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On the Topological Resonance Energy of Heteroconjugated Molecules

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It is demonstrated that the reference polynomial of a heteroconjugated π -electron system with arbitrary Coulomb and resonance integrals has real zeros. Some other properties of the reference polynomial are presented.

INTRODUCTION

Topological resonance energy (*TRE*) is a theoretical index which was discovered a few years ago^{1,2} and which can be used for describing the aromaticity and related properties of conjugated π -electron systems. Although the *TRE* method has limitations and fails in the case of some conjugated radicals and ions³, for a large number of systems of interest in chemistry (i. e. singlet ground state molecules for which at least one Kekulé structural formula can be written), the agreement between the predictions based on *TRE* and the experimental findings is quite good⁴.

TRE is computed according to the formula

$$TRE = E(G) - E^R(G) \quad (1)$$

where $E(G)$ is the HMO total π -electron energy of the molecule considered (usually expressed in the units of β), while $E^R(G)$ is the pertinent reference energy. G indicates the molecular graph of the conjugated system. The crucial idea of the *TRE* method is to construct the reference energy $E^R(G)$ as

$$E^R(G) = \sum_{j=1}^n g_j y_j \quad (2)$$

where the y_j 's are the zeros of the reference polynomial⁵ $R(G, x)$ and g_j symbolizes the occupation number of the j -th molecular orbital⁶. From eq. (2) is evident that for the success of the *TRE* method it is of utmost importance that all the numbers y_j be real.

For the case of conjugated hydrocarbons a proof of the reality of the y_j 's was recently offered⁷, although the same fact was already known in statistical physics⁸ (of course, within a completely different conceptual framework). However, for the case of heteroconjugated molecules the reality of

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the zeros of $R(G, x)$ has not yet been demonstrated. In the present paper we shall prove that for an arbitrary choice of the Coulomb integrals α_r and the resonance integrals β_{rs} in the HMO description of any π -electron system, these zeros are real indeed.

ON THE REFERENCE POLYNOMIAL OF HETEROCONJUGATED MOLECULES

The topological resonance energy of heteroconjugated molecules has been considered in a number of papers (for example in^{1,2,4b,9}). The corresponding reference polynomials were also precisely determined¹⁰ using a Sachs graph formalism. In this section we shall present two novel statements about the reference polynomial (of arbitrary heteroconjugated systems) which are not explicitly based on the notion of Sachs graphs, but which may be, if desired, used as alternative definitions of $R(G, x)$.

Let H be the HMO Hamiltonian matrix of a conjugated system having n conjugated centers. If β is the resonance integral of a carbon-carbon bond (in a hydrocarbon), then we shall write

$$H_{rr} = \alpha_r = a + h_r \beta \quad (3a)$$

$$H_{rs} = \beta_{rs} = k_{rs} A_{rs} \beta \quad (r \neq s) \quad (3b)$$

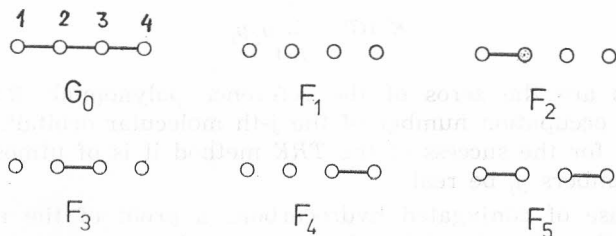
where $A_{rs} = 1$ if the centers r and s are adjacent and $A_{rs} = 0$ otherwise. There will be no restriction on the value of the parameters h_r and k_{rs} (except that they must be real numbers).

The matrix $\mathbf{A} = A_{rs}$ is the adjacency matrix of the molecular graph G . Note that the graph G defined in this manner has no weighted loops or weighted edges. Hence G is a simple graph.

The vertices of G will be labelled by v_1, v_2, \dots, v_n , and e_{rs} will denote the edge connecting the vertices v_r and v_s .

An F -cover of the graph G is a spanning subgraph¹¹ of G having as components only isolated vertices and/or isolated edges (assuming, of course, that an isolated edge contains its end vertices).

For example, G_0 , the molecular graph of the butadiene-like conjugated molecules has the following five F -covers: F_1, F_2, F_3, F_4 and F_5 .



Following the theory which has been recently developed by Farrell¹², we shall say that the weight of the vertex v_r is $x - h_r$ and that the weight of the edge e_{rs} is $-(k_{rs})^2$. The weight of an F -cover is the product of the weights of its components.

Let F denote an F -cover and $w(F)$ its weight. For example,

$$w(F_1) = (x - h_1)(x - h_2)(x - h_3)(x - h_4) \tag{4a}$$

$$w(F_2) = -(k_{12})^2(x - h_3)(x - h_4) \tag{4b}$$

$$w(F_3) = -(k_{23})^2(x - h_1)(x - h_4) \tag{4c}$$

$$w(F_4) = -(k_{34})^2(x - h_1)(x - h_2) \tag{4d}$$

$$w(F_5) = (k_{12})^2(k_{34})^2 \tag{4e}$$

Proposition 1. The reference polynomial of a heteroconjugated molecule whose HMO Hamiltonian is defined via eqs. (3) is given by the expression

$$R(G, x) = \sum_F w(F) \tag{5}$$

with the summation going over all the F -covers of the graph G .

In our example, $R(G_0, x) = \sum_{i=1}^5 w(F_i)$, where the $w(F_i)$'s are determined by the eqs. (4).

It is not difficult to see that Proposition 1 is just a reformulation of the »Sachs graph type« definition of a reference polynomial¹⁰. Nevertheless, this Proposition has a conceptual advantage in that all the required topological operations (i. e. the search for all F -covers) are performed on a simple graph, while the original definition¹⁰ of $R(G, x)$ is based on the consideration of the Sachs graphs of a multigraph with weighted edges and loops.

It is evident that every F -cover containing k edges corresponds to a distinct k -matching in the graph G . Consequently, the total number of F -covers (of a graph G) is equal to the total number of matchings in G , this latter quantity being also known¹³ as Hosoya's topological index Z_G . In the case of hydrocarbons, where $h_1 = h_2 = \dots = h_n = 0$, and $k_{rs} = 1$ for all pairs of adjacent vertices, all F -covers containing k edges have the same weight $w_k = (-1)^k x^{n-2k}$ and thus eq. (5) can be rewritten as

$$R(G, x) = a(G, x) \tag{6}$$

where

$$a(G, x) = \sum_{k=0}^{[n/2]} (-1)^k p(G, k) x^{n-2k} \tag{7}$$

and where $p(G, k)$ is the number of k -matchings in the graph G , i. e. the number of F -covers with k edges. The polynomial defined by eq. (7) is, for obvious reasons, called^{7,12,14} the matching polynomial of the graph G . Thus we have reached the conclusion that *in the case of conjugated hydrocarbons the reference polynomial coincides with the matching polynomial.*

Several recurrence relations have been obtained for matching polynomials^{14,15}. Two of them, namely

can easily be generalized for reference polynomials of heteroconjugated molecules:

$$R(G) = R(G - e_{rs}) - (k_{rs})^2 R(G - v_r - v_s) \quad (10)$$

$$R(G) = (x - h_r) R(G - v_r) - \sum_s (k_{rs})^2 R(G - v_r - v_s) \quad (11)$$

These latter formulae can be used as the basis for another definition of reference polynomials. Such a definition would thus be a purely algebraic one and would not require the use of either the concept of Sachs graphs or the concept of F -covers.

Let O_n be the graph with n vertices and without edges. (In the above example, $F_1 = O_4$.)

Proposition 2. The statements (a) and (b) fully determine the reference polynomials of all heteroconjugated systems.

(a) For $n = 0$, $R(O_n) = 1$. For $n > 0$, $R(O_n) = (x - h_1)(x - h_2) \dots (x - h_n)$.

(b) The formula (10) holds for all graphs G with $n \geq 2$ vertices.

In addition we note that eq. (11) can be obtained from eq. (10), when (10) is repeatedly applied to all edges e_{rs} being incident to the vertex v_r .

THE ZEROS OF THE REFERENCE POLYNOMIAL ARE REAL

The proof of the statement given in the title of this section will be similar to the argumentation used in ref.⁷, and therefore we shall omit the details. Let $y_1(G), y_2(G), \dots, y_n(G)$ are the zeros of $R(G)$ and $y_1(G - v_r), y_2(G - v_r), \dots, y_{n-1}(G - v_r)$ are the zeros of $R(G - v_r)$.

THEOREM

The zeros of $R(G)$ and $R(G - v)$ are real and the interlacing relation

$$y_j(G) \geq y_j(G - v_r) \geq y_{j+1}(G) \quad (12)$$

holds for all $j = 1, 2, \dots, n - 1$.

Proof follows by induction on the number of vertices of the graph. For the (unique) graph G_1 with one vertex ($G_1 = O_1$), we have $R(G_1) = x - h_1$ and the single zero of $R(G_1)$ is equal to h_1 . There exist two graphs with two vertices: G_2 and G'_2 , where $G_2 = O_2$ and G'_2 possesses an edge. Since $R(G_2) = (x - h_1)(x - h_2)$, the zeros of $R(G_2)$ are h_1 and h_2 and eq. (12) obviously holds for G_2 and G_1 . From $R(G'_2) = (x - h_1)(x - h_2) - (k_{12})^2$ we compute that the zeros of $R(G'_2)$ are

$$y_1 = h_1 + \frac{\sqrt{(h_2 - h_1)^2 + 4(k_{12})^2} + (h_2 - h_1)}{2} \quad (13a)$$

and

$$y_2 = h_1 - \frac{\sqrt{(h_2 - h_1)^2 + 4(k_{12})^2} - (h_2 - h_1)}{2} \quad (13b)$$

Hence $y_1 \geq h_1 \geq y_2$ and eq. (12) holds for G'_2 and G_1 . Thus the Theorem is true for the graphs G with two vertices.

We will now assume that the Theorem is true for all graphs with less than n vertices and deduce its validity for graphs with n vertices. Thus the induction hypothesis is that all the zeros of $R(G - v_r)$ and $R(G - v_r - v_s)$ are real and that

$$y_j(G - v_r) \geq y_j(G - v_r - v_s) \geq y_{j+1}(G - v_r) \tag{14}$$

for all $j = 1, 2, \dots, n - 2$ and for all vertices v_s being adjacent to v_r .

It is sufficient to examine the situation when all the zeros of $R(G - v_r)$ are distinct. (If this is not the case and y is a multiple zero of $R(G - v_r)$, then by (14) y is also a zero of $R(G - v_r - v_s)$ and by (11) y is also a zero of $R(G)$. Then we can divide eq. (11) with the greatest common divisor of $R(G)$, $R(G - v_r)$ and $R(G - v_r - v_s)$'s and continue to consider only the distinct zeros⁷.) Thus instead of (14) we will have

$$y_j(G - v_r) > y_j(G - v_r - v_s) > y_{j+1}(G - v_r) \tag{15}$$

for $j = 1, 2, \dots, n - 2$. Then $R(G - v_r - v_s, y_1(G - v_r)) > 0$, $R(G - v_r - v_s, y_2(G - v_r)) < 0$, $R(G - v_r - v_s, y_3(G - v_r)) > 0$ etc. for all s . From eq. (11) follows now

$$R(G, y_1(G - v_r)) = - \sum_s (k_{rs})^2 R(G - v_r - v_s, y_1(G - v_r)) < 0 \tag{16a}$$

$$R(G, y_2(G - v_r)) = - \sum_s (k_{rs})^2 R(G - v_r - v_s, y_2(G - v_r)) > 0 \tag{16b}$$

$$R(G, y_3(G - v_r)) = - \sum_s (k_{rs})^2 R(G - v_r - v_s, y_3(G - v_r)) < 0 \tag{16c}$$

since, of course, $(k_{rs})^2 > 0$ and

$$(x - h_r) R(G - v_r, y_j(G - v_r)) = 0 \tag{17}$$

In order to complete the proof note that for sufficiently large x , $R(G, x)$ must be positive and therefore from the inequalities (16) we conclude that in the interval $(-\infty, +\infty)$, $R(G, x)$ changes sign n times and consequently $R(G, x)$ has n real zeros.

From the inequalities (16) we also see that the zeros of $R(G - v_r)$ must lie between the zeros of $R(G)$ and thus (12) follows. Hence the Theorem is true for graphs with n vertices. Q. E. D.

With respect to the above proof it is worth noting that its essential step was the determination of the inequalities (16). It is a rather fortunate and under no conditions obvious fact that the value of the polynomial $R(G, x)$ for $x = y_j(G - v_r)$, $j = 1, 2, \dots, n - 1$ is independent of the parameter h_r . Therefore also the inequalities (16) hold for all values of h_r which significantly simplified our task.

As a consequence of our Theorem, the reference energy and the topological resonance energy are now proved to have real values for any parametrization of the HMO Hamiltonian.

Note added in proof. — Bojan Hohar (Ljubljana) recently obtained a result which is equivalent to the present Theorem¹⁶.

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SAŽETAK

O topološkoj rezonancijskoj energiji heterokonjugiranih molekula

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Pokazano je da referentni polinom jednog heterokonjugiranog π -elektronskog sustava s proizvoljnim Coulombovskim i rezonancijskim integralima ima realne nule. Izložena su i neka druga svojstva referentnog polinoma.

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