Electronic Properties of Möbius Systems

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The main π-electron properties (energy level distribution, total electron energy, charge distribution) of Möbius systems are analysed. A number of results, known previously for Hückel systems is generalized and/or modified for Möbius systems. The main conclusions of the work are summarized in Rules 1–7.

In two recent publications [1] Graovac and Trinajstić developed the graph-theoretical description of the Möbius-type conjugated systems. For the role which the Möbius strip concept plays in the chemistry of annulenes and in the theory of the electrocyclic closures, see [1] and the papers cited therein. Möbius graphs differ from simple molecular graphs (also called [1] Hückel graphs) in having an edge of weight -1. We shall denote this edge by e_{pq} and the two incident vertices by p and q. The adjacency matrix $\boldsymbol{A} = \| A_{ij} \|$ of a Möbius graph is then defined by

$$A_{ij} = \begin{cases} +1 & \text{if the vertices } i \text{ and } j \text{ are adjacent } (i, j \neq p, q), \\ -1 & \text{for a particular pair of adjacent vertices } p \text{ and } q, \\ 0 & \text{otherwise.} \end{cases} \quad (1)$$

In the general case also Möbius graphs with more than one edge of weight -1 can be conceived, but their chemical significance is obscure and they will not be considered here.

In [1] mainly the monocyclic Möbius graphs were analysed. The aim of the present paper is to examine in more detail the basic π-electron properties of general polycyclic Möbius-type conjugated systems. In Section 2 we consider the total π-electron energy and in Section 3 the charge distribution in Möbius systems. In Section 1 a number of elementary properties of Möbius graphs is presented.

We shall denote by G^* the Möbius graph [as defined by Eq. (1)] and by G the corresponding Hückel graph. Both G and G^* have N vertices. Further notation and terminology will be the same as in Ref. [2] and is not introduced here once again. Exceptionally, the summation over all cycles Z containing the edge e_{pq} will be symbolized by $\sum_{(pq)}$ and not by $\sum_{Z}$ as previously [2].

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1. Some Properties of the Characteristic Polynomial of Möbius Graphs

Let G_k be a graph having an edge e_{pq} of the weight k, between the vertices p and q [2]. Then the following recursion relation is valid for the charcteristic polynomial [2, 3].

$$P(G_k) = P(G - e_{pq}) - k^2 P(G - p, q) - 2k \sum_{(pq)} P(G - Z) . \quad (2)$$

Now, for $k = -1$, G_k is just the Möbius graph, while for $k = +1$, G_k is a simple Hückel graph. In other words,

$$P(G^*) = P(G - e_{pq}) - P(G - p, q) + 2 \sum_{(pq)} P(G - Z) , \quad (2\text{a})$$

$$P(G) = P(G - e_{pq}) - P(G - p, q) - 2 \sum_{(pq)} P(G - Z) . \quad (2\text{b})$$

Subtracting (2b) from (2a), one obtains the relation between the characteristic polynomials of G^* and G,

$$P(G^*) = P(G) + 4 \sum_{(pq)} P(G - Z) . \quad (3)$$

First we deduce some straightforward consequences of Equation (3). If an edge does not belong to any cycle in a graph, it is called a bridge.

Rule 1. If e_{pq} is a bridge, then $P(G^*) = P(G)$.

Since all edges in acyclic graphs are bridges, we have the following specialisation of Rule 1.

Rule 2. If G is an acyclic graph, then $P(G^*) = P(G)$, for an arbitrary position of the -1 edge.

Let the vertex q be of degree two and its two neighbours be the vertices p_1 and p_2. Then the edge e_{p_1q} belongs to a cycle Z if, and only if the edge e_{p_2q} belongs to Z. Therefore,

$$\sum_{(p_1q)} P(G-Z) = \sum_{(p_2q)} P(G-Z)\,. \tag{4}$$

The Eqs. (3) and (4) together yield the following rule.

Rule 3. If $G^*_{p_1q}$ and $G^*_{p_2q}$ are Möbius graphs with the -1 edge in the position p_1q and p_2q, respectively, then $P(G^*_{p_1q}) = P(G^*_{p_2q})$. For example,

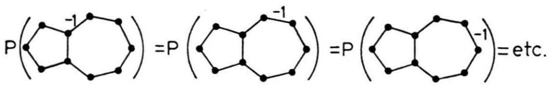

Fig. 1

Rules 1 and 2 are the mathematical formulation of the physically evident fact that Möbius systems are possible only within cyclic topologies. Rule 3 shows in addition that the -1 edge can be shifted within a particular cycle without changing the characteristic polynomial of G^*. This is again in full agreement with the fact that the precise position of the site of the sign inversion (positive-negative overlap between adjacent $2p_z$-orbitals) in a Möbius system is immaterial.

2. Total π-Electron Energy of Möbius Systems

It is long known [4] that the monocyclic Möbius systems obey the "anti-Hückel rule", namely the $(4m)$-membered Möbius rings are relatively stable moieties, while the $(4m+2)$-membered Möbius rings are much less stable. We show now that the anti-Hückel rule is valid for a general polycyclic alternant Möbius system.

First note that for alternant systems it is $b_{2j+1} = 0$ for all j, and therefore $B \equiv 0$. From Eq. (3) it follows that

$$\frac{P(G^*, i\,x)}{P(G, i\,x)} = \frac{A(G^*)}{A(G)} = 1 + 4 \sum_{(pq)} (-1)^{z/2} \frac{A(G-Z)}{A(G)} \tag{5}$$

where we have used the fact that the graphs $G-Z$ have $N-z$ vertices. Now, all the terms $A(G-Z)/A(G)$ are necessarily positive because of the inequalities $b_{2j} \geqq 0$, which are valid for all alternant molecular graphs [2].

Equation (5) is to be substituted into the integral formula (6) for the difference between the total π-electron energies of isomeric molecules [5].

$$E(G^*) - E(G) = \left\langle \log \frac{P(G^*, i\,x)}{P(G, i\,x)} \right\rangle . \tag{6}$$

This yields

$$E(G^*) - E(G) = \left\langle \log \left[1 + 4 \sum_{(pq)} (-1)^{z/2} \frac{A(G-Z)}{A(G)} \right] \right\rangle$$

and the following rule is obvious.

Rule 4 (the anti-Hückel rule). All $(4m)$-membered cycles in a Möbius graph G^*, containing the -1 edge, increase $E(G^*)$ relative to $E(G)$. All $(4m+2)$-membered cycles in G^*, containing the -1 edge, decrease $E(G^*)$ relative to $E(G)$.

3. π-Electron Charge Distribution in Möbius Systems

The π-electron charge on a conjugated atom is given by [6]

$$Q_r(G) = \left\langle \frac{P(G-r, i\,x)}{P(G, i\,x)} \right\rangle . \tag{7}$$

It can be shown that a non-uniform charge distribution ($Q_r \neq 0$) occurs if, and only if at least one of the coefficients b_{2j+1} in Eq. (7) is different from zero [7]. Since Eq. (7) is equally well applicable to Möbius systems, we immediately have the extension of a well-known property of alternant molecules.

Rule 5 (the Pairing theorem for Möbius systems). The charge distribution in alternant Möbius systems is uniform, $Q_r(G^*) = 0$ for all r.

It can be also shown that the charge distribution in non-alternant Möbius systems is not uniform [7]. Nevertheless, the extension of the pairing theorem to Möbius graphs is not complete. Namely, in Hückel graphs the equation

$$P(G, x) = (-1)^N P(G, -x) \tag{8}$$

is valid if, and only if G is bipartite. Therefore a "pairing" between the orbital energy levels exists only in alternant molecules. This is not the case with Möbius graphs, where Eq. (8) can be fulfilled also in certain non-bipartite systems. Two such examples are the Möbius graphs G_1^* and G_2^*.

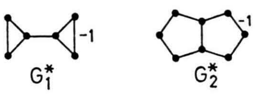

Fig. 2.

Calculation shows that

$$P(G_1{}^*) = x^6 - 7x^4 + 11x^2 - 5$$

and

$$P(G_2{}^*) = x^8 - 9x^6 + 24x^4 - 20x^2 + 4.$$

A detailed examination of Eq. (3) gives the following result.

Rule 6. A non-alternant Möbius graph G^* obeys Eq. (8) if, and only if

a) G^* contains exactly two odd-membered cycles Z_1 and Z_2 of the same size, and

b) $P(G^* - Z_1) = P(G^* - Z_2)$, and

c) the edge e_{pq} belongs either to Z_1 or to Z_2, but not both to Z_1 and Z_2.

Since the requirements of Rule 6 are rather severe, almost all non-alternant Möbius graphs of chemical interest violate Equation (8).

It is known [6] that in Hückel systems the $(4m+1)$-membered cycles decrease, while the $(4m+3)$-membered cycles increase the π-electron charge. We demonstrate now that in Möbius systems exactly the opposite rule is valid.

In order to avoid the rather cumbersome discussion of the general case, we shall consider a special situation here, namely when $G^* - e_{pq}$ is bipartite (but G^* is, of course, not). Then all cycles which contain the -1 edge e_{pq} are odd and from Eq. (2) we have

$$A(G^*) = A(G); \qquad B(G^*) = -B(G), \quad (9)$$
$$A(G^* - r) = A(G - r); \; B(G^* - r) = -B(G - r).$$

Formula (7) can be transformed into [6]

$$Q_r(G) = \left\langle \frac{A(G-r)\,B(G) - A(G)\,B(G-r)}{A^2(G) + B^2(G)} \right\rangle. \quad (10)$$

Substituting Eqs. (9) back into (10), the final result (11) is obtained.

$$Q_r(G^*) + Q_r(G) = 0. \quad (11)$$

Hence, in the considered special case the charges in the Möbius system are precisely opposite to those in the Hückel system. Although Eq. (11) holds not in the general case, one of its consequences is still valid.

Rule 7. All $(4m+1)$-membered cycles in a Möbius graph G^*, containing the -1 edge, increase $Q_r(G^*)$ relative to $Q_r(G)$. All $(4m+3)$-membered cycles in G^* containing the -1 edge, decrease $Q_r(G^*)$ relative to $Q_r(G)$.

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[6] A detailed discussion on the charge distribution in conjugated Hückel systems and further references can be found in: I. Gutman and N. Trinajstić, Croat. Chem. Acta **48**, 19 (1976).
[7] The charge distribution in non-alternant Hückel and Möbius systems is always non-uniform, except in the few cases where the uniform charge distribution is a consequence of the molecular symmetry.