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Topological Localized Molecular Orbitals of Hückel and Möbius Annulenes*

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A localization method in the framework of Hückel MO theory which relies only on molecular topology, and which can be regarded to as the topological version of well established localization criteria, has been applied to the series of (n)annulenes. The calculations have been effected for both Hückel and Möbius topologies, and several aspects of the resulting localized orbitals (homogeneity, equivalence, continuous degeneracy and localizability of degenerate levels) have been considered. It is thus seen that the parallelism between Hückel and Möbius systems also holds for their localized molecular orbitals.

INTRODUCTION

It is generally accepted that aromaticity is due to the delocalization of π electrons. It is therefore not surprising that the localization of MO's in conjugated hydrocarbons has deserved considerable attention.[1-6] In particular, England and Ruedenberg[3] have proposed that the delocalization energy of these compounds is due to the »local delocalization« of each localized π-orbital, which is still more delocalized than the ethylene π-orbital. A systematic study of localized molecular orbitals (LMO's) in the (n)annulenes was not undertaken, however, until 1975 when Kleier, Dixon and Lipscomb[4] applied the Boys criterium[7] for the complete and π-only localization of several monocyclic aromatic rings containing six and ten π-electrons. These authors found evidence for $\sigma - \pi$ separation in the complete localization for some of these molecules, and on the other hand they found that the π-orbital localizations were always indeterminate, result which they considered to be a corollary of Hückel's $(4n + 2)$ rule of aromaticity.

In 1959, Craig[8] first showed that the aromatic character of a ring would change if there was an odd number of phase inversions resulting from a mixed cyclic array of p and d orbitals. Later on Heilbronner[9] indicated that

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the same should apply to a twisted ring of p orbitals, and proposed the name »Möbius ring« for such systems, which up to date have been neither isolated nor detected. After the publication of the Woodward-Hoffman selection rules, Dewar[10] and Zimmermann[11] pointed out that the transition states of pericyclic reactions were isoconjugate to Hückel or Möbius annulenes, and used the Hückel-Möbius aromaticity rules to predict whether a pericyclic reaction was thermally allowed or forbidden, leading to the so-called Dewar-Zimmermann selection rules. There is until now a lack of localization studies on Möbius systems, in particular at the level of Möbius (n)annulenes.

In the present work, a localization method for π-MO's which relies only on molecular topology,[12] therefore constituting the most coherent way to localize MO's obtained from Hückel calculations, is used to study the π-LMO's of Hückel and Möbius annulenes.

LOCALIZATION PROCEDURE

Let $\{\chi_r\}_{r=1,\dots,n}$ be the set of $2p_z$ atomic orbitals (AO's) centered on the carbon atoms of a conjugated hydrocarbon with 2 m electrons, and let φ_i be a MO built as a linear combination of these AO's:

$$\varphi_i = \sum_r^n \chi_r C_{ri} = \chi\, C_i \qquad i = 1,\dots,m \tag{1}$$

In the Hückel formalism, the canonical MO's (CMO's) are those satisfying

$$T\, C = C\, \varepsilon \tag{2}$$

where T is the topological (adjacency) matrix, C is an nxm matrix whose columns are the C_i 's and ε is a diagonal mxm matrix whose diagonal elements are the CMO's energies expressed in β units and taking $\alpha = O$ as the origin. An orthogonal transformation O of the CMO's leaves eq. (2) invariant, i. e. $C' = CO$ with $O^tO = OO^t = 1$ implies $TC' = C'\varepsilon'$ with $\varepsilon' = O^t\,\varepsilon O$, where ε' is in general no longer diagonal but still a symmetric matrix. This flexibility allows for selecting a set of MO's which exhibit a maximum degree of localization. Intrinsic localization criteria require that the orbitals maximize the localization sum

$$S = \sum_1^m [\varphi_i\,\varphi_i\,|\,\varphi_i\,\varphi_i] \tag{3}$$

where $[\varphi_i\,\varphi_j\,|\,\varphi_k\,\varphi_l] = \int \varphi_i\,(r_1)\,\varphi_j\,(r_1)\,f\,(r_{12})\,\varphi_k\,(r_2)\,\varphi_l\,(r_2)\,d\,\tau_1\,d\,\tau_2$, $f\,(r_{12})$ being a different function of r_{12} for each criterium.

Introducing the expansion (1) in the localization sum (3) and making use of the ZDO approximation we obtain

$$S = \sum_{i\,r,t}^{m\,n} C_{ri}{}^2\, L_{rt}\, C_{ti}{}^2 \tag{4}$$

where a matrix L has been introduced whose elements are defined as

$$L_{rt} \equiv [\chi_r\,\chi_r\,|\,\chi_t\,\chi_t] \tag{5}$$

and which will be referred to as the »localization matrix«. Eq. (4) can be

expressed in a more compact way by introducing a matrix Q with elements $Q_{ri} \equiv (C_i\, C_i^t)_{rr} = C_{ri}^2$, giving

$$S = Tr\,(Q^t\, L\, Q) \tag{6}$$

Our topological approach to the localization problem has shown[12] that sensible results are obtained when matrix L is taken in the form

$$L = 1 + kT \tag{7}$$

where k is an adjustable parameter. The resulting orbitals are referred to as topological LMO's (TLMO's). With this choice of the localization matrix, the localization sum (6) becomes

$$S = Tr\,(Q^t\, Q) + kTr\,(Q^t\, T\, Q) \tag{8}$$

It is interesting to compare this expression with those of the number of π--electrons

$$2\,m = 2\,Tr\,(C^t\, C) \tag{9}$$

and of the total π-electron energy

$$E_\pi = 2\,Tr\,(C^t\, T\, C) \tag{10}$$

of the molecule, which are invariant under orthogonal transformations of the MO's. The substitution of matrix C by matrix Q breaks down this invariance, and in this way the resulting quantities can be used as localization variables.

The maximization of S is effected through an iterative sequence of 2×2 rotations[13], which requires the knowledge of

$$A_{ij} \equiv \sum_{r,\,t}^{n} L_{rt}\,\{C_{ri}\,C_{rj}\,C_{ti}\,C_{tj} - 1/4\,(C_{ri}^2 - C_{rj}^2)\,(C_{ti}^2 - C_{tj}^2)\} \tag{11}$$

$$B_{ij} \equiv \sum_{r,\,t}^{n} L_{rt}\,(C_{ri}^2 - C_{rj}^2)\,C_{ti}\,C_{tj} \qquad i,\,j = 1,\ldots,m \tag{12}$$

in order to calculate the angle α of each partial rotation:

$$\sin\,(4\alpha) = B_{ij}/(A_{ij}^2 + B_{ij}^2)^{1/2}; \quad \cos\,(4\alpha) = -\,A_{ij}/(A_{ij}^2 + B_{ij}^2)^{1/2} \tag{13}$$

Localization is achieved when $\alpha = 0$ for every pair of MO's.

In the case of Möbius annulenes, the CMO's have been obtained as eigenvectors of the switch[14] matrix obtained assigning connectivity -1 to an arbitrary pair of consecutive vertices, and the localization matrix elements L_{rt} have been taken as $\delta_{rt} + k\,|\,T_{rt}\,|$ given that they can be considered as the topological reduction of the non-negative integrals obtained taking $f\,(r_{12}) = r_{12}^{-1}$ in expression (5).[12] It should be noted that the parallelism between (8) and (10) does not hold for Möbius systems.

The LMO's thus obtained are comparable with those resulting from Hückel systems, except for a sign inversion appearing whenever a localized orbital embraces the arbitrary edge in which connectivity -1 has been located.

AROMATIC (CLOSED SHELL) ANNULENES

England and Ruedenberg[3] have defined a set of LMO's to be homogeneous if they have the same energy, which, for annulenes, equates to the average orbital

energy of the molecule. Homogeneous LMO's result in the following cases:

Number of atoms		Net charge
Hückel	Möbius	
4p + 1	4p + 3	anions
4p + 2	4p	neutral
4p + 3	4p + 1	cations
4p	4p + 2	dications

Homogeneous orbitals are said to be equivalent if they can be interconverted by a symmetry operation of the molecule. Equivalent LMO's are obtained (or can be obtained if continuous degeneracy occurs) whenever a Kekulé structure can be written in which all the pairs are themselves equivalent. LMO's of this kind appear therefore in systems of the form:

	Number of atoms	Net charge
Hückel	2p + pm	pm +
Möbius	4p + pm	pm +

with p odd and m = 0, 1, 2, . . .

A subset of the LMO's is said to be continuously degenerate if their localization sum is invariant under a non-discrete set of orthogonal transformations. There is therefore an infinite number of sets of LMO's corresponding to a plateau in the localization sum hypersurface, and for any pair of this subset A_{ij} and B_{ij} must vanish (see eq. (13)). Although according to Kleier, Dixon and Lipscomb[4] the Boys criterium produces continuously degenerate LMO's for all of the aromatic Hückel annulenes, the Edmiston-Ruedenberg[13] criterium must lead to a unique set of LMO's in the case of the Hückel cyclobutadiene dianion, as it has been shown by England[15] using a group-theoretical approach. The appearance of continuous degeneracy in TLMO's of annulenes agrees closely with England's results.

ANTIAROMATIC (OPEN SHELL) ANNULENES

In open shell systems the problem of localizing the MO's is not so well defined as in the case of closed shell ones and there is not a unique way of tackling it.
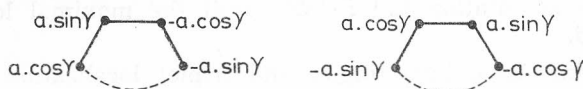
A plausible approach consists in localizing open and closed shells separately.[16] The localization of the closed shells of annulenes has already been discussed in the previous section, so that we shall only consider the localization of the degenerate, half-filled shell. It can be shown[15] that a pair of degenerate MO's spanning an irreducible representation of E symmetry is not localizable (i. e., is continuously degenerate) if and only if
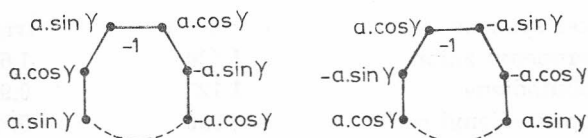
$$E \otimes E = A_1 \oplus A_2 \oplus E' \tag{14}$$

where the A_i's and E' are irreducible representations of dimension 1 and 2, respectively. According to this, the only localizable degenerate levels of Hückel and Möbius (n)annulenes are the NBMO's of neutral (4p)Hückel and (4p + + 2)Möbius systems.

It is interesting to note that, since the pairing theorem also holds for LMO's[17], and since the localization sum is independent of the sign of MO coefficients, the localization sums of paired degenerate levels are equal.

In the framework of our topological approach to LMO's, one can derive general expressions for the localized form of an (n)annulene degenerate, zero--energy level. In effect, the general form of the NBMO's for a Hückel (4p)annulene is:

and, for a Möbius (4p + 2)annulene,

where $a = (2/n)^{1/2}$, n being the number of carbon atoms. Introducing these coefficients in the expressions (11) and (12) and making use of (7) it can be seen, after some manipulation, that (11) and (12) reduce to

$$A_{12} = (2k - 1)/n \; \cos(4\gamma) \qquad (17)$$

$$B_{12} = (2k - 1)/n \; \sin(4\gamma) \qquad (18)$$

According to eqs. (13), the most localized form of the HOMO must give $B_{12} = 0$ and A_{12} negative, which corresponds to taking $\gamma = 0$ in (15) or (16) if $0 \leq k < 1/2$, and $\gamma = \pi/4$ if $k > 1/2$. If $k = 1/2$ the localization is indeterminate, and the HOMO presents an accidental continuous degeneracy.

Another way to approach the problem of orbital localization in open shell systems, which has been related to Linnett's[18] theory of electronic structure, is to localize electrons with α and β spin separately.[19] This procedure would be strictly correct only for the $|M_s| = 1$ states of the $^3A_2$ term corresponding to the electron configuration (closed shells)^{2m} (e)^2, since only in this case the molecular state can be described by a single Slater determinant. Both α and β electrons occupy complete shells, and the corresponding TLMO's will be the same we have discussed in the previous section. However it could be worthwhile to apply the localization procedure for α and β electrons of one of the determinants appearing in the wave function of singlet states*, keeping in mind that the results will vary in general when the HOMO's are modified by an orthogonal transformation. According to this, the localization of singlet determinants of open shell annulenes allows for distinguishing three different situations:

i) *Neutral (4p)Hückel/(4p + 2)Möbius annulenes:* The HOMO is localizable, and the total localization sum depends on the particular choice made for the HOMO, being maximal for its most localized form. Peaked tricentric or bicentric LMO's are obtained, depending on whether k in matrix (7) is smaller or bigger than 1/2.

ii) *(4p + 1)Hückel/(4p + 3)Möbius cations and (4p + 2)Hückel/(4p)Möbius dications:* The HOMO is not localizable, and the total localization sum is invariant under rotations of the HOMO's, thus giving a continuum set of equally localized MO's.

iii) *(4p + 3)Hückel/(4p + 1)Möbius anions* and *(4p + 2)Hückel/(4p)Möbius dianions:* The HOMO is not localizable, and the total localization sum is not invariant under HOMO's rotations. In this case the most localized structure must be found by rotating the HOMO until the maximal localization sum value is reached.

The following table lists singlet and triplet localization sums of some representative annulenes, calculated adding up the partial sums of α and β electrons. When the localization sum depends on HOMO rotations, its maximum value has been listed. This results have been obtained taking $L = 1$.

Hückel systems	singlet	triplet
cylopropenyl anion	1.500	1.667
cyclobutadiene	1.125	0.945
cyclopentadienyl cation	0.850	0.734
benzene dication	0.708	0.611
Möbius systems		
cyclobutadiene dianion	2.188	2.375
cyclopentadienyl anion	1.688	1.486
benzene	1.425	1.172
cycloheptatrienyl cation	1.198	1.000

The localization sums are in general greater for singlet than for triplet TLMO's, which agrees with chemical intuition. Nevertheless the reverse is found in the case of Hückel cyclopropenyl and Möbius cyclobutadiene anions, because in these cases the α-electron MO's of the triplet state span the whole AO space and therefore the absolute maximum of the localization sum can be reached.

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* In principle, one should distinguish whether the HOMO electrons are described by the same or different spatial functions. However symmetry considerations show that the localization sum will be the same in both cases.

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SAŽETAK

Topološke lokalizirane molekularne orbitale Hückelovih i Möbiusovih anulena

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Na niz anulena primijenjen je postupak lokaliziranja u okviru Hückelove MO metode, koji počiva samo na molekularnoj topologiji i koji se može smatrati topološkom verzijom dobro poznatih lokalizacijskih kriterija. Račun je izveden za Hückelove i Möbiusove topološke sisteme i razmatrani su neki aspekti dobivenih lokaliziranih orbitala (homogenost, ekvivalencija, kontinuirana degeneracija i lokalizabilnost degeneriranih nivoa). Konstatirano je da paralelizam između Hückelovih i Möbiusovih sistema važi također i za njihove lokalizirane molekularne orbitale.