CROATICA CHEMICA ACTA CCACAA 56 (3) 389—395 (1983)

CCA-1386

YU ISSN 0011-1643
UDC 541;547.534.2
Original Scientific Paper

Perturbational Self-Consistent Orbitals for Open-Shell Systems. An Application to Xylylenes*

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Received August 8, 1982

An extension of the Lefebvre-Daudey method of building self-consistent localized MO's for closed-shell systems by use of the perturbation theory is given for open-shell systems. By avoiding the eigenvalue problem, and then the diagonalization process, a convenient set of SCF MO's is build so that the results of the Configuration Interaction calculations can be qualitatively understood from a chemical point of view. An application to the ortho-meta- and para-xylylenes is given.

INTRODUCTION

The ortho- meta- and para-xylylenes can be considered as resulting from the interaction of a benzene ring with two methylene groups in ortho- meta- or para-positions. This kind of systems can be studied by purely topological methods such as Q.D.M.P.T.[1,2] (Quasi Degenerate Many-Body Perturbation Theory) and N.O.O.N.[3] (Natural Orbital Occupation Number) or by Valence-Bond wave functions[4]. It is well known[2,3] that in the ortho- and para-systems the singlet state is lower than the triplet while in the meta- the triplet state is lower than the singlet.

For a study by Configuration Interaction method of the singlet-triplet energy difference of these systems two kind of M.O.'s can be used to build ground and excited state determinants:

— The first set is made of the canonical delocalized SCF M.O.'s of xylylenes araising from the usual Hartree-Fock variational method. The main problem with the use of these orbitals results from their complete delocalization over the radical centers and the benzene ring; then it is difficult to give a chemical interpretation of the Configuration Interaction calculations.

— A second set of M.O.'s is made of the localized orbitals which can be chosen by purely chemical intuition: the benzene ring occupied and vacant orbitals and the orbitals associated with the two methylene groups; after normalization this set of orbitals can be used to build the ground and the excited state determinants. Although it is easy to give a chemical interpretation in these kind of determinants, the Configuration Interaction calculations does not

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* Presented at *The IUPAC International Symposium on Theoretical Organic Chemistry,* held in Dubrovnik, Croatia, August 30 — September 3, 1982.

converge rapidly due to the local character of the chosen orbitals; in practice one have to go, at least, to the fourth order terms to reach the convergence. On the other hand a perturbation expansion beyond the second order cannot be easily understood in a qualitatively manner. Therefore the conceptual advantage of the use of the perturbation theory is lost. Therefore we need a convenient set of semilocalized M.O.'s which allows fastly convergent Configuration Interaction calculations.

For this purpose we shall build S.C.F. M.O.'s by a perturbational method. The starting orbitals of the S.C.F. process will be totally localized on the benzene ring or on the two methylene fragments; by avoiding the eigenvalue problem, and then the diagonalization process[5,6] we hope to preserve at the end of the S.C.F. process the identity of the initially chosen orbitals.

THE OPEN-SHELL SELF CONSISTENT PERTURBATIONAL METHOD

A. Method

Many years ago Lefebvre[5] proposed to use the perturbation theory to calculate SCF M.O.'s instead of the variational theory in the traditional Hartree-Fock method. A few years later Daudey[6] used the Lefebvre theory in order to obtain SCF M.O.'s for a closed-shell system close to the initial guess of orbitals; furthermore he demonstrated how one can determine directly *self-consistent localized* M.O.'s for a closed shell system.

Following the Lefebvre-Daudey method one can build[7] a set of SCF M.O.'s Φ_i', Φ_p' and $\Phi_j{}^*$ for an open-shell system starting from an initial guess of M.O.'s Φ_i, Φ_p and $\Phi_j{}^*$ in the following manner:

$$\Phi_i' = \Phi_i + \sum_{p} C_{ip}\,\Phi_p + \sum_{j^*} C_{ij}{}^*\,\Phi_j{}^* \tag{1}$$

$$\Phi_p' = \Phi_p - \sum_{i} C_{ip}\,\Phi_i + \sum_{j^*} C_{pj}{}^*\,\Phi_j{}^* \tag{2}$$

$$\Phi_j{}^{*\prime} = \Phi_j{}^* - \sum_{i} C_{ij}{}^*\,\Phi_i - \sum_{p} C_{pj}{}^*\,\Phi_p \tag{3}$$

where *i*, *p* and *j** index correspond to the doubly occupied, partially occupied and vacant M.O.'s respectively.

In eq. (1), (2) and (3) the mixing coefficients C_{ip}, $C_{ij}{}^*$ and $C_{pj}{}^*$ are supposed to be small. Then using these modified M.O.'s Φ_i', Φ_p' and $\Phi_j{}^{*\prime}$ one can build a ground state, determinant, Φ_o'.

$$\Phi_o' = \|\,\Phi_1'\,\Phi_2' \ldots \Phi_i' \ldots \Phi_p' \ldots\| \qquad \text{or} \tag{4a}$$

$$\begin{aligned}\Phi_o' = \|\,&(\Phi_1 + \sum_{p} C_{1p}\,\Phi_p + \sum_{j^*} C_{1j}{}^*\,\Phi_j{}^*)\,(\Phi_2 + \sum_{p}{}' C_{2p}\,\Phi_p + \sum_{j^*} C_{2j}{}^*\,\Phi_j{}^*) \ldots \\ &\ldots (\Phi_i + \sum_{p} C_{ip}\,\Phi_p + \sum_{j^*} C_{ij}{}^*) \ldots (\Phi_p - \sum_{i} C_{ip}\,\Phi_i + \sum_{j^*} C_{pj}{}^*\,\Phi_j{}^*) \ldots \|\end{aligned} \tag{4b}$$

Because coefficients C_{ip}, $C_{ij}{}^*$ and $C_{pj}{}^*$ supposed to be small one can neglect in eq. (4b) the terms of an order higher than order two with respect to these coefficients; developping the determinant (4b) leads to:

$$\begin{aligned}\Phi_o' = {}&\|\,\Phi_1\,\Phi_2 \ldots \Phi_i \ldots \Phi_p \ldots\| + \|\,(\sum_{p} C_{1p}\,\Phi_p)\,\Phi_2 \ldots \Phi_i \ldots \Phi_p \ldots\| + \ldots + \\ &+ \|\,\Phi_1\,\Phi_2 \ldots (\sum_{p} C_{ip}\,\Phi_p) \ldots \Phi_p \ldots\| + \ldots + \|\,\Phi_1\,\Phi_2 \ldots \Phi_i \ldots (-\sum_{i} C_{ip}\,\Phi_i) \ldots\| +\end{aligned}$$

$$+ \| (\sum_{j^*} C_{1j^*} \Phi_{j^*}) \Phi_2 \ldots \Phi_i \ldots \Phi_p \ldots \| + \ldots + \| \Phi_1 \Phi_2 \ldots (\sum_{j^*} C_{ij^*} \Phi_{j^*}) \ldots \Phi_p \ldots \| + \ldots + \| \Phi_1 \Phi_2 \ldots \Phi_i \ldots (\sum_{j^*} C_{pj^*} \Phi_{j^*}) \ldots \| + \ldots \tag{5}$$

The 2nd ... 4th determinants are zero; after factorization of the other determinants, the relation (5) becomes:

$$\Phi_o' = \| \Phi_1 \Phi_2 \ldots \Phi_i \ldots \Phi_p \ldots \| + \sum_i \sum_{j^*} C_{ij^*} \| \Phi_1 \Phi_2 \ldots \Phi_{j^*} \ldots \Phi_p \ldots \| + \sum_p \sum_{j^*} C_{pj^*} \| \Phi_1 \Phi_2 \ldots \Phi_i \ldots \Phi_{j^*} \ldots \| \tag{6a}$$

or

$$\Phi_o' = \Phi_o + \sum_i \sum_{j^*} C_{ij^*} \Phi_{i \to j^*} + \sum_p \sum_{j^*} C_{pj^*} \Phi_{p \to j^*} \tag{6b}$$

where Φ_o and $\Phi_{i \to j^*}$, $\Phi_{p \to j^*}$ represents ground and excited state determinants respectively.

The coefficients in eq. (1), (2), (3) and (6b) are chosen as (see below):

$$\left.\begin{aligned} C_{ij^*} &= \frac{F_{ij^*}}{\varepsilon_i - \varepsilon_{j^*}} \\ C_{ip} &= \frac{F_{ip}}{\varepsilon_i - \varepsilon_p} \\ C_{pj^*} &= \frac{F_{pj^*}}{\varepsilon_p - \varepsilon_{j^*}} \end{aligned}\right\} \tag{7}$$

where ε and F are the diagonal and off-diagonal elements of the Fock matrix in the M.O.'s basis.

At each SCF cycle the new set of M.O.'s Φ_p', Φ_p' and Φ'_{j^*} which is obtained from the previous one (Φ_i, Φ_p and Φ_{j^*}) by means of eq. (1), (2) and (3) is orthonormalized by a mixed Löwdin-Smith procedure[7]. The same process is the repeated until convergency is reached i. e. until the following relations are fulfilled

$$\left.\begin{aligned} F^{(n)}_{ij^*} &= F^{(n+1)}_{ij^*} = 0 \\ F^{(n)}_{ip} &= F^{(n+1)}_{ip} = 0 \\ F^{(n)}_{pj^*} &= F^{(n+1)}_{pj^*} = 0 \end{aligned}\right\} \tag{8}$$

where n represents the nth iterative cycle.

As it can be demonstrated[8] when the mixing coefficients and the convergence conditions are given by relations (7) and (8) respectively then eq. (6b) corresponds to the first order correction of the ground state determinant, Φ_o, by all the monoexcited state determinants, $\Phi_{i \to j^*}$ and $\Phi_{p \to j^*}$, in the framework of the Nesbet approximation[9] for the open-shell systems.

The whole SCF perturbative proces has been tailored so as:

(*i*) to avoid the mixing of M.O.'s with the same occupation number. In particular we need to avoid the mixing of the singly occupied orbitals which are in general degenerate or quasi-degenerate in an open-shell system and then have a tendancy to mix together.

(*ii*) to follow in a simple and concise manner the evolution of the M.O.'s along the SCF procedure. Indeed as it can be seen from eq. (1), (2) and (3) in each SCF cycle each M.O. is obtained from the previous one mixed with a small fraction of the others M.O.'s. By avoiding the traditional eigenvalue problem and then the diagonalization process the final SCF M.O.'s — as in the Lefebvre-Daudey method — have a strong memory of the starting in the initial guess M.O.'s.

However this perturbational method needs a careful choice of the initial guess of M.O.'s so that the mixing coefficients C_{ip}, $C_{ij}{}^*$ and $C_{pj}{}^*$ be actually small in the perturbational development. Most often, these conditions can be satisfied by choosing as initial guess, a set of orbitals which are localized or quasi-localized in well chosen molecular fragments; these molecular fragments can be determined from on chemical intuition grounds.

B. Application to Xylylenes

B1. Minimal Basis Calculations in the ab Initio Level

Because the initial guess orbitals are crucial for the final M.O.'s in the SCF perturbational method we have chosen them in the following manner: The eight π-orbitals of each xylylene isomer are the six canonical delocalized π-MO's of the benzene ring plus two P_z atomic orbitals for each methylene group. The σ-orbitals are the canonical σ-M.O.'s obtained by a preliminary Hartree-Fock variational calculation for each xylylene isomer. The whole set of these orbitals is then orthonormalized by a $s^{-1/2}$ process.

In the above set of orbitals each xylylene isomer is considered as a pure diradical system with a single electron in each P_z atomic orbital: therefore these two orbitals are, in the beginning, the two N.B.M.O.'s (Non-Bonding M.O.'s). At the end of the SCF perturbative process each N.B.M.O. contains — as was expected by the theory — only one P_z atomic orbital plus some delocalized tails on the benzene ring. These delocalized tails are the consequence of the interaction (see next paragraph) of each P_z orbital with the occupied and vacant orbitals of the benzene ring fragment.

Our calculations show further that the main rearrangements of the guessed orbitals occur in the first iterative SCF cycle; the remaining cycles lead to small numerical refinements. This is specific to the π-electron systems and can be also observed in the traditional variation methods when Hückel type orbitals are used in the initial guess.

B2. Rationalization of the ab Initio Results at the Hückel Level

As the first SCF cycle for the π-electrons of the xylylenes has a decisive role in the final results one can use the Hückel approximation to understand this. At this level of approximation the M.O.'s of the benzene ring can be given by the simple and well known analytical expressions [10] for a $4N+2$ cyclic polyene.

By using these expressions one can obtain[8] analytical expressions for the mixing coefficients $C_{ij}{}^*$, C_{ip} and $C_{pj}{}^*$ given by eq. (7); further by making the corresponding trigonometrical summations in eq. (2) one can obtain[8] for the

NBMO's, for example, the following expressions (given here before normalization):

$$C_{A,\,q} = -\frac{K_N}{2\,\beta N}\sin\frac{\pi}{2}\left|q-(q_o)_1\right|\cdot\left[\frac{N}{2}+\sin\frac{\pi}{2}\left|q-(q_o)_1\right|\right]$$

$$C_{A,\,p_{z_1}} = 1 \tag{9}$$

$$C_{B,\,q} = -\frac{K_N}{2\,\beta N}\sin\frac{\pi}{2}\left|q-q_o)_2\right|\left[\frac{N}{2}+\sin\frac{\pi}{2}\left|q-(q_o)_2\right|\right]$$

$$C_{B,\,p_{z_2}} = 1 \tag{10}$$

$C_{A,q}$ and $C_{B,q}$ are the L.C.A.O. coefficients in the q^{th} A.O. of the $4N+2$ polylene in the A and B N.B.M.O.'s respectively;

p_{z_1} and p_{z_2} are the two methylene p_z A.O.'s;

$(q_o)_1$ and $(q_o)_2$ are the numbers of the two A.O.'s of the $4N+2$ polyene in which the p_{z_1} and p_{z_2} A.O.'s are lying;

K_N is a constant which depends on the size of the $4N+2$ polyene

$$K_N = <\Phi_{q_o}\left|\hat{h}(1)\right|p_{z_1}> + \sum_k\sum_\nu \; Bk_\nu B_{kq_o}(\Phi_{q_o}p_{z_1}\left|\Phi_{q_o}\Phi_\nu\right.) + (\Phi_{q_o}p_{z_1}\,|$$

$$|p_{z_2}p_{z_2}) + \frac{1}{q}(\Phi_{q_o}p_{z_1}\left|p_{z_1}p_{z_2}\right.)$$

here $\hat{h}(1)$ is the monoelectronic operator and $B_{k\nu}$, B_{kq_o} are respectively the LCAO coefficients in the Φ_ν and Φ_{q_o} A.O.'s of the k^{th} doubly occupied M.O. of the $4N+2$ polyene.

The differential overlap of the NBMO's, crucial to the Configuration Interaction analysis, is proportional to the products of eq. (9) by eq. (10); the investigation of this products gives:

when $(q_o)_1$ and $(q_o)_2$ are
both odd (stared)
or both even (unstared)

$$C_{Aq}\times C_{Bq}\left\}\begin{array}{l}\neq 0 \text{ when } q = \text{even (unstared)}\\[2ex] = 0 \text{ when } q = \text{odd (stared)}\end{array}\right.$$

when $(q_o)_1$ and $(q_o)_2$ are
even and odd (unstared and stared)

$$C_{Aq}\times C_{Bq} = 0 \quad \text{for each } q$$

The above relations reflect the alternant character of the xylylene systems; they show also that each xylylene isomer can be visualized as the superposition of two benzyl radicals. It should be noticed here that this kind of N.B.M.O. can be also obtained[11] by a $\pi/4$ rotation of the HOMO and LUMO canonical MO's of xylylenes; however in this case the origin of the N.B.M.O.'s cannot be given.

THE CONFIGURATION INTERACTION CALCULATIONS FOR THE SINGLET-TRIPLET ENERGY DIFFERENCE

As it is well known[12,13] perturbation theory allows the direct calculation of the energy difference between the ground and the excited states. For the direct calculation of the singlet-triplet energy difference Malrieu has proposed[13,14] a Nesbet-Eipstein barycentric partition of the exact, $\hat{H}_{ex}$, hamiltonian

$$\hat{H}_{ex} = \hat{H}_o + \hat{V}$$

with

$$\hat{H}_o = E_o [\,|S><S| + |T><T|\,] + \sum_{\Phi_k} [<\Phi_k|\hat{H}_{ex}|\Phi_k>|\Phi_k><\Phi_k|\,]$$

where $|S>$ and $|T>$ are the zero order singlet and triplet wave functions respectively;

E_o is the barycentric zero order energy;

Φ_k are all the excited state determinants.

Under the above partition of the exact hamiltonian the energy difference, $\Delta E^{(2)}_{S-T}$, of the singlet-triplet state in the second order is given[13,14] by

$$\Delta E^{(2)}_{S-T} = 2 \sum_{\Phi_k} \frac{<\Phi_1|\hat{H}_{ex}|\Phi_k><\Phi_k|\hat{H}_{ex}|\Phi_2>}{E_o - <\Phi_k|\hat{H}_{ex}|\Phi_k>} \qquad (11)$$

where $|\Phi_1 = \|\Phi_1 \Phi_2 \ldots |\Phi_i \ldots A\bar{B}\|$ and $|\Phi_2 = \|\Phi_1 \Phi_2 \ldots |\Phi_i \ldots B\bar{A}\|$

TABLE

Compound / Contribution	ORTHO- ev	META- ev	PARA- ev
Exchange	+ 0.0301	+ 1.6197	+ 0.0263
Super Exchange	— 1.5010	— 0.0001	— 1.7386
Double (on Dynamic) Spin-Polarization	— 1.2263	+ 1.1367	— 1.2311
Doubly Excitations	+ 0.0640	— 0.2978	— 0.0107
Charge Transfert A, B → j*	— 0.0056	— 0.8802	— 0.0117
Charge Transfert i → A, B	— 0.0132	— 0.9628	— 0.0090
SUM	— 2.6520	+ 0.6155	— 2.9749

where the plus sign means that the corresponding contribution favors the triplet state and the minus favors the singlet state;

A and B are the two N.B.M.O.'s;

i and j* are the occupied and vacant M.O.'s.

The main advantage of formula (11) is that it can give in a simple and concise manner the contribution of each excited state determinant in both the singlet and triplet zero order states.

The final results are given in the table. The full analysis of these results will be given in a forthcoming paper.

CONCLUSION

The SCF perturbative process gives, as expected by the theory, N.B.M.O.'s which have a strong memory of the initial guess orbitals; furthermore the use of these orbitals in the Configuration Interaction Calculations of the singlet-triplet energy difference gives a satisfying convergence even to second order.

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SAŽETAK

Perturbacijske samousklađene orbitale za sisteme s otvorenom ljuskom. Primjena na ksililene

P. Karafiloglou

Prikazano je proširenje Lefebvre-Daudeyeve metode izgradnje samousklađenih lokaliziranih MO za sisteme sa zatvorenom ljuskom, pomoću perturbacijske teorije, na sisteme s otvorenom ljuskom. Uklanjanjem problema vlastitih vrijednosti i procesa dijagonalizacije izgrađen je pogodan set samousklađenih MO tako da se rezultati dobiveni metodom konfiguracijskih interakcija mogu kvalitativno sagledati s kemijskog aspekta. Predočena je primjena na orto-, meta- i para-ksililene.