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An extension of the Coulson–Rushbrooke–Longuet-Higgins theorem

II. A topological method for calculation of the number of nonbonding molecular orbitals*

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Summary. A novel topological method which predicts the number of Hückel nonbonding molecular orbitals and the set of atomic orbitals of which they are composed is put forward. It may be applied to a large class of homo-, heteronuclear, alternant, and nonalternant systems.

Key words: Nonbonding molecular orbitals — Topological method — Organic radicals

1. Introduction

Organic radicals and polyradicals have become targets of intense research due to the possibility of synthesizing organic ferromagnets [1–3]. Several unpaired electrons may give rise to overall states of various multiplicity. The case of parallel spin alignment is of special interest because macroscopic spin may be achieved by incorporating radicals or polyradicals in a molecular crystal or in a single polymer. A number of high spin conjugated alternant hydrocarbons [4] have been synthesized. The Hückel MO (molecular orbital) method suggest there are nearly degenerate partially occupied orbitals. This degeneracy was termed topological since it depends only upon the molecular skeleton [5, 6]. In most cases it may be predicted by simple graph-theoretical approaches.

According to the Coulson–Rushbrooke–Longuet-Higgins theorem [7–9] an alternant hydrocarbon has at least $\overset{*}{N} - \overset{\circ}{N}$ nonbonding molecular orbitals

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(NBMO's), where $\overset{*}{N}$ and $\overset{\circ}{N}$ are the number of starred and unstarred π-centers, respectively. A more accurate approach deals with the resonance structures. As pointed out by Longuet-Higgins [9], an alternant hydrocarbon of N conjugated atoms has at least $N-2D$ NBMO's, where D is the maximum number of double bonds occurring in any resonance structure. Both methods yield a lower limit for the number of NBMO's. Exact graph-theoretical approaches for the number of NBMO's in conjugated hydrocarbons [10] and the MO pattern of conjugated compounds in general [11, 12] have also been developed.

In the present paper, we prove a new criterion for the minimum number of NBMO's in conjugated compounds. It is applicable to nonalternant molecules, and to molecules with heteroatoms, and may be viewed as a generalization of the Coulson–Rushbrooke–Longuet-Higgins theorem [7–9] to these two cases. The investigations reported in this paper are a continuation of those presented in [13, 14], where the Coulson–Rushbrooke–Longuet-Higgins theorem was generalized for some classes of alternant hydrocarbon heteroanalogues.

2. Formulation and proof of the method

Let R denote the maximal set of disjoint homonuclear π-centers of a conjugated compound, i.e. the set R contains neither adjacent π-centers nor heteroatoms, and hence the Coulomb integrals α_r are equal for all the π-centers r of the set R (i.e., for all $r \in R$). In the case where the number of π-centers in the maximal disjoint set, N_R, is greater than half the total number of π-centers in the compound N, there are at least $2N_R - N$ nonbonding MO's, i.e. $N_0 \geqslant 2N_R - N$.

We shall denote the number of π-centers in the complement of the maximal disjoint set by $N_S = N - N_R$. In contrast to the case of an alternant system, the set S may comprise heteroatomic π-centers and/or pairs of adjacent π-centers. When constructing the Hückel matrix, we shall assume an appropriate labelling of the π-centers of the sets R and S: $r = 1, 2, \ldots, N_R, r \in R$; $s = N_R + 1, N_R + 2, \ldots, N, s \in S$. Further, since the Coulomb integrals α_r for the set R are equal, we choose the energy reference level $E_0 = \alpha_r$, so that in the Hückel matrix the diagonal elements for the set R vanish, i.e. $H_{rr} = 0$ for $r \in R$. Since the atoms in R are not bonded, the off diagonal elements $H_{rr'}$, $r, r' \in R$, are also zero and the Hückel hamiltonian matrix has a block form:

$$H = \begin{vmatrix} 0 & A^+ \\ A & B \end{vmatrix}. \tag{1}$$

The upper left zero submatrix corresponds to the AO's (atomic orbitals) of the set R. The matrix element H_{sr} of the Hückel hamiltonian for AO's $s \in S$ and $r \in R$ are represented by the matrix A of N_S rows and N_R columns. Matrix A^+ stands for the transpose of A. The square matrix B with elements $H_{ss'}$, $s, s' \in S$, is of order N_S. Representing the Hückel matrix as

$$H = H_1 + H_2$$

where

$$H_1 = \begin{vmatrix} 0 & A^+ \\ 0 & 0 \end{vmatrix}, \qquad H_2 = \begin{vmatrix} 0 & 0 \\ A & B \end{vmatrix}$$

and applying the theorem that the rank of the sum of matrices is not greater than the sum of the ranks of the addends, we obtain that

$$\operatorname{rank}(H) \leqslant \operatorname{rank}(H_1) + \operatorname{rank}(H_2) \leqslant N_S + N_S$$

since $\operatorname{rank}(H_1) \leqslant N_S$, $\operatorname{rank}(H_2) \leqslant N_S$. As a consequence of $\operatorname{rank}(H) \leqslant 2N_S$, there are at least $N - 2N_S = 2N_R - N$ zero eigenvalues corresponding to NBMO's.

Corollary 1. *The nonbonding MO's are composed only of AO's of the maximal disjoint set R. The eigenvectors C for zero eigenvalues (represented by columns) satisfy the matrix equation:*

$$H \cdot C = 0. \tag{2}$$

Let X and Y denote the components of the eigenvectors for the sets R and S, respectively:

$$C = \begin{vmatrix} X \\ Y \end{vmatrix}; \qquad \begin{aligned} X &= (x_i)^+, \quad i = 1, 2, \ldots, N_R; \\ Y &= (y_k)^+, \quad k = 1, 2, \ldots, N_S. \end{aligned}$$

Taking into account the block form of the Hückel matrix (1), Eq. (2) takes the form:

$$H \cdot C = \begin{vmatrix} 0 & A^+ \\ A & B \end{vmatrix} \cdot \begin{vmatrix} X \\ Y \end{vmatrix} = \begin{vmatrix} A^+ \cdot Y \\ A \cdot X + B \cdot Y \end{vmatrix} = \begin{vmatrix} 0 \\ 0 \end{vmatrix}$$

and splits into the following two equations

$$A^+ \cdot Y = 0, \tag{2a}$$

$$A \cdot X + B \cdot Y = 0. \tag{2b}$$

Since we treat here only the NBMO's due to the block form of the Hückel matrix, we may assume that matrix A (and A^+, respectively) has the greatest possible rank, N_S. In such a case, Eq. (2a) has only a trivial solution, $Y = 0$, corresponding to zero AO coefficients for the set S. Consequently,

$$A \cdot X = 0. \tag{3}$$

The above equation represents a system of N_S homogeneous linear equations for N_R variables, X_r, $r = 1, 2, \ldots, N_R$, and has $N_R - \operatorname{rank}(A) = N_R - N_S = 2N_R - N$ nontrivial linearly independent solutions corresponding to the AO coefficients of NBMO's for the maximal disjoint set R.

Corollary 2. *If the conjugated system has various maximal disjoint sets, R_k, $k = 1, 2, \ldots, K$, the NBMO's are composed only of the AO's of their intersection $R_1 \cap R_2 \cap \cdots \cap R_K$. According to Corollary 1, AO coefficients are zero for any complement S_k, i.e. they vanish for their union $S_1 \cup S_2 \cup \cdots \cup S_K$ which is identical to the complement of $R_1 \cap R_2 \cap \cdots R_K$.*

3. Application of the method

When applied to alternant hydrocarbons, our method gives the same results about the number of NBMO's as the Longuet-Higgins theorem [9]. Still, as a result of Corollary 1, the set of AO's from which the NBMO's are composed, may also be obtained. In the case of tetramethyleneethene, whose Hückel graph is given in Fig. 1, the maximal disjoint set (marked by "*") comprises all terminal π-centers.

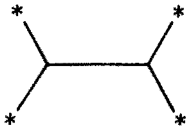

Fig. 1

The system has two NBMO's, localized on these π-centers. The substitution of the π-centers not included in the maximal disjoint set has no effect upon the NBMO's.

In the case of the isobutylene radical, which is an odd alternant system,

Fig. 2

the theorem of Coulson and Longuet-Higgins [8] predicts that the NBMO is composed of AO's of π-sites 1, 3, 5. However, since there are two maximal disjoint sets comprising positions 1, 3, 5 and 1, 4, 5, respectively, it follows from Corollary 2 that the NBMO coefficients are nonzero only for sites 1 and 5.

An example for a nonalternant system is the model hydrocarbon 2,4-dimethyleneazulene:

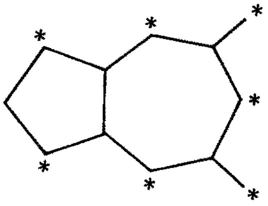

Fig. 3

Molecule 3 has $N = 12$ π-centers, and the number of π-sites in the maximal disjoint set is $N_R = 7$. Therefore, 3 has two NBMO's and, if electrically neutral, should represent a diradical. The same result is derived from the characteristic polynomial for 3, which is

$$x^2(x^{10} - 13x^8 + 60x^6 + 2x^5 - 118x^4 - 10x^3 + 91x^2 + 12x - 18) = 0$$

(where α and β for $x = (\alpha - e)/\beta$ are the Coulomb and resonance integrals, respectively. Consequently, the polynomial has two roots $x = 0$ which correspond to two NBMO's of energy $e = \alpha$).

The heteronuclear nonalternant system 4 has $N = 5$ π-centers and $N_R = 3$.

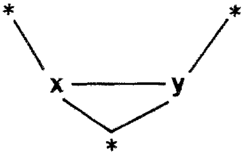

Fig. 4

Therefore 4 has one NBMO. This is seen also from the characteristic polynomial for 4 ($\alpha_x = \alpha + Q\beta$; $\alpha_y = \alpha + R\beta$):

$$x\{x^4 + (Q + R)x^3 - (5 - QR)x^2 + (2 - 2Q - 2R)x + 3\} = 0$$

which has one root $x = 0$.

The Hückel graph of 2-methylenefulvene 5 has two maximal disjoint subsets of cardinality 4.

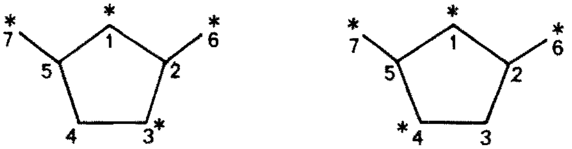

Fig. 5

According to Corollary 2, the NBMO is composed of AO's 1, 6, and 7.

The method may be applied to some one-dimensional systems, representing models of nonclassical polymers [6, 15]. Their common feature is that they cannot be represented by a classical (Kekulé) formula and the number of NBMO's is proportional to the number of unit cells. An example of such a system is the nonalternant polymer

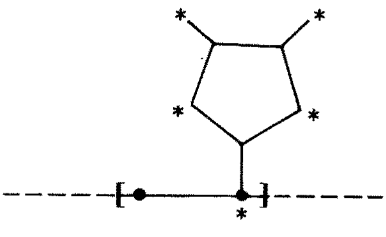

Fig. 6

which has a degenerate NBMO, since each unit cell comprising 9 π-sites has a maximal disjoint set of cardinality 5.

4. Concluding remarks

Proceeding from a simple topological criterion, the method permits us to predict whether a given model compound represents a radical or a polyradical, and to determine the set of carbon atoms whose substitution has no effect upon the NBMO's. It may serve as a guiding principle in the design of homo- and heteronuclear high-spin organic systems.

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