called the Virtual Orbital approximation) is obtained by the substitution of a virtual MO P_{j^*} to an occupied one P_i. In the 2nd quantization formalism, this may be written as:

$$\Phi\begin{pmatrix} j^* \\ i \end{pmatrix} = a_{j^*}^{+} a_0 \Phi_0 \,. \tag{6}$$

Expressing the canonical creation and annihilation operators in terms of local creation and annihilation operators (through Eqs. (2) and (4)) one gets an equivalent expression of the excitation procedure

$$\Phi\begin{pmatrix} j^* \\ i \end{pmatrix} = \frac{2}{n+1} \sum_r \sum_s \sin\frac{i\pi r}{n+1} \sin\frac{j\pi s}{n+1} a_{p_{s*}}^{+} a_{p_r} \Phi_0 \tag{7}$$

where Φ_0 may expressed now as the antisymmetrized product of local MO's

$$\Phi\begin{pmatrix} j^* \\ i \end{pmatrix} = \frac{2}{n+1} \sum_r \sum_s \sin\frac{i\pi r}{n+1} \sin\frac{j\pi s}{n+1} \Phi\begin{pmatrix} s^* \\ r \end{pmatrix}. \tag{8}$$

The single excitation from P_i to P_{j*} appears as the linear combination of local excitations from the bonds r toward the antibonding MO of the bonds s. These excitations may be described in general as electron transfer from one region to another. Some of the local excitations, for which $s = r$, do not imply such an electron transfer since they simply represent a ($\pi\pi^*$) excitation in the ethylenic system of a (double) bond. These excitations ($r = s$) will be called local excitations (LEs) while the former ones ($r \neq s$) will be called Charge Transfer excitations (CTEs). The CTEs will be characterized by the amplitude of the electron jump through the quantity $p = |r - s|$ and identified as ^{p}CTE.

Let us analyze now the relative weight of local and charge transfer excitations in the (lowest) excitations. The weight of LE is given by

$$d_{\mathrm{LE}}\begin{pmatrix} j^* \\ i \end{pmatrix} = \left(\frac{2}{n+1}\right)^2 \sum_r \left(\sin\frac{j\pi r}{n+1} \sin\frac{i\pi r}{n+1}\right)^2. \tag{9}$$

Since $\sin^2\alpha \leqq 1$

$$d_{\mathrm{LE}}\begin{pmatrix} j^* \\ i \end{pmatrix} \leqq \frac{4}{n+1}. \tag{10}$$

A more accurate calculation gives $d_{\mathrm{LE}}\begin{pmatrix} j^* \\ i \end{pmatrix} = \frac{1}{n+1}\left[1 + \frac{f(i,j,n)}{n+1}\right]$ where f is bounded by a constant whatever i, j, n.

Therefore the relative weight of LE in the Virtual Orbital description of excited states decreases as $1/n$ when the dimension n of the conjugated system increases[6].

On the contrary the weight of the CTE increases towards 1. The excitations are treated almost democratically, whatever the distance between the departure and arrival bonds, i.e. the amplitude of the electron jump. It will be seen in Appendix 1 that a jump over p intermediate bonds becomes as probable as the local excitations when n is much larger than p.

2. The Excitonic Wave-Function

Let us turn back now towards the excitonic model, in order to analyze the structure of the lowest excited states. The excitonic matrix appears as built from several blocks. One block deals with the LE excitations $\begin{pmatrix} p^* \\ p \end{pmatrix}$ and their matrix

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[6] These results are not modified by considering the proper S^2 eigenfunctions for the excited state

$$\Psi\begin{pmatrix} j^* \\ i \end{pmatrix}^{1,3} = 1/\sqrt{2}\left(\Phi\begin{pmatrix} j^* \\ i \end{pmatrix} \pm \Phi\begin{pmatrix} \bar{j}^* \\ \bar{i} \end{pmatrix}\right)$$

instead of the single determinant $\Phi\begin{pmatrix} j^* \\ i \end{pmatrix}$ of Eq. (6).

elements. For singlet states these matrix elements are essentially transition dipole-transition dipole interactions

$$\left\langle \Phi\begin{pmatrix} r^* \\ r \end{pmatrix} \middle| \boldsymbol{H} \middle| \Phi\begin{pmatrix} s^* \\ s \end{pmatrix} \right\rangle = 2(p_r p_r^*, p_s p_s^*) - (p_r p_s^*, p_s p_r^*) . \tag{11}$$

The second term decreases exponentially with the distance R_{rs} between the bonds r and s, and the first one decreases as $1/R_{rs}^3$. For the triplet state the dipolar interaction disappears. In both cases one may consider that the only important off diagonal elements occur between excitations on adjacent bonds

$$(p_r p_r^*, p_{r+1} p_{r+1}^*) = (p_r p_r^*, p_{r-1} p_{r-1}^*) = b . \tag{12}$$

The LE are less energetic than the CTE, as may be seen from the zeroth-order

$$\Delta E\begin{pmatrix} s^* \\ r \end{pmatrix} = \langle p_s^* | \boldsymbol{F} | p_s^* \rangle - \langle p_r | \boldsymbol{F} | p_r \rangle - J p_r p_s^* + K p_r p_s^* \pm K p_r p_s^* . \tag{13}$$

In this expression the difference between the diagonal elements of the Fock operator are independant on the distance between r and s, while the charge-charge interaction $J p_r p_s^*$ decreases as R_{rs}^{-1}. $K p_r p_s^*$ decreases exponentially with R_{rs} but remains always much smaller than $J p_r p_s^*$ and the localized transition energies may be ordered in the following way:

$$\begin{gathered} \left(\Delta E_0 = \Delta E\begin{pmatrix} r^* \\ r \end{pmatrix}\right) < \left(\Delta E_1 = \Delta E\begin{pmatrix} (r\pm 1)^* \\ r \end{pmatrix}\right) < \left(\Delta E_2 = \Delta E\begin{pmatrix} (r\pm 2)^* \\ r \end{pmatrix}\right) \\ < \cdots < \left(\Delta E_p = \Delta E\begin{pmatrix} (r\pm p)^* \\ r \end{pmatrix}\right) < \cdots < (\langle p_s^* | \boldsymbol{F} | p_s^* \rangle - \langle p_r | \boldsymbol{F} | p_r \rangle) . \end{gathered} \tag{14}$$

One may build therefore the excitonic matrix in a basis of localized excited determinants in which the LE occur first, followed by CTExcitations between adjacent bonds, and so on ... The LE determinants are coupled with the CTE ones, through

$$\left\langle \Phi\begin{pmatrix} r^* \\ r \end{pmatrix} \middle| \boldsymbol{H} \middle| \Phi\begin{pmatrix} s^* \\ t \end{pmatrix} \right\rangle = \langle p_r p_{t^*} | p_r^* p_s \rangle .$$

If r, s and t are all different this matrix element may be approximated through the Mulliken's approximation

$$\left\langle \Phi\begin{pmatrix} r^* \\ r \end{pmatrix} \middle| \boldsymbol{H} \middle| \Phi\begin{pmatrix} s^* \\ t \end{pmatrix} \right\rangle = 1/2 \langle p_s | p_t^* \rangle \left[\langle rs | r^* s \rangle + \langle rt^* | r^* t^* \rangle\right] \tag{15}$$

$\langle ps | pt^* \rangle$ decreases exponentially as $\exp(-R_{st})$, and the two integrals decrease as R_{rs}^{-2} and R_{rt}^{-2} respectively. The matrix element will be negligible except when $t = r$ or $s^* = r^*$. In such a case

$$\begin{aligned} \left\langle \Phi\begin{pmatrix} r^* \\ r \end{pmatrix} \middle| \boldsymbol{H} \middle| \Phi\begin{pmatrix} s^* \\ r \end{pmatrix} \right\rangle &= \langle p_r^* | \boldsymbol{F} - \boldsymbol{J}_r | p_s^* \rangle \\ \left\langle \Phi\begin{pmatrix} r^* \\ r \end{pmatrix} \middle| \boldsymbol{H} \middle| \Phi\begin{pmatrix} r^* \\ s \end{pmatrix} \right\rangle &= \langle p_r | \boldsymbol{F} + \boldsymbol{J}_{r^*} | p_s \rangle . \end{aligned} \tag{16}$$

If s and r are adjacent bonds ($s = r \pm 1$), these matrix elements are rather important

$$\begin{aligned} \left\langle \Phi\begin{pmatrix} r^* \\ r \end{pmatrix} \middle| H \middle| \Phi\begin{pmatrix} (r\pm 1)^* \\ r \end{pmatrix} \right\rangle &= \langle p_r^* | F - J_r | p_{r\pm 1}^* \rangle = A_1 \\ \left\langle \Phi\begin{pmatrix} r^* \\ r \end{pmatrix} \middle| H \middle| \Phi\begin{pmatrix} r^* \\ (r\pm 1) \end{pmatrix} \right\rangle &= -\langle p_r | F + J_{r^*} | p_{r\pm 1} \rangle = B_1 \end{aligned} \tag{17}$$

and we shall keep only these interactions, as we did when diagonalizing the ground state Fock operator. In the same way the CTE between adjacent bonds are coupled with some CTE at two bonds distances.

$$\begin{aligned} \left\langle \Phi\begin{pmatrix} (r+1)^* \\ r \end{pmatrix} \middle| H \middle| \Phi\begin{pmatrix} (r+2)^* \\ r \end{pmatrix} \right\rangle &= \langle p_{r+1}^* | F - J_r | p_{r+2}^* \rangle = A_2 \\ \left\langle \Phi\begin{pmatrix} (r+1)^* \\ r \end{pmatrix} \middle| H \middle| \Phi\begin{pmatrix} (r+1)^* \\ r+2 \end{pmatrix} \right\rangle &= -\langle p_r | F + J_{(r+1)}^* | p_{r+2} \rangle = B_2 \,. \end{aligned} \tag{18}$$

The structure of the excitonic CI matrix is shown in Fig. 2. Then, taking benefit of the fact that $\Delta E_0 < \Delta E_1 < \Delta E_2$ etc… one may try to search the eigenfunctions of the CI matrix by a two steps procedure.

a) diagonalization of the CI matrix of the LE only. This is the original excitonic treatment proposed by Simpson [11]. This step gives some zeroth order wave-functions Ψ_m^0.

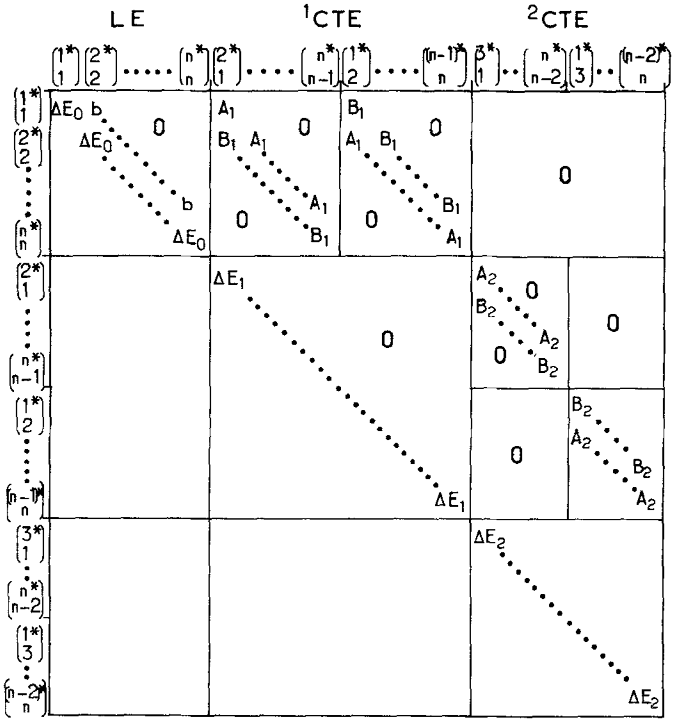

Fig. 2. Structure of the excitonic matrix

b) perturbation of these zeroth order wave functions under the influence of the CTE, through a classical RS procedure.

Since the CI matrix restricted to the LE has a Hückel-type structure, one knows its eigenfunctions and eigenvalues

$$\Psi_m^0 = \sum_{r=1}^{n} C_{mr} \Phi\begin{pmatrix} r^* \\ r \end{pmatrix} \quad \text{with} \quad C_{mr} = \sqrt{\frac{2}{n+1}} \sin \frac{m\pi r}{n+1}, \tag{19}$$

$$\Delta E_m^0 = \Delta E_0 + 2b \cos \frac{m\pi}{n+1}. \tag{20}$$

Then one may perturb Ψ_m^0 under the influence of the CTE. The theoretical details of such a procedure may be found elsewhere [17]. Due to the structure of the CI matrix when one neglects the long distances overlap distributions, the first order wave-function Ψ_m^1 will only involve the ^{1}CTE, i.e. the CTE between adjacent bonds.

$$\Psi_m^1 = \sum_r \left[\left\langle \Psi_m^0 \middle| \boldsymbol{H} \middle| \Phi\begin{pmatrix} (r+1)^* \\ r \end{pmatrix} \right\rangle \Phi\begin{pmatrix} (r+1)^* \\ r \end{pmatrix} + \left\langle \Psi_m^0 \middle| \boldsymbol{H} \middle| \Phi\begin{pmatrix} (r-1)^* \\ r \end{pmatrix} \right\rangle \Phi\begin{pmatrix} (r-1)^* \\ r \end{pmatrix} \right] \times (\Delta E_m^0 - \Delta E_1)^{-1}. \tag{21}$$

In order to analyse the relative weight of the LE and CTE in that model, we must calculate the norm of the first order perturbed wave-function.

$$\begin{aligned} \langle \Psi_m^1 | \Psi_m^1 \rangle &= (\Delta E_m^0 - \Delta E_1)^{-2} \sum_r \left\langle \Psi_m^0 \middle| \boldsymbol{H} \middle| \Phi\begin{pmatrix} (r+1)^* \\ r \end{pmatrix} \right\rangle^2 \\ &\quad + \left\langle \Psi_m^0 \middle| \boldsymbol{H} \middle| \Phi\begin{pmatrix} (r-1)^* \\ r \end{pmatrix} \right\rangle^2 \left\langle \Psi_m^0 \middle| \boldsymbol{H} \middle| \Phi\begin{pmatrix} (r+1) \\ r \end{pmatrix}^* \right\rangle \\ &= C_{mr} \left\langle \Phi\begin{pmatrix} r^* \\ r \end{pmatrix} \middle| \boldsymbol{H} \middle| \Phi\begin{pmatrix} (r+1)^* \\ r \end{pmatrix} \right\rangle + C_{m(r+1)} \left\langle \Phi\begin{pmatrix} (r+1)^* \\ (r+1) \end{pmatrix} \middle| \boldsymbol{H} \middle| \Phi\begin{pmatrix} (r+1)^* \\ r \end{pmatrix} \right\rangle \\ &= C_{mr} A_1 + c_{m(r+1)} B_1 . \end{aligned} \tag{23}$$

Thus

$$\langle \Psi_m^1 | \Psi_m^1 \rangle = \frac{2}{n+1} (\Delta E_m^0 - \Delta E_1)^{-2} \sum_{r=1}^{n-1} \left(\sin \frac{mr\pi}{n+1} A_1 + \sin \frac{m(r+1)\pi}{n+1} B_1 \right)^2. \tag{24}$$

This summation is easy to perform through elementary trigonometrical transformations and gives

$$\langle \Psi_m^1 | \Psi_m^1 \rangle = 4 \left(\frac{A_1 + B_1}{\Delta E_m^0 - \Delta E_1} \right)^2 + \frac{1}{n+1} f(n,m) = N_1 + \frac{1}{n+1} f(n,m) \tag{25}$$

where $f(n,m)$ is a trigonometric function of n and m bounded by a constant. Therefore the weight of the CTE in the first order perturbed wave functions tends towards a constant when n increases. Since $\langle \Psi_m^0 | \Psi_m^0 \rangle = 1$, the ratio of the LE in the first order perturbed wave function tends towards a constant

$$\frac{\langle \Psi_m^0 | \Psi_m^0 \rangle}{\langle \Psi_m^0 | \Psi_m^0 \rangle + \langle \Psi_m^1 | \Psi_m^1 \rangle} \simeq \frac{1}{1 + N_1} \quad \text{when} \quad n \to \infty . \tag{26}$$

The further ^{p}CTE excitations would appear with exponentially decreasing weights: in the first order wave-function the coefficients would imply exponentially decreasing overlap distributions $\varphi_r \varphi_{(r+p)}$, and if one only keeps the interactions between adjacent bonds, they would only appear at the p^{th} order of perturbation with a weight proportional to x^p (See Appendix 2).

3. Discussion of the Electronic Delocalization in the Excited State

This analysis rests upon the convergence of the perturbation expansion. This convergence is questionable for the higher eigenfunctions of the LE CI matrix, but is certainly valid for the lowest excitations. The numerical diagonalizations of the full excitonic matrix actually show that the relative weight of LE tends towards 45% in the series of linear polyenes [18].

The result of the CI procedure gives therefore a description of the excited states which differs qualitatively from the Virtual Orbital single determinant description. The single determinant built from canonical delocalized MO's represents the excited state as a "democratic" mixture of Charge Transfer Excitations. The long distance electron jumps are highly probable while the local excitations in the bonds have a vanishing weight when the dimension increases. On the contrary the excitonic treatment describes the excited state as mainly built from local excitations in the bond (the corresponding probability decreases but tends towards a constant when the number of equivalent bonds increases) and from ^{1}CTE between adjacent bonds. The electron jumps probabilities decrease exponentially with the amplitude of the jump.

It had been noticed already that in the Hückel theory the Orbital description of the excited state only involves exchange or delocalization effects which are therefore overestimated to reproduce implicitely the bielectronic effects[7] One sees here that going from the Hückel to the SCF model does not change quatitatively the validity of the single determinantal description of the excited state as regard the electronic delocalization.

This result concerns not only the excitonic treatment but the usual Configuration Interaction between the singly excited configurations; since the canonical MO's are obtained from the localized ones by two unitary transformations in the spaces of occupied and virtual MO's, the space of the singly excited determinants is invariant in these changes of the MO's, and the eigenvectors of the CI matrix of singly excited determinants are the same, regardless of the localized or delocalized character of the MO's. The excitonic treatment gives therefore some insight upon the physical effect of the CI of singly excited states, which, in the delocalized scheme, seems rather intricate and difficult to analyse, since all the matrix elements loose their local character. Once again the localized picture demonstrates its higher handiness and its interpretative power.

But the most surprising result is that the canonical orbital model of the excitation in a certain sense overestimates the electronic delocalization in the excited state. Of course quantum mechanics describes the excitation as delocalized. In the statistical interpretation of quantum mechanics [20] the Hamiltonian and the wave-function only deal with a set of similarly prepared systems, not

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[7] See Refs. [12] and [19].

with a unique system, and we cannot know what happens in the excitations of a given molecule. The delocalization is linked to the symmetry properties of the Hamiltonian and does not prove anything about the local or global character of the excitation in each molecular system. Even in the excitonic model which only implies the local excitations, the excitation is delocalized, and, this "delocalization" due to the basic principles, cannot be removed in homogenous symmetrical systems.

But the delocalization of the electrons is completely different from the delocalization of the excitation. In this loge theory [21], Daudel has proposed some intrinsic criteria to analyse the extent of electronic delocalization; the probability of finding two and only two electrons in each loge of a partition of space may be maximized with respect to the definition of the loge and this maximum gives an estimate of the physical electronic localization. The higher this probability, the less probable are the situations with 1 electron in loge *i* and 3 electrons in loge *j*.

Along the same direction, and according to the statistical interpretation of the wave-function we proposed to study the fluctuation of the number of electrons in each loge [22]. When the fluctuations are important, the system is not well localizable. One may also consider as a measure of the electronic delocalization the fluctuations of the dipole moment; in a symmetric or non polar system, the "permanent" or mean dipole moment will be zero but the ionic structures in which one electron has jumped from its box *i* to the box *j* introduce some transient dipoles. This concept may be applied to the excited states, and from that point of view it is clear that the orbital description of the excited state overestimates the electronic delocalization. This description (Eq. (8)) is very close the "fully democratic" delocalized description of the excited state where each configuration $\Phi\begin{pmatrix} s^* \\ r \end{pmatrix}$ would appear with a probability $1/n^2$.

$$\Psi = 1/n \sum_r \sum_s \Phi\begin{pmatrix} s^* \\ r \end{pmatrix} \tag{27}$$

for a linear system, the configuration $\Phi\begin{pmatrix} s^* \\ r \end{pmatrix}$ introduces a dipole moment equal to

$$\vec{\mathcal{M}}_{rs} = e\overrightarrow{Rrs} = e\vec{l}(r-s) \tag{28}$$

where l is the standard distance between two bonds $(\vec{r}, \vec{r}+1)$. We shall neglect here the transition dipole moment between different CTE excitations, even when they differ by two adjacent MO's

$$\left\langle \Phi\begin{pmatrix} s^* \\ r \end{pmatrix} \middle| \overrightarrow{\Sigma \boldsymbol{R}} \middle| \Phi\begin{pmatrix} (s+1)^* \\ r \end{pmatrix} \right\rangle = \langle s^* | \boldsymbol{R} | (s+1)^* \rangle \simeq 0 ,$$

as would be done in the CNDO hypotheses for fully localized MO's. All the configurations where $r-s=q$ contribute to the same value $\vec{\mathcal{M}}_q = e\vec{l}q$, which appears with the probability $p_q = \frac{n-|q|}{n^2}$. One knows therefore the full histogram of the dipole moment of the excited state, i.e. the spectral decomposition of the dipole moment in the excited state, which is reported in Fig. 3.

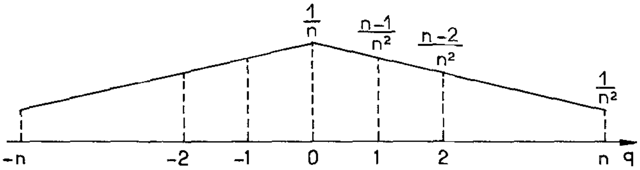

Fig. 3. Distribution of the dipole moment of the excited state for the delocalized single determinantal description

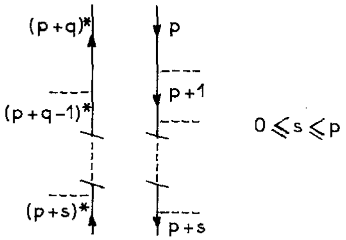

Fig. 4. Appearance of the $\begin{pmatrix}(p+q)^*\\ p\end{pmatrix}^q$ CTE's configurations from the $\begin{pmatrix}(p+s)^*\\ (p+s)\end{pmatrix}$ LE's configurations

The fluctuation of the dipole moment in the excited state may be calculated immediately

$$\mathcal{F} = 2\sum_{q=1}^{n-1} \mathcal{M}_q^2\, p_q = 2\Sigma(el)^2\, q^2\, \frac{n-q}{n^2} = 2(el)^2 \sum_{q=1} (nq^2 - q^3).$$

Since

$$\sum_{q=1}^{n-1} q^2 \simeq \frac{n^3}{3} \quad \text{and} \quad \sum_{q=1}^{n-1} q^3 \simeq \frac{n^4}{4}$$

$$\mathcal{F} = 2(el)^2\, n^2/6\,.$$

The fluctuation of the dipole moment increases as n^2 when the dimension of the system increases. One may see easily that this feature is kept when one uses Eq. (8) for the wave-function, instead of the "fully democratic" single determinantal representation of Eq. (27).

On the contrary the excitonic model (i.e. the full CI of singly excited determinants, whatever the basis set of MO's) will give a completely different histogram. Since the wave-function appears as mainly built from the LE and ^{1}CTE between adjacent bonds, in a ratio which tends towards a constant, the histogram tends towards a constant shape and the fluctuation of the dipole moment also increases towards a constant when n increases.

This result remains valid when one takes into account the long distances ^{p}CTE with their exponentially decreasing weight e^{ap} (cf. Appendix 2). Their contribution to the fluctuation of the dipole moment is indeed proportional to $2\sum_{p=1}^{n-1} p^2 e^{ap}$. This sum may be bracketed through the integration

$$\int_1^n p^2 e^{ap} dp < \sum_{p=1}^{n-1} p^2 e^{ap} < \int_0^{n-1} p^2 e^{ap} dp\,.$$

$\int_0^n p^2 e^{ap} dp = e^{an}\left(\frac{n^2}{a} - \frac{2n}{a^2} + \frac{2}{a^3}\right)$ is bonded whatever n and therefore the fluctuation of the dipole moment is bonded, a being negative as may be seen from Appendix 2.

The configuration Interaction between the singly excited configurations qualitatively changes the picture of the excited state. In the Orbital description, the mean number of electrons per bond is correct, but the fluctuations of electronic positions are much too large. The CI tends to bring back the electrons two by two in each loge. One may say that the orbital description of the excited state is too disordered, and that the CI brings some order in the excited state, diminishes the entropy of the description. The excitonic model looses the single determinantal character and its related advantages, but it gives immediately a more correct representation of the excited state. Table 1 summarizes the main conclusions of this work.

In the following paper, we shall demonstrate that the qualitative differences between the Orbital and Excitonic descriptions of the excited state imply some qualitative differences in the descriptions of the $\sigma-\pi$ coupling effect on the $\pi\pi^*$ transition, and in the orbital reorganisation of the excited states.

Table 1. Summary of the comparison between delocalized and localized pictures of the excitation

	Delocalized picture		Localized picture
MO's	Delocalized P_i, P_{j*}		Localized p_r, p_{s*} $\{p\} = \underset{\sim}{\mathbb{U}}\{\mathbb{P}\}$ $\underset{\sim}{\mathbb{U}}$ unitary
Ground State determinant	Φ_0	identical	Φ_0
Excited determinants	$\Phi\begin{pmatrix} j^* \\ i \end{pmatrix}$		Local excitations $\Phi\begin{pmatrix} r^* \\ r \end{pmatrix}$ charge transfer excitations $\Phi\begin{pmatrix} (r+p)^* \\ r \end{pmatrix}$
Representation of the excited state			
Single determinantal approx.	*Virtual orbital approximation* $\Phi\begin{pmatrix} j^* \\ i \end{pmatrix}$ may be expressed in terms of $\Phi\begin{pmatrix} s^* \\ r \end{pmatrix}$ $\left.\begin{array}{l}\text{The weight of LE's} \rightarrow 0 \\ \text{of PCTE's} \rightarrow 1\end{array}\right\}$ when $n \rightarrow \infty$ The fluctuation of the dipole moment in the excited state behaves like n^2		no single determinantal approximation
CI between the single excited determinants	*Usual* CIS *approximation* This treatment is identical to the excitonic one. The conclusions obtained for the excitonic treatment hold for the CIS approximation, which therefore relocalizes the excitation with respect to the VO approximation.	$\equiv$	*Excitonic method* The weight of LE's → constant C (~ 50%) ^{1}CTE's → 1–C (~ 50%) when $n \rightarrow \infty$ The fluctuation of the dipole moment in the excited state → constant.

Appendix 1

Weight of the ${}^pCTEs$ in the Orbital Model

According to Eq. (8) the weight of the ^{p}CTEs in the orbital model is given by

$$Q(n,p)=\frac{8}{(n+1)^2}\sum_{r=1}^{n-p}\sin^2\frac{i\pi r}{n+1}\sin^2\frac{j\pi(r+p)}{n+1}$$

for the transition $i \to j^*$. For sake of simplicity, the analysis will be limited to the lowest transition, the $N-V$ transition, corresponding to $i=j=n$. Then

$$\begin{aligned}Q(n,p)&=\frac{8}{n+1^2}\sum_{r=1}^{n-p}\sin^2\frac{n\pi r}{n+1}\sin^2\frac{2n\pi(r+p)}{n+1}\\&=\frac{8}{(n+1)^2}\sum_{r=l}^{n-p}\left(\sin\frac{\pi r}{n+1}\sin\pi\frac{r+p}{n+1}\right)^2\\&=\frac{2}{(n+1)^2}\sum_{r=1}^{n-p}\left(\cos\frac{\pi p}{n+1}-\cos\frac{2\pi}{n+1}(r+p/2)\right)^2\\&=\frac{2}{(n+1)^2}\sum_{r=1}^{n-p}\left(\cos^2\frac{\pi p}{n+1}+\cos^2\frac{2\pi(r+p/2)}{n+1}-2\cos\frac{\pi p}{n+1}\frac{\cos 2\pi(r+p/2)}{n+1}\right)\end{aligned}$$

$$\Sigma\cos^2\frac{\pi p}{n+1}=(n-p-1)\cos^2\frac{\pi p}{n+1}$$

$$\Sigma\cos^2\frac{\pi(2r+p)}{n+1}=\frac{n-p-1}{2}+\sin\frac{2p\pi}{n+1}-\cos\frac{2p\pi}{n+1}\left(1+tg\frac{2\pi}{n+1}\right)$$

$$-\Sigma 2\cos\frac{p\pi}{n+1}\cos\frac{(2r+p)\pi}{n+1}=\sin\frac{2p\pi}{n+1}-1+\cos\frac{2p\pi}{n+1}\left(1+\mathrm{tg}\frac{\pi}{n+1}\right).$$

Therefore

$$Q(n,p)=\frac{2}{(n+1)^2}\left[(n-p-1)\left(1/2+\cos\frac{2\pi p}{n+1}\right)+f(n,p)\right]$$

where $f(n,p)$ is a trigonometric function bonded by a constant. $Q(n,p)$ behaves as $\frac{n-p}{(n+1)^2}\left(1+2\cos^2\frac{\pi p}{n+1}\right)$, and when n increases for a fixed value of p, this quantity tends towards $3/n$.

Appendix 2

Weight of the Long Distances Charge Transfer Excitations in the Excitonic Model

The configuration $\begin{pmatrix}(r+p)^*\\ r\end{pmatrix}$ may be reached from the LE $\begin{pmatrix}(r+s)^*\\ (r+s)\end{pmatrix}$ in Ψ_m^0 (where $0 \leqq s \leqq p$) by changing progressively the hole from r to $r+s$ through s hole-hole interactions, and by changing progressively the particle from $(r+s)^*$ to $(r+p)^*$ through $(p-s)$ particle particle interactions. The corresponding diagram is drawn in Fig. 4. For a given value of s, the s hole-hole interaction lines and the

$p-s$ particle-particle interaction lines may have any relative position. The number of relative positions of s balls in $p-s+1$ boxes is $\binom{s}{p}$ and the total number of different diagrams is $N=\sum_{s=0}^{p}\binom{s}{p}=2^p$. One may have an estimate of the corresponding propagator by assuming all the denominators to be equal to ΔE_1 (which is a minorant). If one takes

$$\left.\begin{array}{l} \left\langle \binom{u^*}{t} \middle| \boldsymbol{H} \middle| \binom{u^*}{t+1} \right\rangle = B \\ \left\langle \binom{u^*}{t} \middle| \boldsymbol{H} \middle| \binom{(u+1)^*}{t} \right\rangle = A \end{array}\right\} \quad \forall u, t$$

as occurs in the CNDO hypotheses, the $\binom{s}{p}$ diagrams with s hole-hole interaction lines give a contribution

$$\binom{s}{p} B^s A^{p-s}/\Delta E^p .$$

The coefficient of the configuration $\binom{(r+p)^*}{r}$ in the p^{th} order correction Ψ_m^p is equal to

$$\begin{aligned} \left\langle \Psi_m^p \middle| \Phi\binom{(r+p)^*}{r} \right\rangle &= \sum_{s=0}^{p}\binom{s}{p} B^s A^{p-s} \Delta E^{-p} \\ &= [(A+B)/\Delta E]^p . \end{aligned}$$

Therefore the ^{p}CTE's appear with coefficients exponentially decreasing with the amplitude of the electron jump. Their weight in the perturbed wave function follows the same variation.

References

1a. McWeeny, R., Ohno, K.: Proc. Royal Soc. (London) A **255**, 367 (1960) – Tsuchida, A., Ohno, K.: J. chem. Physics **39**, 600 (1963) – McWeeny, R., Del Re, G.: Theoret. chim. Acta (Berl.) **10**, 13 (1968).

1b. Petke, J. D., Whitten, J. L.: J. chem. Physics **51**, 3166 (1969).

1c. Hoyland, J. R.: J. Amer. chem. Soc. **90**, 2227 (1968); J. chem. Physics **50**, 473 (1969).

2a. Masson, A., Levy, B., Malrieu, J. P.: Theoret. chim. Acta (Berl.) **18**, 193 (1970) – Berthier, G., Meyer, A. Y., Praud, L.: In: Jerusalem Symposia on Quantum Chemistry and Biochemistry **3**, 174 (1971). – Serre, J., Praud, L., Berthier, G.: Jerusalem Symposia on Quantum Chemistry and Biochemistry, p. 198; Bonaccorsi, R., Petrongolo, C., Scrocco, E., Tomasi, J.: Theoret. chim. Acta (Berl.) **15**, 332 (1969).

2b. Diner, S., Malrieu, J. P., Jordan, F., Claverie, P.: Theoret. chim. Acta (Berl.) **15**, 86 (1970).

3. Diner, S., Malrieu, J. P., Claverie, P.: Theoret. chim. Acta (Berl.) **13**, 1, 18 (1969). – Diner, S., Jordan, F., Gilbert, M.: Theoret. chim. Acta (Berl.) **15**, 100 (1969). – Jordan, F., Gilbert, M., Malrieu, J. P., Pincelli, U.: Theoret. chim. Acta (Berl.) **15**, 211 (1969). – Diner, S., Malrieu, J. P., Claverie, P., Jordan, F.: Chem. Physics Letters **2**, 319 (1969). – Daudey, J. P., Diner, S.: Int. J. quant. Chemistry **6**, 575 (1972).

4. Sovers, O. J., Kern, C. W., Pitzer, R. M., Karplus, M.: J. chem. Physics **49**, 2592 (1968); Cadioli, R., Pincelli, U., Levy, B.: Chem. Physics Letters (in press). – Lehn, J. M., Munsch, B., Levy, B., Millié, Ph.: Theoret. chim. Acta (Berl.) **18**, 143 (1970).

5a. McConnell, H.: J. chem. Physics **24**, 764 (1956).
5b. Maeder, F., Berthier, G., Millié, Ph.: Int. J. quant. Chemistry **4** s, 175 (1970). – Levy, B., Berthier, G., Millié, Ph.: Int. J. quant. Chemistry **6**, 155 (1972). – Ellinger, Y., Rassat, A., Subra, R., Berthier, G., Millié, Ph.: Chem. Physics Letters **11**, 362 (1971).
5c. Langlet, J., Malrieu, J. P.: Theoret. chim. Acta (Berl.) **22**, 80 (1971).
6a. Hiroike, E.: J. physic. Soc. Japan **22**, 379 (1967). – Armour, E. A. G., Stone, A. J.: Proc. Royal Soc. (London) A **302**, 25 (1967). – Barbier, C., Gagnaire, D., Berthier, G., Levy, B.: J. Magn. Res. **5**, 11 (1971). – Barbier, C., Lêvy, B., Millié, Ph.: Chem. physic. Letters **17**, 122 (1972).
6b. Pople, J. A., Santry, D. P.: Molecular Physics **8**, 1 (1964). – Denis, A., Malrieu, J. P.: Molecular Physics **23**, 581 (1972).
7. Trindle, C.: J. Amer. chem. Soc. **91**, 4054 (1969); 3251, 3255 (1970); Theoret. chim. Acta (Berl.) **18**, 261 (1970).
8. Langlet, J., Malrieu, J. P.: J. Amer. chem. Soc. **94**, 7254 (1972).
9. See the discussion of the report by G. Berthier about localized pictures, Colloque international du CNRS Menton (1970), related in "Aspects de la Chimie Quantique Contemporaine, CNRS, (Paris) p. 49 (1971).
10. Malrieu, J. P.: J. Photochem. Photobiol. **7**, 531 (1968).
11. Simpson, W. T.: J. Amer. chem. Soc. **73**, 5363 (1951); **77**, 6164 (1955).
12. Pople, J. A., Walmsley, S. M.: Trans. Faraday Soc. **58**, 441 (1962).
13. Murrell, J. N.: J. chem. Physics **37**, 1162 (1962).
14. Langlet, J.: Theoret. chim. Acta (Berl.), **27**, 223 (1972).
15. Edmiston, C., Ruedenberg, K.: J. chem. Physics **43**, 597 (1963); Rev. mod. Physics **35**, 457 (1963). – Gilbert, T. L.: In: Molecular orbitals in chemistry, Physics and Biology, Löwdin, P. O., Pullman, B. (Eds.) p. 405. New York: Acad. Press 1964. – Foster, J. M., Boys, S. F.: Rev. mod. Physics **32**, 300 (1960). – Magnasco, V., Perico, A.: J. chem. Physics **47**, 971 (1967).
16. Lennard-Jones, J. E.: Proc. Royal Soc. (London) A **198**, 114 (1949). – Hall, G. G., Lennard-Jones, J. E.: Proc. Royal Soc. (London) A **202**, 155 (1950); A **205**, 367 (1951); Hall, G. G.: Proc. Royal Soc. (London) A **202**, 166 (1950); A **203**, 102 (1952).
17. Huron, B., Malrieu, J. P., Rancurel, P.: J. chem. Physics (in press).
18. Langlet, J., Malrieu, J. P.: Theoret. chim. Acta, (Berl.) (in press).
19. Salem, L.: The molecular orbital theory of conjugated systems. p. 448-452. New York: W. A. Benjamin (1966).
20. See e.g. Ballantine: Rev. mod. Physics **42**, 358 (1970).
21. Daudel, R.: Les fondements de la chimie théorique. Paris: Gauthier Villars 1956.
22. Diner, S., Claverie, P., Malrieu, J. P., to be published.

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