Theoret. Chim. Acta (Berl.) 66, 43–49 (1984)

THEORETICA CHIMICA ACTA

On cyclic conjugation

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A novel approach to the theory of cyclic conjugation is proposed, which is free of some disadvantages of the previously used methods. It is shown that in the general case the effect of cyclic conjugation is an additive function of individual ring effects.

An expression for the effect of an individual ring on total π-electron energy is obtained. Some difficulties of the theory are pointed out.

Key words: Cyclic conjugation–graph theory

1. Introduction

A general theory of cyclic conjugation has been recently developed, using the μ-polynomial technique [1]. The theory enabled the unification of some previously introduced concepts: topological resonance energy [2], effect of individual rings on total π-electron energy [3], Möbius systems [4] and other [5]. The μ-polynomial technique was applied [1] to several π-electron indices of conjugated hydrocarbons such as total π-electron energy, charge density and bond order, and a few generally valid rules about their dependence on the cycles contained in the molecule have been deduced. In the present paper we shall reexamine the effect of cyclic conjugation on total π-electron energy. Such a reexamination was necessary because of the difficulties which have been recently pointed out by Herndon [6]. Namely, the zeros of the μ-polynomial may, in certain cases, be complex numbers. Therefore a formal application of the μ-polynomial technique may sometimes result in complex-valued individual ring effects [6], which, of course, are without any physical meaning.

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The analysis given in the present work will show how these difficulties can be avoided, but will also exhibit the limitations of the μ-polynomial technique. Our considerations, as well as those in Ref. [1], are graph-theoretical in nature and are, therefore, applicable within the framework of the Hückel (topological) molecular orbital model.

The theory of cyclic conjugation is essentially based on the following ideas. If a conjugated molecule G contains r cycles $Z_1, Z_2, \dots, Z_r$, then we associate a variable t_a (a real number) to each cycle Z_a, $a = 1, 2, \dots, r$. The choice $t_a = 1$ means that the effect of Z_a is normally taken into account; the choice $t_a = 0$ means that the effect of Z_a is fully disregarded.

The parameters t_a form a vector $\mathbf{t} = (t_1, t_2, \dots, t_r)$. The μ-polynomial $\mu(G, \mathbf{t}, x)$ is a polynomial in the variable x, depending on $\mathbf{t}$. If $\mathbf{t} = \mathbf{1}$, then the μ-polynomial reduces to the characteristic polynomial $\phi(G, x)$:

$$\mu(G, \mathbf{1}, x) = \phi(G, x).$$

In the present paper we shall use the same symbolism as in Ref. [1], where the theory of the μ-polynomial is described in detail. In particular, we shall often need the following two abbreviations: if $t_a = 0$ for all a, then $\mathbf{t} = \mathbf{0}$: if $t_a = 1$ for all a, then $\mathbf{t} = \mathbf{1}$.

If a (Hückel) molecular orbital quantity J can be calculated from the characteristic polynomial of the molecular graph according to a mapping f:

$$f\colon \phi(G, x) \to J \equiv J(\mathbf{1}),$$

then we define the function $J(\mathbf{t})$ via

$$f\colon \mu(G, \mathbf{t}, x) \to J(\mathbf{t}).$$

The quantity $J(\mathbf{t})$ needs not to have any physical interpretation, except for $\mathbf{t} = \mathbf{1}$. Moreover, for $\mathbf{t} \neq \mathbf{1}$, $J(\mathbf{t})$ may be complex valued.

In a number of previous papers [2–5] it has been proposed (using, of course, a different terminology) to measure the effect of cyclic conjugation by a difference $J(\mathbf{t}^A) - J(\mathbf{t}^B)$, where $\mathbf{t}^A$ and $\mathbf{t}^B$ are two suitably chosen $\mathbf{t}$-vectors. As a matter of fact, $\mathbf{t}^A$ was always chosen to be equal to $\mathbf{1}$. In the TRE model [2] as well as in the papers [5], $\mathbf{t}^B = \mathbf{0}$. In the theory of Möbius systems [4] one has $t_a^B = -1$ if Z_a is a Möbius ring and $t_a^B = 1$ otherwise. In [3] the effect of an individual ring Z_a on the total π-electron energy E has been defined as $E(\mathbf{1}) - E(\mathbf{t}^B)$, where $t_a^B = 0$ and $t_b^B = 1$ for $b \neq a$. This latter definition, however, may lead to complex-valued results [6].

Hence we see that in the models proposed in Refs. [2–5] the calculated effect of cyclic conjugation depends on the value of the function $J(\mathbf{t})$ in two different points. In at least one of these points $J(\mathbf{t})$ has no sound physical meaning and therefore all the schemes given in [2–6] suffer from the well-known [7] disadvantages of resonance-energy-like quantities.

Another approach to measuring the effect of cyclic conjugation would be in selecting $\mathbf{t}^A = \mathbf{1}$ and choosing $\mathbf{t}^B$ as close to $\mathbf{1}$ as possible. In this manner we would have to examine the function $J(\mathbf{t})$ only in the neighborhood of the point $\mathbf{1}$, hence in the neighborhood of the only point in which $J(\mathbf{t})$ is a physically meaningful quantity. By this approach we shall overcome the difficulties mentioned above and in Ref. [6].

2. The local definition of the effect of cyclic conjugation

In this section we derive some general properties of cyclic conjugation, provided its effect is measured according to the following "local" definition.

Definition A. Let $\mathbf{t}^A = \mathbf{1}$ and $\mathbf{t}^A - \mathbf{t}^B = \boldsymbol{\delta} = (\delta_1, \delta_2, \dots, \delta_r)$, and assume that the components of δ are sufficiently small. Then the effect of cyclic conjugation on J is determined by the behavior of the function $J(\mathbf{t}^A) - J(\mathbf{t}^B)$.

We call this approach to cyclic conjugation local because it is (explicitly) based on the behavior of $J(\mathbf{t})$ at a single point, namely at $\mathbf{t} = \mathbf{1}$. Therefore it differs essentially from the previously used non-local models [2–6], based on the behavior of $J(\mathbf{t})$ at two distinct points.

The above definition can be made more precise if we assume that in the neighborhood of the point $\mathbf{t} = \mathbf{1}$ the function $J(\mathbf{t})$ can be presented in the form

$$J(\mathbf{t}) = \sum_a [J^a \cdot (\delta_a)^h + 0(|\delta_a|^{h+1})], \tag{1}$$

where h is a certain exponent which will be determined later on. From Eq. (1) is immediately seen that[1]

$$J^a = \left. \frac{\partial J(\mathbf{t})}{\partial (\delta_a)^h} \right|_{\mathbf{t}=\mathbf{1}}. \tag{2}$$

Now we can extend Definition A as follows.

Definition B. The (local) effect of an individual cycle Z_a on the quantity J is equal to J^a, Eq. (2).

For reasons which will become clear later on, we shall say that J^a is an effect of order h^{-1}.

As a straightforward consequence of Eq. (1) and the above definition, we have the following simple but rather convenient results.

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[1] Note that in Ref. [1] an apparently similar quantity J_a has been considered, which is the partial derivative of $J(\mathbf{t})$ at the point $\mathbf{0}$. However, the physical interpretation, the mathematical properties and the dependence on molecular topology of J_a and J^a are completely different, and these two quantities should be strictly distinguished

Rule 1. According to the local approach, the effect of cyclic conjugation on any molecular orbital quantity is an additive function of individual ring contributions.

Rule 2. The joint (local) effect of all cycles on J is equal to $J^1+J^2+\ldots+J^r$. It is worth mentioning here that similar rules for non-locally defined cyclic conjugation effects hold only as rough approximations [1, 5, 8].

3. Effect of cyclic conjugation on total π-energy

As a consequence of Rule 1, it is sufficient to consider individual ring effects only. Let us therefore choose the vector δ so that $\delta_a=\delta$ and $\delta_b=0$ for $b\neq a$. Then according to the results of Ref. [1],

$$\mu(G, t^B, x)=\phi(G,x)-2\phi(G-Z_a,x)\cdot\delta. \tag{3}$$

Let $x_1, x_2, \ldots, x_n$ be the zeros of the characteristic polynomial $\phi(G,x)$ i.e. the eigenvalues of the graph G [9, 10]. The following consideration will be based upon the well-known result [9] that the Hückel MO energy levels E_i of a conjugated molecule are related to the eigenvalues x_i of the corresponding molecular graph as $E_i=\alpha+x_i\beta$. If we express the MO energies in β units, then simply $E_i=x_i$. The total π-electron energy E is then given by

$$E=\sum_{i=1}^{n} g_i x_i$$

where g_i is the occupation number of the i-th MO.

Suppose first that the eigenvalue x_i is non-degenerate. Then (as shown in Appendix) the zero of $\mu(G, t^B, x)$, Eq. (3), which corresponds to x_i is given by

$$x_i+2[\phi(G-Z_a,x_i)/\phi^{(1)}(G,x_i)]\delta \tag{4}$$

with the error in the approximation (4) being of order δ^2. This means that a cycle Z_a has an effect of order one on a non-degenerate MO energy E_i. This effect (in β units) is given by

$$E_i^a=2\phi(G-Z_a,x_i)/\phi^{(1)}(G,x_i). \tag{5}$$

E_i^a is necessarily a real quantity.

Rule 3. If all the occupied MO's are non-degenerate, then the effect of a cycle Z_a on the total π-electron energy E is of order one and is given by

$$E^a=2\sum_i g_i\phi(G-Z_a,x_i)/\phi^{(1)}(G,x_i)$$

with the summation going over all eigenvalues of the molecular graph.

E^a is a real quantity, irrespective of the number of π-electrons and their distribution in MO's.

The case of degenerate MO energy levels is somewhat more complicated. If the energy level E_i is doubly degenerate, then as a consequence of the theorem which is given in the Appendix, the corresponding two zeros of $\mu(G, t^B, x)$ are

$$x_i + 2\sqrt{[\phi(G - Z_a, x_i)/\phi^{(2)}(G, x_i)] \cdot \delta} \tag{6a}$$

$$x_i - 2\sqrt{[\phi(G - Z_a, x_i)/\phi^{(2)}(G, x_i)] \cdot \delta} \tag{6b}$$

and the error in (6) is of order $|\delta|$. These two zeros are either both real or both complex, depending on the sign of the term $[\phi(G - Z_a, x_i)/\phi^{(2)}(G, x_i)] \cdot \delta$.

If the degeneracy of the MO's is higher than two, then complex zeros of $\mu(G, t^B, x)$ necessarily occur, no matter how close are the points t^B and **1**. This follows from the theorem given in the Appendix and the fact that among the k-th root of every number there are at least k-2 complex roots.

We conclude therefore that if a MO is doubly degenerate, then the (local) effect of cyclic conjugation on its energy may be complex valued. If, however, the MO is more than doubly degenerate, then the (local) effect of cyclic conjugation on its energy must be complex valued.

If the MO is k-times degenerate, then the effect of a cycle on its energy is of order k.

The occurrence of complex valued individual ring effects on molecular orbital energies is certainly a serious shortcoming of the μ-polynomial technique, both in its local and non-local variant. The local approach has, however, the fortunate advantage that the effect of a ring on total π-electron energy is a real quantity in all chemically relevant cases. The following rule holds.

Rule 4. If the degenerate MO's are occupied with the same number (two or one or zero) of π-electrons, then the effect of a cycle Z_a on the total π-electron energy is of order one and is given by

$$E^a = 2 \sum_i{}' g_i \phi(G - Z_a, x_i)/\phi^{(1)}(G, x_i)$$

with the summation going over all non-degenerate eigenvalues of the molecular graph.

In order to prove Rule 4 consider an eigenvalue x_i of G which is k-times degenerate. Then according to Definition B and the result from the Appendix, the effect of Z_a on the k degenerate MO energy levels is given by the k different solutions E_i^a of the equation

$$(E_i^a)^k = -k!\, \phi(G - Z_a, x_i)/\phi^{(k)}(G, x_i).$$

By a well-known result of algebra, the sum of these solutions is zero, provided $k > 1$. Hence whenever the degenerate orbitals are occupied with equal numbers of electrons, the contributions to E^a coming from the degenerate energy levels mutually cancel. Thus only the non-degenerate energy levels contribute to E^a and their effect is of order one. Rule 4 follows.

The only situation which is not covered by Rules 3 and 4 is when the number of π electrons in a set of k degenerate molecular orbitals is neither 0 nor k nor

$2k$. Then the present method fails. However, in this case the Hückel model is also completely inadequate to describe the electronic structure of the molecule. Therefore Rules 3 and 4 embrace all relevant electronic configurations.

4. Concluding remarks

Following the criticism of Herndon [6] we have revisited the μ-polynomial technique [1] for measuring the effect of cyclic conjugation and proposed a modification of it. The main advantage of this novel approach is its local character, namely the auxiliary function $J(t)$ has to be examined in a single point $t = 1$ only.

In the local variant of the theory, the total effect of cyclic conjugation has been shown to be simply the sum of individual ring effects.

A novel method for the calculation of the individual ring effects on total π-electron energy is proposed. Contrary to a previous method [3, 6], the present one always gives real-valued results. Exceptionally, our approach is not applicable to certain degenerate electronic states (where, however, the Hückel model cannot be used either).

The μ-polynomial technique can be applied to molecular orbital energy levels, but reasonable results are obtained only in the non-degenerate case. It is not possible to avoid complex-valued ring effects on more than doubly degenerate MO energies.

This seems to be an inevitable pitfall of the graph-theoretical approach to cyclic conjugation and indicates the limits of its applicability.

Acknowledgement. The author is grateful to Professor W. C. Herndon (El Paso) for helpful discussions.

Appendix

The theorem which we prove in this appendix is a generalization of a result from the book [11].

Let $P(x)$ be a polynomial and x_0 its zero, having algebraic multiplicity $k (k \geq 1)$. Let $P^{(i)}(x)$ denote the i-th derivative of $P(x)$. Let further $Q(x)$ be another polynomial and u a parameter.

If $|u|$ is sufficiently small, then the zeros of the polynomial $P(x) + uQ(x)$ will lie near to the zeros of the polynomial $P(x)$. A more precise localization of the zeros of $P(x) + uQ(x)$ is given by the following theorem.

Theorem. *If ρ_i, $i = 1, \ldots, k$ are the k-th roots of the expression*

$$-uk!\,Q(x_o)/p^{(k)}(x_o),$$

then the polynomial $P(x) + uQ(x)$ has k zeros of the form

$$x_0 + \rho_i + O(|u|^{2/k}), \quad i = 1, \ldots, k.$$

Proof. Define another polynomial $P(x)+z^kQ(x)$ and let $x(z)$ be its zero. Then the equation

$$P(x(z))+z^kQ(x(z))=0 \tag{A-1}$$

holds for all values of z. Let $x(z)$ has been chosen so that $x(0)=x_0$.

For $|z|$ being sufficiently small, one can expand $x(z)$ in a power series

$$x(z)=x_0+A\cdot z+B\cdot z^2+\dots$$

Then obviously

$$x(z)=x_0+A\cdot z+0(z^2)$$

and

$$A=\left.\frac{\partial x(z)}{\partial z}\right|_{z=0} \tag{A-2}$$

Differentiate the identity (A-1) k times with respect to z and then set $z=0$. Using Eq. (A-2) and the facts that by hypothesis $P(x_0)=P^{(1)}(x_0)=\dots=P^{(k-1)}(x_0)=0$ and $p^{(k)}(x_0)\neq 0$, we arrive to the equation

$$A^kP^{(k)}(x_0)+k!\,Q(x_0)=0,$$

from which we conclude that

$$x(z)=x_0+[-k!\,Q(x_0)/P^{(k)}(x_0)]^{1/k}\cdot z+0(z^2).$$

The theorem follows now by putting $z^k=u$.

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Received October 19, 1983