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# Cyclic Conjugation and the Hückel Molecular Orbital Model**

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A new graphic polynomial, $\mu(G, t)$, has been introduced which depends on a vector $t$ and which reduces to the characteristic and matching polynomial of the graph $G$ for certain choices of $t$. This leads to a unification of a great part of the previously developed theories of the characteristic and matching polynomials. The basic properties of $\mu(G, t)$ are determined.

A method has been developed by which a function $J(t)$ can be associated with every $\pi$-electron index $J$. Since the component $t_a$ of the vector $t$ is interpreted as the extent by which a particular cycle $Z_a$ of the molecular graph $G$ influences the polynomial $\mu(G, t)$, it is possible to use the function $J(t)$ in the study of the effect of $Z_a$ on the $\pi$-electron index $J$.

Total $\pi$-electron energy, $\pi$-electron charge and $\pi$-electron bond order have been analysed by this method and a number of topological rules of the modulo 4 type have been formulated. It is indicated that all these rules have a common algebraic background.

**Key words:** Graph theory – Hückel rule.

## 1. Introduction

One of the most intriguing features of the chemistry of unsaturated conjugated hydrocarbons is the fact that cyclic conjugation of the $\pi$-electron system causes drastically different effects, depending on whether the size of the cycle is $4m$,

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** Dem Andenken Erich Hückels gewidmet.

$4m+1$, $4m+2$ or $4m+3$. Furthermore, the properties of the polycyclic conjugated compounds differ significantly from those of acyclic systems.

An early success of quantum theory in chemistry was the ability to reproduce a part of these chemical phenomena by means of a simple topological model, which is usually called the Hückel molecular orbital (HMO) theory [1].

The limitations of the Hückel theory are well known (see e.g. [1b], pp. 134–147). In spite of encouraging reports which from time to time appear in the chemical literature about the agreement of the HMO results with experimental measurements [2] or with the results of more advanced quantum chemical calculation schemes [3], it seems that the HMO theory is nowadays obsolete for *quantitative* description of chemical facts. In problems where *qualitative* answers suffice, the HMO model can be often applied with considerable success [4, 5], although caution is always necessary [6].

Another reason for the use of the HMO theory is its simplicity, which enables one to formulate and mathematically prove statements valid for a large (often infinite) class of conjugated systems. This would hardly be possible within any other more sophisticated quantum chemical model. Unfortunately, however, the approximations which lead to the elegant algebraic and combinatorial form of the HMO theory, make the theory oversimplified and thus fully incapable to describe certain types of chemical phenomena [6]. On the other hand, those properties of conjugated molecules which we will analyse in the present work are, at least in a qualitative manner, correctly reproduced by the HMO model.

A particularly deep insight into the dependence of the HMO results on the structure of the conjugated molecule was obtained in the last ten years using the mathematical methods of graph theory [7].

In the present paper we shall develop a new graph theoretical technique which will enable the unification of a great deal of the modulo 4 rules of the Hückel theory. We will exemplify our method on three HMO $\pi$-lectron indices of conjugated hydrocarbons: total $\pi$-electron energy, $\pi$-electron charge density and $\pi$-electron bond order. We will be able to answer the question how cyclic conjugation in a molecule influences these $\pi$-electron characteristics, which is a problem of certain importance in the topological theory of conjugated molecules [7]. We will obtain statements within and about the HMO model, which, when correctly and cautiously interpreted, lead to some useful qualitative chemical conclusions.

The paper is divided into two parts. In the first part we shall present the mathematical formalism of our method whereas in the second we shall apply it to the Hückel theory.

## 2. The $\mu$-Polynomial

Two graphic polynomials have been extensively studied within the topological theory of conjugated molecules, namely the characteristic polynomial $\phi(G)$

[7, 8] and the matching polynomial $\alpha(G)$ [9, 10] of the molecular graph $G$. These polynomials have applications also in a number of other fields of natural sciences and mathematics [8, 9, 11–13].

If $\boldsymbol{A}$ is the adjacency matrix of $G$, then by definition [7, 8],

$$\phi(G)=\phi(G,x)=\det(x\boldsymbol{I}-\boldsymbol{A}). \tag{1}$$

If $p(G, k)$ is the number of $k$-matchings in $G$, then by definition [9],

$$\alpha(G)=\alpha(G,x)=\sum_{k=0}^{m}(-1)^k p(G,k)x^{n-2k}. \tag{2}$$

From the form of these two definitions one could hardly anticipate any similarity between $\phi(G)$ and $\alpha(G)$. However, detailed studies [9, 12–14] show that $\phi(G)$ and $\alpha(G)$ possess a surprisingly large number of analogous combinatorial and algebraic properties. In connection with this the problem was set whether the theory of these two polynomials could be unified by means of a reasonably chosen function $\mu(G, t)$, which would continuously transform $\alpha(G)$ into $\phi(G)$ when the parameter $t$ changes from zero to unity.

Indeed, such a function could be designed and it appeared to be of some relevance for the topological theory of conjugated molecules [15, 16].

We shall use the following standard graph theoretical notation and terminology. $G$ will denote a graph with $n$ vertices: $v_1, v_2, \dots, v_n$ and $m$ edges; the edge connecting the vertices $v_i$ and $v_j$ is denoted by $e_{ij}$. The subgraphs $G-v_i$ and $G-e_{ij}$ are obtained from $G$ by deletion of the vertex $v_i$ and the edge $e_{ij}$, respectively.

Let $G$ contain $r$ cycles: $Z_1, Z_2, \dots, Z_r$. (These cycles, of course, need not be all mutually independent.) Then $G-Z_a$ is the subgraph obtained by deleting all the vertices (and incident edges) of $Z_a$ from $G$.

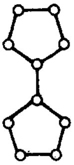
We shall say that $Z_a$ and $Z_b$ are disjoint cycles if they have no vertex in common. Let $Z_a, Z_b, Z_c, \dots$ be a collection of mutually disjoint cycles of $G$. Then the subgraph $G-Z_a-Z_b-Z_c-\cdots$ is obtained from $G$ by deletion of all the vertices of $Z_a, Z_b, Z_c, \dots$.

The deletion of cycles from a graph may result in a subgraph without vertices – the empty graph $\varnothing$.

For this subgraph we shall define

$$\alpha(\varnothing)=\phi(\varnothing)=\mu(\varnothing)=1.$$

For example, the molecular graph $G_0$ of fulvalene contains two cycles $Z_1$ and $Z_2$ which are disjoint.

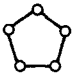


$G_0$

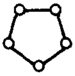
$Z_1$

$Z_2$

The three possible subgraphs resulting when the cycles are deleted from $G_0$ are given as follows:



$G_0 - Z_1$



$G_0 - Z_2$

$\varnothing$

$G_0 - Z_1 - Z_2$

The concept of Sachs graphs has been already introduced in a number of previous publications [7, 8, 17]. Let $s$ be a Sachs graph. Then $n(s)$, $c(s)$ and $r(s)$ are the number of vertices, components and cycles, respectively, of $s$. The empty graph will be also considered as a Sachs graph with the properties $n(\varnothing) = c(\varnothing) = r(\varnothing) = 0$.

Let $\boldsymbol{S}$ be the set of all Sachs graphs which are contained in $G$ as subgraphs and let $\boldsymbol{S}^0$ be the set of all Sachs graphs from $\boldsymbol{S}$ which have the property $r(s) = 0$. Note that $\varnothing$ is element of both $\boldsymbol{S}$ and $\boldsymbol{S}^0$.

The following two relations, which have closely resembling form, exist between $\phi(G)$ and $\boldsymbol{S}$ and between $\alpha(G)$ and $\boldsymbol{S}^0$, respectively:

$$\phi(G) = \sum_{s \in \boldsymbol{S}} (-1)^{c(s)} 2^{r(s)} x^{n-n(s)} \tag{3}$$

$$\alpha(G) = \sum_{s \in \boldsymbol{S}^0} (-1)^{c(s)} 2^{r(s)} x^{n-n(s)} = \sum_{s \in \boldsymbol{S}^0} (-1)^{c(s)} x^{n-n(s)}. \tag{4}$$

However, while (3) is the important Sachs theorem [7, 8, 17], Eq. (4) should be understood as just another form of definition (2). In fact, the Sachs theorem (3) is a graphical representation of the expansion of the determinant (1), that is of an antisymmetrized summation over all $n!$ permutations. If in such an expansion we consider only the transpositions, then we obtain the matching polynomial, Eq. (4).

The set $\boldsymbol{S}^0$ is obtained from $\boldsymbol{S}$ by abandoning all the cyclic Sachs graphs. Therefore $\alpha(G)$ can be understood as being derived from $\phi(G)$ if in the Sachs formula (3) one *fully* neglects the contributions of all Sachs graphs which possess cycles. Having in mind this point of view, we arrive at the idea to try to *partially* neglect the cyclic Sachs graphs in (3). This can be realized in the following way.

Let $\boldsymbol{t} = (t_1, t_2, \ldots, t_r)$ be an $r$-dimensional vector, whose components are arbitrary numbers (or functions). The component $t_a$ of $\boldsymbol{t}$ is associated to the cycle $Z_a$ of the graph $G$, $a = 1, 2, \ldots, r$.

Let us consider a Sachs graph $s$ which is composed of $r(s)$ cycles $Z_{a_1}, Z_{a_2}, \ldots, Z_{a_{r(s)}}$, $r(s) > 0$. Then the product $t_{a_1} t_{a_2} \cdots t_{a_{r(s)}}$ will be denoted by $T(s)$. For acyclic Sachs graphs $s \in \boldsymbol{S}^0$ (for which $r(s) = 0$), we define $T(s) = 1$.

*Definition.* The $\mu$-polynomial of the graph $G$ is

$$\mu(G) = \mu(G, \boldsymbol{t}) = \mu(G, \boldsymbol{t}, x) = \sum_{s \in \boldsymbol{S}} (-1)^{c(s)} 2^{r(s)} x^{n-n(s)} T(s). \tag{5}$$

The components of the vector $\boldsymbol{t}$ can be thus interpreted as the weights of the corresponding cycles, by which they contribute to the Sachs-type summation formula (5).

Recently Farrell [18] has introduced a general class of graphic polynomials, the so called $F$-polynomials. The $\mu$-polynomial appears to be a special case of an $F$-polynomial.

Let the vectors $(0, 0, \ldots, 0)$ and $(1, 1, \ldots, 1)$ be denoted by $\mathbf{0}$ and $\mathbf{1}$, respectively. If $\boldsymbol{t} = \mathbf{0}$, then all cyclic Sachs graphs have a zero contribution to the summation (5) and thus Eq. (5) reduces to Eq. (4). In the case of $\boldsymbol{t} = \mathbf{1}$, all $T(s)$'s are equal to one and (5) reduces to (3). Thus,

(*a*) $\mu(G, \mathbf{0}) = \alpha(G)$,

(*b*) $\mu(G, \mathbf{1}) = \phi(G)$,

which shows that $\mu(G)$ fulfills the desired requirements.

The $\mu$-polynomial is a generalization also of the characteristic polynomial of Möbius graphs. Let $G^*$ be the molecular graph of a Möbius system. Then a particular edge $e$ of $G^*$ is weighted by $-1$. Therefore,

(*c*) if $t_a = -1$ whenever the cycle $Z_a$ contains $e$

and $t_a = +1$ otherwise, then $\mu(G, \boldsymbol{t}) = \phi(G^*)$.

For details on the Möbius graphs see [19].

It can be proved that

$$\mu(G) = \mu(H) \tag{6}$$

when the graphs $G$ and $H$ are isomorphic and their cycles are equally labelled, and

$$\mu(G_1 \dot{+} G_2) = \mu(G_1)\mu(G_2), \tag{7}$$

with $G_1 \dot{+} G_2$ denoting a graph having two disconnected components $G_1$ and $G_2$. Eqs. (6) and (7) show that $\mu(G)$ is correctly defined from a graph theoretical point of view.

By collecting in (5) all those Sachs graphs which contain the same cycles, we deduce:

*Proposition 1a.*

$$\mu(G) = \alpha(G) - 2\sum_{a=1}^{r} t_a\alpha(G - Z_a) + 4\sum_{a,b} t_a t_b\alpha(G - Z_a - Z_b)$$

$$-8\sum_{a,b,c} t_a t_b t_c\alpha(G - Z_a - Z_b - Z_c) + \cdots. \tag{8}$$

The second, third etc. summation in (8) goes over all pairs, triplets etc. of mutually disjoint cycles in $G$. This combinatorial identity can be inverted, thus leading to

$$\alpha(G) = \mu(G) + 2\sum_{a=1}^{r} t_a\mu(G - Z_a) + 4\sum_{a,b} t_a t_b\mu(G - Z_a - Z_b)$$

$$+8\sum_{a,b,c} t_a t_b t_c\mu(G - Z_a - Z_b - Z_c) + \cdots. \tag{9}$$

The $\mu$-polynomial can also be expressed in terms of the characteristic polynomials, namely:

*Proposition 1b.*

$$\mu(G) = \phi(G) + 2\sum_{a=1}^{r} (1 - t_a)\phi(G - Z_a) + 4\sum_{a,b} (1 - t_a)(1 - t_b)\phi(G - Z_a - Z_b)$$

$$+8\sum_{a,b,c} (1 - t_a)(1 - t_b)(1 - t_c)\phi(G - Z_a - Z_b - Z_c) + \cdots \tag{10}$$

and the inversion of (10) yields

$$\phi(G) = \mu(G) - 2\sum_{a=1}^{r} (1 - t_a)\mu(G - Z_a) + 4\sum_{a,b} (1 - t_a)(1 - t_b)\mu(G - Z_a - Z_b)$$

$$-8\sum_{a,b,c} (1 - t_a)(1 - t_b)(1 - t_c)\phi(G - Z_a - Z_b - Z_c) + \cdots. \tag{11}$$

For $\boldsymbol{t} = \mathbf{1}$ we obtain from (8)

$$\phi(G) = \alpha(G) - 2\sum_{a} \alpha(G - Z_a) + 4\sum_{a,b} \alpha(G - Z_a - Z_b)$$

$$-8\sum_{a,b,c} \alpha(G - Z_a - Z_b - Z_c) + \cdots. \tag{12}$$

while for $\boldsymbol{t} = \mathbf{0}$ Eq. (10) implies

$$\alpha(G) = \phi(G) + 2\sum_{a} \phi(G - Z_a) + 4\sum_{a,b} \phi(G - Z_a - Z_b)$$

$$+8\sum_{a,b,c} \phi(G - Z_a - Z_b - Z_c) + \cdots. \tag{13}$$

Note that the above expansion formulas (8)–(13) are finite and contain at most $r$ summations. They show that a certain symmetry exists between $\mu(G)$, $\alpha(G)$ and $\phi(G)$.

As an example we shall calculate the $\mu$-polynomial of $G_0$, the molecular graph of fulvalene. According to (8),

$$\begin{aligned}\mu(G_0) &= \alpha(G_0) - 2t_1\alpha(G - Z_1) - 2t_2\alpha(G - Z_2) + 4t_1t_2\alpha(G - Z_1 - Z_2)\\ &= x^{10} - 11x^8 + 41x^6 - 61x^4 + 31x^2 - 1 - 2(t_1 + t_2)(x^5 - 5x^3 + 5x) + 4t_1t_2.\end{aligned}$$

The necessary matching polynomials can be obtained using appropriate recursion techniques [10].

*Corollary 1.1.* If $G$ is acyclic, then $\mu(G, \boldsymbol{t}) = \phi(G) = \alpha(G)$, since the vector $\boldsymbol{t}$ then has no components.

Thus for acyclic graphs the $\mu$-polynomial trivially reduces to the matching and characteristic polynomials. Therefore in the following we will consider only cyclic molecular graphs.

*Corollary 1.2.* If $G$ possesses a single cycle, then

$$\begin{aligned}\mu(G) &= \alpha(G) - 2t\alpha(G - Z)\\ &= \phi(G) + 2(1 - t)\phi(G - Z)\\ &= (1 - t)\alpha(G) + t\phi(G).\end{aligned}$$

According to definition, the $\mu$-polynomial is a linear function of each of the parameters $t_a$. Differentiation of Eq. (8) with respect to $t_a$ gives

$$\begin{aligned}\frac{\partial \mu(G)}{\partial t_a} &= -2\alpha(G - Z_a) + 4\sum_b t_b\alpha(G - Z_a - Z_b)\\ &\quad - 8\sum_{b,c} t_bt_c\alpha(G - Z_a - Z_b - Z_c) + \cdots.\end{aligned}$$

Thus we have proved

*Proposition 2.*

$$\frac{\partial \mu(G)}{\partial t_a} = -2\mu(G - Z_a).$$

*Corollary 2.1.*

$$\frac{\partial^2 \mu(G)}{\partial t_a\,\partial t_b} = \begin{cases} 4\mu(G - Z_a - Z_b) & \text{if } Z_a \text{ and } Z_b \text{ are disjoint,}\\ 0 & \text{otherwise.}\end{cases}$$

*Corollary 2.2.*

$$\alpha(G)=\mu(G)-\sum_a t_a\frac{\partial\mu(G)}{\partial t_a}+\sum_{a,b} t_a t_b\frac{\partial^2\mu(G)}{\partial t_a\,\partial t_b}$$

$$-\sum_{a,b,c} t_a t_b t_c\frac{\partial^3\mu(G)}{\partial t_a\,\partial t_b\,\partial t_c}+\cdots,$$

$$\phi(G)=\mu(G)+\sum_a(1-t_a)\frac{\partial\mu(G)}{\partial t_a}+\sum_{a,b}(1-t_a)(1-t_b)\frac{\partial^2\mu(G)}{\partial t_a\,\partial t_b}$$

$$+\sum_{a,b,c}(1-t_a)(1-t_b)(1-t_c)\frac{\partial^3\mu(G)}{\partial t_a\,\partial t_b\,\partial t_c}+\cdots.$$

*Corollary 2.3.* If $t_a=t$ for all $a=1,\ldots,r$, then

$$\frac{\partial\mu(G)}{\partial t}=-2\sum_a\mu(G-Z_a).$$

In graph spectral theory it is well known [8] that

$$\frac{d\phi(G)}{dx}=\sum_{j=1}^{n}\phi(G-v_j). \tag{14}$$

If we differentiate Eq. (10) with respect to $x$ and take into account (14), we obtain:

*Proposition 3.*

$$\frac{\partial\mu(G)}{\partial x}=\sum_{j=1}^{n}\mu(G-v_j). \tag{15}$$

Note that (15) holds for arbitrary $t$, but under the assumption that $t$ is independent of $x$.

Let $e_{ij}$ be an edge of the graph $G$. This edge may eventually belong to some of the cycles $Z_a$ of $G$. Then $\boldsymbol{S}$ can be partitioned into the subsets $\boldsymbol{S}_-$, $\boldsymbol{S}_+$ and $\boldsymbol{S}_a$, $a=1,2,\ldots,r$, $\boldsymbol{S}=\boldsymbol{S}_-\cup\boldsymbol{S}_+\bigcup_{a=1}^{r}\boldsymbol{S}_a$, such that $\boldsymbol{S}_-$ contains the Sachs graphs of $G$ which do not possess $e_{ij}$, $\boldsymbol{S}_+$ contains the Sachs graphs of $G$ in which $e_{ij}$ is an isolated edge and $\boldsymbol{S}_a$ contains those Sachs graphs in which the edge $e_{ij}$ belongs to the cycle $Z_a$. (If $e_{ij}$ does not belong to $Z_a$, then $\boldsymbol{S}_a$ is an empty set. An edge cannot, of course, belong to more than one component of a Sachs graph.)

According to the definition of the $\mu$-polynomial,

$$\sum_{s\in\boldsymbol{S}_-}(-1)^{c(s)}2^{r(s)}x^{n-n(s)}T(s)=\mu(G-e_{ij}), \tag{16}$$

$$\sum_{s\in\boldsymbol{S}_+}(-1)^{c(s)}2^{r(s)}x^{n-n(s)}T(s)=-\mu(G-v_i-v_j). \tag{17}$$

If $e_{ij}$ belongs to the cycle $Z_a$, then

$$\sum_{s\in\boldsymbol{S}_a}(-1)^{c(s)}2^{r(s)}x^{n-n(s)}T(s)=-2t_a\mu(G-Z_a). \tag{18}$$

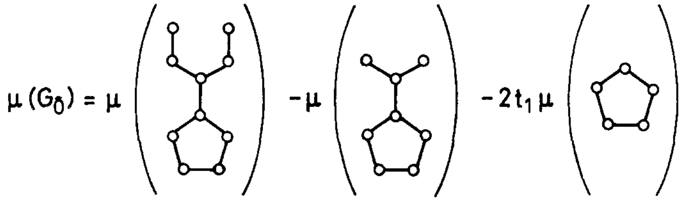
Otherwise the left hand side of (18) is equal to zero, Combining Eqs. (16)–(18) we obtain the following recursion formula:

*Proposition 4.*

$$\mu(G)=\mu(G-e_{ij})-\mu(G-v_i-v_j)-2\sum_a t_a\mu(G-Z_a), \tag{19}$$

where the summation goes over all cycles $Z_a$ which contain the edge $e_{ij}$.

For example,



*Corollary 4.1.* For $t=\mathbf{1}$ and $t=\mathbf{0}$, Eq. (19) reduces to the previously known [8, 10] recursion relations for $\phi(G)$ and $\alpha(G)$,

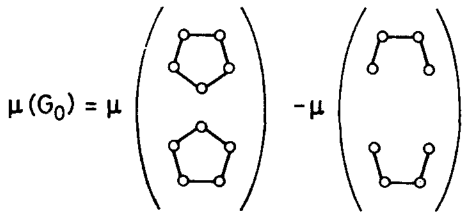
$$\phi(G)=\phi(G-e_{ij})-\phi(G-v_i-v_j)-2\sum_a \phi(G-Z_a),$$

$$\alpha(G)=\alpha(G-e_{ij})-\alpha(G-v_i-v_j).$$

*Corollary 4.2.* If $e_{ij}$ is a bridge[1], then

$$\mu(G)=\mu(G-e_{ij})-\mu(G-v_i-v_j).$$

For example, the edge connecting the two five membered cycles of the fulvalene graph $G_0$ is a bridge. Therefore,



*Corollary 4.3.* Let $g$ and $h$ be vertices of the graphs $G$ and $H$, respectively. Let $G\cdot H$ be obtained by identifying $g$ with $h$. Then

$$\mu(G\cdot H)=\mu(G)\mu(H-h)+\mu(G-g)\mu(H)-x\mu(G-g)\cdot\mu(H-h).$$

Propositions 1–4 summarize the main relations which exist between the polynomials $\mu$, $\alpha$ and $\phi$ and also present a few combinatorial identities for $\mu(G)$;

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[1] An edge $e$ of the graph $G$ is called a bridge if $G-e$ has more components than $G$. Consequently, $e$ cannot belong to a cycle of $G$, and $\boldsymbol{S}=\boldsymbol{S}_+\cup\boldsymbol{S}_-$.

these latter are generalizations of the previously known results for $\alpha(G)$ and $\phi(G)$ and reduce to them when we set $\mathbf{t} = \mathbf{0}$ and $\mathbf{t} = \mathbf{1}$, respectively.

The polynomials $\alpha(G)$ and $\phi(G)$ have the distinguished algebraic property that all their zeros are real. If $\mathbf{t} \neq \mathbf{0}, \mathbf{1}$, the zeros of $\mu(G, \mathbf{t})$ are not necessarily real numbers, as it was shown on the example of the complete graph with five vertices [15]. Fortunately, there is a considerably large class of graphs (which includes also the molecular graphs of numerous conjugated systems, e.g. fulvalene) for which the following statement applies.

Let $\mathbf{t} \leq \mathbf{1}$ mean $|t_a| \leq 1$ for all $a = 1, 2, \ldots, r$.

*Proposition 5.* If $G$ is a graph whose edges do not simultaneously belong to two or more cycles, then $\mu(G, \mathbf{t})$ has real zeros for all $\mathbf{t} \leq \mathbf{1}$.

This result has been proved in [15] for the special case when all the components of $\mathbf{t}$ are mutually equal. The proof of the general case is essentially the same and will not be reproduced here.

## 3. On the Origin of Modulo 4 Rules in Hückel Theory

The Hückel's $4m+2$ rule was originally formulated for monocyclic molecules [1], but soon thereafter it was extended also to the case of polycyclic systems (see for example [5], pp. 93–95). The question of the generalization of the Hückel rule to polycyclic hydrocarbons seems, however, to be quite difficult, and only recently a full solution of this problem was obtained for alternant hydrocarbons [20].

In the last few years graph theoretical investigations have enabled the discovery of several further modulo 4 regularities within the framework of the HMO model. Modulo 4 rules were observed for total $\pi$-electron energy [20, 21], charge distribution [22, 23], bond order [24] and HOMO-LUMO separation [16, 22, 25] of both Hückel [16, 20–25] and Möbius systems [16, 19, 26]. For completeness we mention also the modulo 4 rules in the Woodward–Hoffmann theory [4] and some of those rules which have been deduced independently of the HMO model [27].

In this section we shall develop a new unified approach to the modulo 4 rules of Hückel theory. The general strategy of our method is the following.

The applicability of graph theory in HMO theory is mainly based on the possibility to express the HMO $\pi$-electron indices as functions of the characteristic polynomial of the molecular graph $G$ and (eventually) of certain of its subgraphs $G_j$, $j = 1, 2, \ldots$.

These expressions are in fact the Coulson–Longuet–Higgins integral formulas [28, 29].

Let $J$ be such a $\pi$-electron index and let the corresponding Coulson–Longuet–Higgins formula be

$$J = f(\phi(G), \phi(G_j)),$$

where $f$ is a certain, analytically well defined function.

We construct now the variable quantity $J(\boldsymbol{t})$, which depends on the vector $\boldsymbol{t}$ as

$$J(\boldsymbol{t}) = f(\mu(G, \boldsymbol{t}), \mu(G_j, \boldsymbol{t})).$$

Obviously, $J(\mathbf{1}) = J$.

$J(\boldsymbol{t})$ can be expanded in a power series

$$J(\boldsymbol{t}) = J(\mathbf{0}) + \sum_a J_a t_a + \sum_a \sum_b J_{ab} t_a t_b + \sum_a \sum_b \sum_c J_{abc} t_a t_b t_c + \cdots,$$

where, of course,

$$J_a = \frac{\partial J(\mathbf{0})}{\partial t_a}, \qquad J_{ab} = \frac{1}{2!} \frac{\partial^2 J(\mathbf{0})}{\partial t_a\, \partial t_b}, \qquad J_{abc} = \frac{1}{3!} \frac{\partial^3 J(\mathbf{0})}{\partial t_a\, \partial t_b\, \partial t_c} \quad \text{etc.}$$

The above series is convergent for $\boldsymbol{t} \leq \mathbf{1}$ at least in the case of the Coulson–Longuet–Higgins formulas considered in this paper. Therefore,

$$J = J(\mathbf{0}) + \sum_a J_a + \sum_a \sum_b J_{ab} + \sum_a \sum_b \sum_c J_{abc} + \cdots. \tag{20}$$

Thus the $\pi$-electron index $J$ is decomposed into a number of terms: $J(\mathbf{0})$, $J_a$, $J_{ab}$, $J_{abc}$, ..., which are in many cases relatively simple functions of the molecular topology. Having in mind that $t_a$ is the weight by which the cycle $Z_a$ contributes to $\mu(G, \boldsymbol{t})$, we can interprete

$J(\mathbf{0})$ as the effect of acyclic structural details on $J$,
$J_a$ as the first order effect of the cycle $Z_a$ on $J$,
$J_{aa}$ as the second order effect of $Z_a$,
$J_{aaa}$ as the third order effect of $Z_a$,
$J_{a,b}$ $(a \neq b)$ as the first order collective effect of the pair of cycles $Z_a$ and $Z_b$,
$J_{aab}$, $J_{abb}$ $(a \neq b)$ as the second order collective effects of $Z_a$ and $Z_b$,
$J_{abc}$ $(a \neq b, c)$ as the first order collective effect of the triplet of cycles $Z_a$, $Z_b$ and $Z_c$ on the $\pi$-electron index $J$, etc.

The total effect $J(a)$ of the cycle $Z_a$ on the index $J$ is thus

$$J(a) = J_a + J_{aa} + J_{aaa} + \cdots \tag{21}$$

and consequently, $J - \sum_a J(a)$ represents the effect of simultaneous cyclic conjugation in two or more cycles.

In the following considerations we shall often need three graphic polynomials $(G)$, $[G]$ and $\{G, \boldsymbol{t}\}$, which are in a simple manner related to the characteristic, matching and $\mu$-polynomial, respectively of the graph $G$, namely

$$(G) = (G, x) = i^{-n} \phi(G, ix), \tag{22}$$

$$[G]=[G,x]=i^{-n}\alpha(G,ix), \tag{23}$$

$$\{G,t\}=\{G,t,x\}=i^{-n}\mu(G,t,ix). \tag{24}$$

Here and later, $i=\sqrt{-1}$.

From Proposition 2 and Eq. (24) follows

$$\frac{\partial\{G,t\}}{\partial t_a}=-2i^{-|Z_a|}\{G-Z_a,t\}. \tag{25}$$

### *3.1. Properties of Some Topological Functions and Their Integrals*

In the present section we shall determine some properties of the topological functions $[G-Z_a]/[G]$, $[G-Z_a-Z_b]/[G]$ etc. These functions and their integrals appear in all expressions which will be derived later within our topological analysis of the total $\pi$-electron energy, $\pi$-electron charge distribution and $\pi$-electron bond order.

In the following we shall adopt the usual abbreviation [20, 24, 30], namely

$$\frac{1}{\pi}\int_{-\infty}^{+\infty}F(x)\,dx\equiv\langle F(x)\rangle\equiv\langle F\rangle.$$

From Eq. (23) and the definition (2) of $\alpha(G)$ it immediately follows that

$$[G]=\sum_k p(G,k)x^{n-2k}.$$

Since the $p(G,k)$'s are non-negative integers for all $k=0,1,\ldots$, we conclude that

(a) if the graph $G$ has an even number of vertices, then $[G,-x]=[G,x]$ and $[G]>0$ for all real values of the variable $x$ $(x\neq 0)$;

(b) if the graph $G$ has an odd number of vertices, then $[G,-x]=-[G,x]$ and sign $[G]=$ sign $x$.

In the later considerations we shall frequently use the fact that whenever $F(x)$ is an odd function, i.e. $F(-x)=-F(x)$, then $\langle F(x)\rangle=0$.

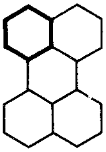
Let $|Z|$ denote the size of the cycle $Z$, that is the number of its vertices.

$[G-Z_a]/[G]$ is an even (odd) function if $|Z_a|$ is even (odd). Similarly, $[G-Z_a-Z_b]/[G]$ is even (odd) if $|Z_a|+|Z_b|$ is an even (odd) number, etc. Consequently, the integrals $\langle[G-Z_a]/[G]\rangle$, $\langle[G-Z_a-Z_b]/[G]\rangle$ etc. are positive if $|Z_a|$, $|Z_a|+|Z_b|$, etc. have even values and vanish whenever $|Z_a|$, $|Z_a|+|Z_b|$ etc. are odd. Therefore in the following considerations we shall assume that $|Z_a|$, $|Z_a|+|Z_b|$ etc. are even numbers.

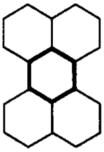
It can be proved (see the Appendix) that for all real values of the variable $x$, the function $2[G-Z]/[G]$ is less than unity. For large values of $x$, $[G-Z]/[G]$ behaves asymptotically as $x^{-|Z|}$.

$[G-Z]/[G]$ is usually a bell-shaped function with a maximum at $x=0$. Exceptionally, if $[G-Z]/[G]=0$ for $x=0$ then $[G-Z]/[G]$ has a minimum at $x=0$ and $[G-Z]/[G] \ll 1$ for all $x$. Therefore, if $Z_1$ and $Z_2$ are two cycles of equal size in a conjugated system $G$, then the integral $\langle [G-Z_1]/[G] \rangle$ is greater than $\langle [G-Z_2]/[G] \rangle$, provided that $[G-Z_1]/[G] \neq 0$ and $[G-Z_2]/[G]=0$ for $x=0$.

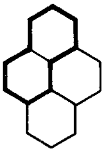
In order to illustrate this, consider the two six-membered cycles $Z_{11}$ and $Z_{12}$ of perylene, $G_1$, and the two ten-membered cycles $Z_{21}$ and $Z_{22}$ of pyrene, $G_2$.



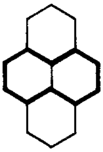
$G_1, Z_{11}$



$G_1, Z_{12}$



$G_2, Z_{21}$



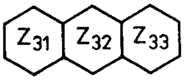
$G_2, Z_{22}$

For $x=0$ the functions $[G_1-Z_{11}]/[G_1]$, $[G_1-Z_{12}]/[G_1]$, $[G_2-Z_{21}]/[G_2]$ and $[G_2-Z_{22}]/[G_2]$ have the values $\frac{1}{3}$ (=maximum), 0 (=minimum), $\frac{1}{6}$ (=maximum) and 0 (=minimum), respectively. The corresponding integrals $\langle [G-Z]/[G] \rangle$ are equal to 0.0935, 0.0207, 0.0325 and 0.0059, respectively.

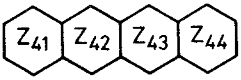
If $H$ is a subgraph of $G$, then $p(H, k) \leq p(G, k)$ for all $k=1, 2, \ldots$. Therefore also $[H] \leq [G]$ for all positive values of $x$. In particular, $[G-Z_a-Z_b]/[G] < [G-Z_a]/[G]$ for all values of $x$.

As a consequence of the above inequality, the integral $\langle [G-Z_a]/[G] \rangle$ is about one order of magnitude larger than $\langle [G-Z_a-Z_b]/[G] \rangle$. (Note also that if the cycles $Z_a$ and $Z_b$ are not disjoint, then $G-Z_a-Z_b$ is meaningless and we must set $[G-Z_a-Z_b] \equiv 0$; thus all the respective integrals vanish. In particular, $\langle [G-Z_a-Z_b]/[G] \rangle = 0$ for $a=b$.)

As an illustration consider anthracene, $G_3$, and tetracene, $G_4$, whose six-membered cycles are denoted by $Z_{31}$, $Z_{32}$, $Z_{33}$ and $Z_{41}$, $Z_{42}$, $Z_{43}$, $Z_{44}$, respectively.



$G_3$

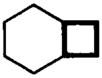


$G_4$

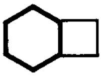
For $H$ being the subgraph $G_3-Z_{31}$, $G_3-Z_{32}$ and $G_3-Z_{31}-Z_{33}$, the integral $\langle [H]/[G_3] \rangle$ is equal to 0.0856, 0.0672 and 0.0023, respectively. For $H$ being the subgraph $G_4-Z_{41}$, $G_4-Z_{42}$, $G_4-Z_{41}-Z_{43}$ and $G_4-Z_{41}-Z_{44}$, the integral $\langle [H]/[G_4] \rangle$ is equal to 0.0782, 0.0557, 0.0014 and 0.0044, respectively. Note in addition that the the integrals $\langle [G_3-Z_{31}-Z_{32}]/[G_3] \rangle$, $\langle [G_4-Z_{42}-Z_{43}]/[G_4] \rangle$ etc. are equal to zero since the respective cycles are not disjoint.

The integrals $\langle [G-Z_a][G-Z_b]/[G]^2\rangle$ and $\langle [G-Z_a]^2/[G]^2\rangle$ are considerably smaller than $\langle [G-Z_a]/[G]\rangle$, provided, of course, that $|Z_a|$ is even.

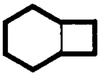
For example, if the four-, six- and eight-membered cycles of benzcyclobutadiene, $G_5$, are denoted by $Z_{51}$, $Z_{52}$ and $Z_{53}$, then $\langle [G_5-Z_{5j}]/[G_5]\rangle$ is equal to 0.1716, 0.1098 and 0.0915 for $j=1,2,3$, while $\langle [G_5-Z_{5j}][G_5-Z_{5k}]/[G_5]^2\rangle$ is equal to 0.0309, 0.0255, 0.0232, 0.0217, 0.0205 and 0.0183 for $(j,k)=(1,1)$, $(1,2)$, $(1,3)$, $(2,2)$, $(2,3)$ and $(3,3)$, respectively.



$G_5, Z_{51}$



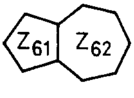
$G_5, Z_{52}$



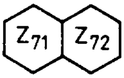
$G_5, Z_{53}$

If both $|Z_a|$ and $|Z_b|$ are odd, then the integral $\langle [G-Z_a][G-Z_b]/[G]^2\rangle$ is positive, but has relatively small value because for $x=0$, $[G-Z_a]=[G-Z_b]=0$.

Thus for example, in the case of azulene, $G_6$, we have $\langle [G_6-Z_{61}]^2/[G_6]^2\rangle=0.0119$, $\langle [G_6-Z_{61}][G_6-Z_{62}]/[G]^2\rangle=0.0066$ and $\langle [G_6-Z_{62}]^2/[G_6]^2\rangle=0.0043$, which should be compared with the analogous integrals for naphthalene, $G_7$: $\langle [G_7-Z_{71}]^2/[G_7]^2\rangle=[G_7-Z_{71}][G_7-Z_{72}]/[G_7]^2\rangle=0.0200$.



$G_6$



$G_7$

We are now prepared to examine how cyclic conjugation influences the main HMO $\pi$-electron indices of conjugated molecules.

### 3.2. *Total π-Electron Energy*

Let $G$ and $G'$ be two molecular graphs with equal number of vertices and $E(G)$ and $E(G')$ be the pertinent total $\pi$-electron energies. Then [29],

$$E(G)-E(G')=\langle \log((G)/(G'))\rangle. \qquad (26)$$

Let us choose $G'$ in Eq. (26) to be a graph with $n$ vertices but without edges. Then $(G')=x^n$ and $E(G')=0$. Consequently, $E=E(G)=\langle \log((G)x^{-n})\rangle$, which can be rewritten as

$$E=E^0+\langle \log((G)/[G])\rangle,$$

with

$$E^0=\langle \log([G]x^{-n})\rangle.$$

According to our method, we construct now the function

$$E(t)=E^0+\langle \log(\{G,t\}/[G])\rangle \qquad (27)$$

and expand it in a power series. It is immediately seen that for $\mathbf{t}=\mathbf{0}$ the second term on the right side of (27) vanishes and thus $E^0=E(\mathbf{0})$. Therefore $E^0$ is the contribution of the acyclic structural elements of the conjugated system to total $\pi$-electron energy. (We note in passing that the difference $E-E^0$ was recently interpreted as a novel type of "topological" resonance energy [31], since it can be understood as the entire effect of cycles on the total $\pi$-electron energy.

Using Eq. (25) one can easily derive from (27)

$$\frac{\partial E(\mathbf{0})}{\partial t_a}=-2i^{-|Z_a|}\left\langle\frac{[G-Z_a]}{[G]}\right\rangle \tag{28}$$

$$\frac{\partial^2 E(\mathbf{0})}{\partial t_a\,\partial t_b}=-4i^{-|Z_a|-|Z_b|}\left\{\left\langle\frac{[G-Z_a][G-Z_b]}{[G]^2}\right\rangle-\left\langle\frac{[G-Z_a-Z_b]}{[G]}\right\rangle\right\}, \tag{29}$$

$$\frac{\partial^k E(\mathbf{0})}{(\partial t_a)^k}=-2^k(k-1)!\,i^{-k|Z_a|}\langle([G-Z_a]/[G])^k\rangle. \tag{30}$$

Examination of formulas (28)–(30) gives a considerable insight into the dependence of total $\pi$-electron energy on molecular structure.

*Rule 1.* The first order (and therefore the most significant) effect of a cycle $Z$ on total $\pi$-electron energy is positive if $|Z|=4m+2$, negative if $|Z|=4m$ and zero if $|Z|=4m+1$ or $4m+3$. The second order effect of a cycle $Z$ is negative if $|Z|$ is even and positive if $|Z|$ is odd.

According to (20) and (30), the $k$th order effect of a cycle $Z_a$ on total $\pi$-electron energy is

$$-\frac{2^k}{k}i^{-k|Z_a|}\langle([G-Z_a]/[G])^k\rangle$$

and therefore the total effect of this cycle is given by

$$E(a)=-\sum_{k=1}^{\infty}\frac{2^k}{k}i^{-k|Z_a|}\langle([G-Z_a]/[G]^k\rangle. \tag{31}$$

In the Appendix it is proved that for even membered cycles the condition

$$2[G-Z]/[G]\leq 1$$

is fulfilled for all $x\in(-\infty,+\infty)$. Consequently, Eq. (31) can be transformed into

$$E(a)=\langle\log(1+2[G-Z_a]/[G])\rangle \quad \text{if } |Z_a|=4m+2, \tag{32a}$$

$$E(a)=\langle\log(1-2[G-Z_a]/[G])\rangle \quad \text{if } |Z_a|=4m. \tag{32b}$$

The analogous relation for odd-membered cycles reads

$$E(a)=\tfrac{1}{2}\langle\log(1+4[G-Z_a]^2/[G]^2)\rangle.$$

From Eqs. (32) is evident that $E(a) > 0$ if $|Z_a| = 4m + 2$ and $E(a) < 0$ if $|Z_a| = 4m$. Thus we have deduced:

*Rule 2.* The effect of a cycle $Z$ on total $\pi$-electron energy is positive if $|Z| = 4m + 2$ and negative if $|Z| = 4m$.

This is exactly the statement of the (generalized) Hückel $4m+2$ rule. We see that as long as the collective effects of pairs, triplets etc. of cycles are disregarded, the Hückel rule is generally valid. It has been shown elsewhere that these collective effects may in certain exceptional cases cause violations of the Hückel rule, but only in the case of $(4m+2)$-membered cycles [20].

*Rule 3a.* A pair of cycles $Z_a$ and $Z_b$ has a non-vanishing first order collective contribution only if $|Z_a| + |Z_b|$ is even.

This contribution depends on two terms which have opposite signs (see Eq. (29)) and therefore it is difficult to predict whether it stabilizes or destabilizes the molecule.

If, however, $Z_a$ and $Z_b$ are not disjoint, then the second integral in (29) vanishes and we have:

*Rule 3b.* The first order collective contribution of the cycles $Z_a$ and $Z_b$ is positive if $Z_a$ and $Z_b$ form one of the following pairs:

$$|Z_a| = 4m + 2 \quad \text{and} \quad |Z_b| = 4m',$$

$$|Z_a| = 4m + 1 \quad \text{and} \quad |Z_b| = 4m' + 1,$$

$$|Z_a| = 4m + 1 \quad \text{and} \quad |Z_b| = 4m' + 3.$$

Otherwise, the effect is negative.

The higher order collective contributions of cycles appear to conform to quite complicated mathematical expressions and therefore their analysis becomes difficult. Since these effects are usually small and chemically insignificant, we shall not continue our considerations along these lines.

### 3.3. *$\pi$-Electron Charge*

Let us denote the $\pi$-electron net charge on the atom $r$ of the conjugated hydrocarbon $G$ by $Q_r$. Then[2] [28],

$$Q_r = Q_r(G) = -i\langle (G - v_r)/(G) \rangle.$$

We introduce now the quantity $Q_r(t)$ as

$$Q_r(t) = -i\langle \{G - v_r, t\}/\{G, t\} \rangle \tag{33}$$

Since $[G - v_r]/[G]$ is necessarily an odd function, it immediately follows that

$$Q_r(0) = -i\langle [G - v_r]/[G] \rangle = 0.$$

---

[2] Note that this equation holds for those conjugated systems which have filled bonding and empty antibonding molecular orbitals; in the following we shall restrict our considerations to such systems.

*Rule 4a.* Acyclic structural elements of the molecular topology have no effect on $\pi$-electron charge.

Using the formula (25) it is easy to determine the expression for the first order effect of the cycle $Z_a$ on $Q_r$. Let us for brevity introduce the symbols $\{G, v_r, Z_a\}$ and $[G, v_r, Z_a]$ as follows:

$$\{G-v_r-Z_a, t\}\{G, t\}-\{G-v_r, t\}\{G-Z_a, t\}=\{G, v_r, Z_a\},$$

$$[G-v_r-Z_a][G]-[G-v_r][G-Z_a]=[G, v_r, Z_a].$$

Then

$$\frac{\partial Q_r(t)}{\partial t_a}=2i^{-|Z_a|+1}\langle\{G, v_r, Z_a\}/\{G, t\}^2\rangle \tag{34}$$

and consequently the first order effect is

$$\frac{\partial Q_r(\mathbf{0})}{\partial t_a}=2i^{-|Z_a|+1}\langle[G, v_r, Z_a]/[G]^2\rangle. \tag{35}$$

In order to determine the $k$th order effect of the cycle $Z_a$, note that according to (25),

$$\frac{\partial}{\partial t_a}\{G, v_r, Z_a\}=-2i^{-|Z_a|}(\{G-v_r-Z_a\}\{G-Z_a\}-\{G-Z_a\}\{G-v_r-Z_a\})=0$$

where we have used the fact that $\{G-v_r-Z_a, t\}$ and $\{G-Z_a, t\}$ cannot depend on $t_a$. Thus also $\{G, v_r, Z_a\}$ is independent of $t_a$. Now a repeated differentiation of Eq. (34) results in the expression (36) for the $k$th order effect of the cycle $Z_a$:

$$i(2i^{-|Z_a|})^k\left\langle\frac{[G-Z_a]^{k-1}}{[G]^{k+1}}[G, v_r, Z_a]\right\rangle. \tag{36}$$

The total effect of $Z_a$ on the $\pi$-electron charge of the atom $r$ is therefore

$$\begin{aligned}Q_r(a)&=i\sum_{k=1}^{\infty}(2i^{-|Z_a|})^k\left\langle\frac{[G-Z_a]^{k-1}}{[G]^{k+1}}[G, v_r, Z_a]\right\rangle\\&=2i^{-|Z_a|+1}\left\langle\frac{[G, v_r, Z_a]}{[G]^2}\sum_{k=1}^{\infty}(2i^{-|Z_a|}[G-Z_a]/[G])^{k-1}\right\rangle\\&=2i^{-|Z_a|+1}\left\langle\frac{[G, v_r, Z_a]}{[G]^2}(1-2i^{-|Z_a|}[G-Z_a]/[G])^{-1}\right\rangle.\end{aligned}$$

Subtracting from this latter expression the term $i\langle[G-v_r]/[G]\rangle$ (which is equal to zero), we obtain after appropriate transformations

$$Q_r(a)=2i^{-|Z_a|+1}\langle[G, v_r, Z_a]/([G]^2+4[G-Z_a]^2)\rangle \tag{37}$$

It is interesting to note that the formulas for the first order effect (35) and for the total effect (37) of the cycle $Z_a$ on $\pi$-electron charge, have closely related algebraic form, contrary to the analogous expressions for total $\pi$-electron energy, Eqs. (28) and (32).

If $|Z_a|$ is even, then both the functions $([G-v_r-Z_a][G])$ and $([G-v_r][G-Z_a])$ are odd functions and consequently $[G, v_r, Z_a]$ is also an odd function. Therefore the integrals in Eqs. (35)–(37) vanish.

*Rule 4b.* $(4m+2)$- and $(4m)$-membered cycles have no $k$th order effect on $\pi$-electron charge for all $k=1, 2, \ldots$ and thus the total effect of such cycles is also equal to zero.

The collective effect of two (or more) cycles on total $\pi$-electron energy conforms to rather complicated topological formulas. For instance, the first order collective effect of two distinct cycles $Z_a$ and $Z_b$ is given by

$$\frac{1}{2}\frac{\partial^2 Q_r(\mathbf{0})}{\partial t_a\,\partial t_b}=2i^{-|Z_a|-|Z_b|-1}\cdot$$

$$\langle([G][G, v_r, Z_a+Z_b]-[G-Z_a][G, v_r, Z_b]-[G-Z_b][G, v_r, Z_a])/[G]^3\rangle$$

and the only simple conclusion which can be drawn is that this effect is equal to zero if the two cycles have the same parity.

It can be shown that also in the general case

$$\frac{\partial^k Q_r(\mathbf{0})}{\partial t_{a_1}\,\partial t_{a_2}\cdots\partial t_{a_k}}=0 \tag{38}$$

whenever $|Z_{a_1}|+|Z_{a_2}|+\cdots+|Z_{a_k}|$ is even, i.e. the collection of $k$ cycles $Z_{a_1}, Z_{a_2}, \ldots, Z_{a_k}$ may have a non-zero collective effect on $\pi$-electron charge only if the number of odd-membered cycles in this collection is odd.

According to the well-known Pairing theorem, alternant hydrocarbons have a uniform HMO $\pi$-electron charge distribution, i.e.

$$Q_r=0 \quad \text{for all } r=1, 2, \ldots, n. \tag{39}$$

Since the alternant systems (by definition) cannot possess odd-membered cycles, we see that any collection of cycles in an alternant hydrocarbon satisfies Eq. (38). This conclusion, together with Rules 4a and 4b results in the following generalization of the statement (39).

*Rule 5.* In the case of alternant hydrocarbons all topological factors which have been considered in the expansion (20) have separately a zero effect on $\pi$-electron charge.

From Rules 4 and 5 it follows that $(4m+1)$- and $(4m+3)$- membered cycles are the only topological factors which determine the $\pi$-electron charge in conjugated hydrocarbons (of course, within the Hückel model).

In the case of odd-membered cycles Eq. (37) can be rewritten as

$$Q_r(a)=Q_{r1}(a)-Q_{r2}(a) \text{ if } |Z_a|=4m+1$$

and

$$Q_r(a)=Q_{r2}(a)-Q_{r1}(a) \text{ if } |Z_a|=4m+3$$

with

$$Q_{r1}(a) = 2\langle[G - v_r - Z_a][G]/([G]^2 + 4[G - Z_a]^2)\rangle$$

$$Q_{r2}(a) = 2\langle[G - v_r][G - Z_a]/([G]^2 + 4[G - Z_a]^2)\rangle.$$

Thus the effect of a cycle on the $\pi$-electron charge is presented by a difference of two terms, which have a rather similar dependence on molecular topology. Therefore it is not easy to formulate any generally valid rule neither about the sign of the effect (37) nor about its magnitude.

There is however an important special case, namely when the vertex $v_r$ belongs to the cycle $Z_a$. Then the subgraph $G - v_r$ contains not the cycle $Z_a$ and consequently the polynomial $[G - v_r - Z_a]$ is identically equal to zero. Therefore the term $Q_{r1}(a)$ vanishes. (The integral $Q_{r2}(a)$ is, of course, always positive.)

*Rule 6.* If the conjugated center $r$ belongs to the odd-membered cycle $Z_a$, then $Z_a$ induces a negative $\pi$-electron charge on this center ($Q_r(a) < 0$) if $|Z_a| = 4m + 1$ and $Z_a$ induces a positive $\pi$-electron charge ($Q_r(a) > 0$) if $|Z_a| = 4m + 3$.

From the present analysis we see that the $\pi$-electron charge in conjugated hydrocarbons is essentially governed by modulo 4 topological rules, although these are much more complex than in the case of total $\pi$-electron energy.

The sign of the $\pi$-electron charge of those atoms which belong to only one odd-membered cycle is completely determined by Rule 6. If, however, the atom belongs to two or more odd-cycles, then its $\pi$-electron charge is a result of a competition between the effect of every particular odd-cycle (as given by Rule 6) and of collective cyclic effects.

### 3.4. *$\pi$-electron bond order*

In order to derive the formulas for the dependence of the bond order on cyclic conjugation in a $\pi$-electron system, we start on with the identity [28]

$$P_{rs} = P_{rs}(G) = \frac{1}{2}\,\frac{\partial E(G_k)}{\partial k}\bigg|_{k=1}, \tag{40}$$

where $P_{rs}$ is the $\pi$-electron bond order of the bond between the atoms $r$ and $s$ of the conjugated system whose molecular graph is $G$, whereas $G_k$ denotes the graph which is obtained from $G$ by setting a (variable) weight $k$ on the edge $e_{rs}$ in order to label this edge; $E(G_k)$ is the total $\pi$-electron energy corresponding to $G_k$.

In the following we shall consider only the case when $v_r$ and $v_s$ are adjacent vertices.

Using Eq. (26) and the fact that $\partial E(G)/\partial k = 0$, we can transform (40) into

$$P_{rs} = \frac{1}{2}\,\frac{\partial}{\partial k}\langle \log\,((G_k)/(G))\rangle\bigg|_{k=1}. \tag{41}$$

From the formula (41) we directly arrive at the function $P_{rs}(t)$,

$$P_{rs}(t)=\frac{1}{2}\frac{\partial}{\partial k}\langle \log(\{G_k,t\}/\{G,t\})\rangle\bigg|_{k=1}. \tag{42}$$

It can be shown that

$$\mu(G_k)=\mu(G-e_{rs})-k^2\mu(G-v_r-v_s)-2k\sum_a t_a\mu(G-Z_a).$$

(Note that for $k=1$ the above formula reduces to that given in Proposition 4).

Substitution of (42) back into (41) gives

$$P_{rs}(t)=\left\langle\frac{\{G-v_r-v_s,t\}}{\{G,t\}}\right\rangle-\sum_a i^{-|Z_a|}t_a\left\langle\frac{\{G-Z_a,t\}}{\{G,t\}}\right\rangle. \tag{43}$$

If we set $t=\mathbf{0}$ in formula (43), then we obtain the effect of acyclic structural details of the molecular topology on bond order, namely

$$P_{rs}(\mathbf{0})=\langle[G-v_r-v_s]/[G]\rangle.$$

Consequently, the difference $P_{rs}-P_{rs}(\mathbf{0})$ represents the joint effect of all cycles on bond order. This quantity has been examined in [32] and called the bond resonance energy, BRE. Whereas $P_{rs}(\mathbf{0})$ is always positive, the bond resonance energy may be both a positive or negative number or zero.

In order to determine the effect of a particular cycle $Z_a$ on $P_{rs}$ we have to distinguish between the case when the edge $e_{rs}$ belongs to $Z_a$ and the case when $e_{rs}$ is not an edge of $Z_a$. Using (25) we calculated for the former case:

$$\frac{\partial P_{rs}(\mathbf{0})}{\partial t_a}=-i^{-|Z_a|}\left\langle\frac{[G-Z_a]}{[G]}\,\frac{[G]-2[G-v_r-v_s]}{[G]}\right\rangle \tag{44}$$

and

$$P_{rs}(a)=-i^{-|Z_a|}\left\langle\frac{[G-Z_a]}{[G]}\,\frac{[G]-2[G-v_r-v_s]}{[G]-2i^{-|Z_a|}[G-Z_a]}\right\rangle \tag{45}$$

when $|Z_a|$ is even,

$$\frac{\partial P_{rs}(\mathbf{0})}{\partial t_a}=0 \tag{46}$$

and

$$P_{rs}(a)=2\left\langle\frac{[G-Z_a]^2}{[G]}\,\frac{[G]-2[G-v_r-v_s]}{[G]^2+4[G-Z_a]^2}\right\rangle \tag{47}$$

when $|Z_a|$ is odd. If the edge $e_{rs}$ does not belong to $Z_a$ we computed:

$$\frac{\partial P_{rs}(\mathbf{0})}{\partial t_a}=-2i^{-|Z_a|}\left\langle\frac{[G,v_r,v_s,Z_a]}{[G]^2}\right\rangle \tag{48}$$

and

$$P_{rs}(a) = -2i^{-|Z_a|}\left\langle \frac{[G, v_r, v_s, Z_a]}{[G]([G]-2i^{-|Z_a|}[G-Z_a])} \right\rangle \tag{49}$$

when $|Z_a|$ is even,

$$\frac{\partial P_{rs}(\mathbf{0})}{\partial t_a} = 0 \tag{50}$$

and

$$P_{rs}(a) = 4\left\langle \frac{[G-Z_a]}{[G]}\,\frac{[G, v_r, v_s, Z_a]}{[G]^2+4[G-Z_a]^2} \right\rangle \tag{51}$$

when $|Z_a|$ is odd. In the above expressions the abbreviation

$$[G-v_r-v_s-Z_a][G]-[G-Z_a][G-v_r-v_s]=[G, v_r, v_s, Z_a]$$

has been used. $P_{rs}(a)$ is the total effect of the cycle $Z_a$ on the bond order $P_{rs}$.

It seems to be a hard task to predict the sign of the expressions (44), (45), (47), (48), (49) and (51). According to the inequality which is proved in the Appendix, if $|Z_a|$ is even, then the polynomial $[G]-2i^{-|Z_a|}[G-Z_a]$ has positive values for all $|x|>0$. Therefore the sign of the integrals (44), (45) and (47) depends on the sign of the function $[G]-2[G-v_r-v_s]$, while the sign of (48), (49) and (51) is determined by $[G, v_r, v_s, Z_a]$. Both functions may change their sign in the interval $(0, \infty)$.

Since $[G]$ is a polynomial with non-negative coefficients of degree $n$ and $[G-v_r-v_s]$ has degree $n-2$, their difference is larger than zero for large values of the variable $x$ (at least for $|x|\geq 1$). Assuming that the integration over the interval where $[G]-2[G-v_r-v_s]$ is positive gives the major contribution to (44) and (45), we can formulate the following:

*Rule 7.* A $(4m+2)$-membered cycle has a positive (increasing) contribution to the $\pi$-electron bond order of all bonds which lie on this cycle. A $(4m)$-membered cycle decreases the $\pi$-electron bond order of the bonds which belong to this cycle.

In addition to this rule, from (46) and (47) is seen that odd-membered cycles have no first order, and a small total effect on the bond order.

Since $[G, v_r, v_s, Z_a]$ is the difference between two polynomials of the same degree $(=2n-2-|Z_a|)$, we conclude that the integrals (48), (49) and (51) are small relative to (44) and (45). Therefore from (48)–(51) results:

*Rule 8.* Cycles which do not contain the bond *rs* have small influence on $P_{rs}$. Their effect may be both positive and negative, depending on finer details of the molecular topology.

## 4. Conclusion

The method exposed in the present paper is in principle applicable to the examination of the effect of cyclic conjugation on all $\pi$-electron indices of the Hückel model. In all cases when modulo 4 type rules could be observed, these regularities had the following common algebraic background.

In calculating the expressions $J_a$, $J_{ab}$, $J_{abc}$ etc. in Eq. (20) we must necessarily use the identity (25). The signs of the integral expressions for $J_a$, $J_{ab}$ etc. are usually determined by the multiplyer $i^{-|Z_a|}$ in Eq. (25). Since $i^{-|Z_a|} = +1, -i, -1$ and $+i$ depending on whether the size of the cycle $Z_a$ is $4m$, $4m+1$, $4m+2$ or $4m+3$, modulo 4 type regularities for the sign of $J_a$, $J_{ab}$ etc. must necessarily arise.

Hence there appears to be a close relation between the mathematical theory of the numerous modulo 4 rules of the Hückel model, and the fact that $+1$, $-1$, $+i$ and $-i$ form a group (of order 4) with respect to multiplication.

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## Appendix

*Proposition*: If $Z$ is an even-membered cycle of a graph $G$, then

$$2[G-Z, x]/[G, x] \leq 1 \tag{52}$$

for all real values of the variable $x$.

*Proof*: Let $G$ possess $n$ vertices and let $n' = n$ if $n$ is even while $n' = n-1$ if $n$ is odd. Then according to eqs. (2) and (23),

$$[G-Z, x]/[G, x] = \frac{\sum_k p(G-Z, k)x^{n'-|Z|-2k}}{\sum_k p(G, k)x^{n'-2k}}, \tag{53}$$

where $|Z|$ is the size of the cycle $Z$ and $p(H, k)$ denotes the number of $k$-matchings of the graph $H$. Note that the subgraph $G-Z$ possesses $n-|Z|$ vertices.

Let the vertices of the cycle $Z$ be labelled by $v_1, v_2, \ldots, v_{|Z|}$ in such a manner that $v_{i-1}$ is adjacent to $v_i$, $i = 2, 3, \ldots, |Z|$ and $v_{|Z|}$ is adjacent to $v_1$. Let $M_k$ be a $k$-matching of the subgraph $G-Z$. Then $M_k \cup \{e_{12}, e_{34}, \ldots, e_{|Z|-1,|Z|}\}$ and $M_k \cup \{e_{23}, e_{45}, \ldots, e_{|Z|,1}\}$ are two distinct $(k+|Z|/2)$-matchings of $G$. Therefore the number of $(k+|Z|/2)$-matchings of $G$ is at least two times larger than the number of $k$-matchings of $G-Z$,

$$2p(G-Z, k) \leq p(G, k+|Z|/2)$$

for all $k = 0, 1, 2, \ldots$.

Since $n'-|Z|-2k$ is an even number, we further conclude that

$$2p(G-Z,k)x^{(n'-|Z|)-2k} \le p(G,k+|Z|/2)x^{n'-2(k+|Z|/2}$$

for all $k$ and for all real values of $x$. Consequently,

$$2\sum_k p(G-Z,k)x^{(n'-|Z|)-2k} \le \sum_k p(G,k+|Z|/2)x^{n'-2(k+|Z|/2)}$$

$$\le \sum_k p(G,k)x^{n'-2k}$$

and the inequality (52) follows from the identity (53). Q.E.D.

If $Z$ is an odd-membered cycle, then there exist graphs for which (52) is not satisfied.

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