Graph Theory and Molecular Orbitals. XVIII. On Topological Resonance Energy*

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Mathematical relations necessary for the calculation of the previously introduced[15] topological resonance energy, *TRE*, are derived. *TRE*, as defined in ref. 15, was rather inconvenient for numerical calculations. In the present work these computing difficulties are overcome.

Acyclic characteristic polynomial P^{ac} and acyclic spectrum of a graph are defined and their close relationship to *TRE* is demonstrated. Hence, the evaluation of P^{ac} is the crucial step in the computation of *TRE*'s. A graphical procedure is described and exemplified for the determination of P^{ac}'s both for simple graphs and for graphs with loops and weighted edges.

INTRODUCTION

Resonance energy, *RE*, is defined as

$$RE = E(\text{molecule}) - E\left(\begin{smallmatrix}\text{reference}\\\text{structure}\end{smallmatrix}\right) \tag{1}$$

where E(molecule) is the total (or total π-electron) energy of a conjugated system, whereas $E\left(\begin{smallmatrix}\text{reference}\\\text{structure}\end{smallmatrix}\right)$ is the analogous quantity for a hypothetical reference structure. Depending on the choice of this reference structure, different *RE*'s have been defined[1-8]. An especially successful concept has proved to be the so called[9] Dewar resonance energy, *DRE*, which is based on an »acyclic polyene-like« reference structure[1,3,4,10].

In DRE the energy of the reference structure is introduced in the following manner. The total energy of certain classes of acyclic systems can be given in a simple additive form[10]

$$E\left(\begin{smallmatrix}\text{acyclic}\\\text{polyene}\end{smallmatrix}\right) = \sum_j n_j E_j \tag{2}$$

where n_j is the number of bonds of a given type contained in the considered molecule and E_j is the corresponding bond energy parameter. Note that eq. (2) holds approximately and the E_j's are determined by a least-squares fitting of this relation to the values of a selected set of acyclic systems and bond types.

The basic idea of DRE is that both aromatic stabilization and antiaromatic destabilization have their origin in the presence of cycles in the molecular

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π-network. Therefore, the aim of the method is to find a reference structure which would contain all, and only, acyclic contributions to E(molecule). Eq. (2) indicates the choice

$$E \left({\text{reference} \atop \text{structure}}\right) = \sum_j n_j E_j \tag{3}$$

In fact, the DRE method is defined by eq. (3). The excellent agreement between DRE's and the experimental findings is well established[1,3,4,9,10] nowadays. It is also worth noting that DRE's calculated within the HMO approximation are not less accurate than the same quantities obtained by other, more sophisticated SCF MO techniques[3,4,11–14].

However, the DRE method is not quite free from conceptual difficulties. Thus,

(a) it contains a large number of fitting parameters (E_j's) which indicate that the method is to some extent arbitrary;

(b) it is not *a priori* certain that eq. (3) contains *all* acyclic and *no* cyclic contributions to E(molecule);

(c) the numbers n_j can be evaluated only for systems possessing a Kekulé structure**, and therefore charged species, radicals *etc.* are outside the scope of the DRE method.

In a previous work[15] topological resonance energy, *TRE*, a novel variant of the DRE has been proposed, which does not suffer from the above listed difficulties. In particular,

(a) TRE requires no fitting parameters;

(b) it is mathematically defined in such a manner that the energy of the TRE reference structure contains exactly *all* acyclic and exactly *no* cyclic contributions to E(molecule);

(c) its applicability is not stipulated by the existence of Kekulé structures.

The starting point in introducing the concept of TRE was a Coulson-type integral formula for the total π-electron energy[16–18], E_π,

$$E_\pi = (1/2\,\pi) \int\limits_{-\infty}^{+\infty} \frac{dx}{x^2} \, \log \, \{[\sum_{s \in S_e} (-1)^{n\,(s)/2\,+\,c\,(s)} \cdot$$

$$\cdot \, 2^{r\,(s)} \, x^{n\,(s)}]^2 + [\sum_{s \in S_o} (-1)^{(n\,(s)\,+\,1)/2\,+\,c\,(s)} \, 2^{r\,(s)} \, x^{n\,(s)}]^2\} \tag{4}$$

where S_e and S_o are the sets of all Sachs graphs[19] of the molecular graphs with even and odd number of vertices, respectively. The summations in (4) go over all elements of the sets S_e and S_o, and $n(s)$, $c(s)$ and $r(s)$ are the number of vertices, components and cyclic components, respectively, of the Sachs graph s. Let in addition $S = S_e \cup S_o$ be the set of all Sachs graphs of the molecular graph. Further details on Sachs graphs are given elsewhere[19,20].

Eq. (4) indicates that every Sachs graph gives a certain contribution to the value of E_π. Then, obviously, the contributions of Sachs graphs with $r(s) = 0$ will represent the acyclic part of the total π-electron energy. Consequently, one can define the »acyclic polyene-like« reference structure as

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** More precisely, n_j's are unique only in systems with exactly one Kekulé structure.

$$E_\pi \genfrac{}{}{0pt}{}{\text{(reference)}}{\text{structure}} = (1/2\,\pi) \int\limits_{-\infty}^{+\infty} \frac{dx}{x^2}\,\log\,\{\,[\ \sum_{s\in S_e^{ac}} (-1)^{n\,(s)/2\,+\,c\,(s)}\cdot$$

$$\cdot\,x^{n\,(s)}]^2 + [\ \sum_{s\in S_o^{ac}} (-1)^{(n\,(s)\,+\,1)/2\,+\,c\,(s)}\ x^{n\,(s)}]^2\} \tag{5}$$

where S_e^{ac} (S_o^{ac}) is the set of all Sachs graphs of the molecular graph with even (odd) number of vertices and with $r(s) = 0$. Let further $S_{ac} = S_e^{ac} \cup S_o^{ac}$.

For graphs representing conjugated hydrocarbons, $S_o^{ac} = \phi$, and eq. (5) becomes

$$E_\pi \genfrac{}{}{0pt}{}{\text{(reference)}}{\text{structure}} = (1/\pi \int\limits_{-\infty}^{+\infty} \frac{dx}{x^2}\,\log\,\{\,[\ \sum_{s\in S^{ac}} (-1)^{n\,(s)/2\,+\,c\,(s)}\cdot x^{n\,(s)}] \tag{6}$$

Eqs. (5) and (6) are the mathematical definitions of TRE[15]. Although these formulae give a proper insight into the topological origin of aromaticity (TRE or $DRE > 0$) and antiaromaticity (TRE or $DRE < 0$), they are rather impractical for performing actual numerical calculations. In the present work a graph theoretical technique that enables simple evaluation of TRE's in the general case will be presented.

THE ACYCLIC CHARACTERISTIC POLYNOMIAL AND THE ACYCLIC SPECTRUM OF A GRAPH

The argument used in the definition of the TRE reference structure (eqs. (5) and (6) can be generalized in a simple and straightforward manner. Let F be any quantity which can be calculated from a given set σ of Sachs graphs. Symbolically,

$$F = f\,(s\,|\,s \in \sigma) \tag{7a}$$

Now the »acyclic F« is, by definition

$$F^{ac} = f\,(s\,|\,s \in \sigma,\ r\,(s) = 0) \tag{7b}$$

or in another notation

$$F^{ac} = f\,(s\,|\,s \in \sigma^{ac}) \tag{7c}$$

where σ^{ac} is the set of all Sachs graphs s from σ with the property $r(s) = 0$.

In the following we will be interested in the »acyclic characteristic polynomial«, $P^{ac}\,(G, x)$, and the »acyclic spectrum« of the graph G. Let the characteristic polynomial $P\,(G, x) = P\,(G)$ of the graph G be of the form

$$P\,(G) = \sum_{n=0}^{N} a_n\,x^{N-n}$$

where N is the number of vertices of G. Since $P\,(G)$ fulfills the relation[19-21]

$$P\,(G) = \sum_{s\in S} (-1)^{c\,(s)}\ 2^{r\,(s)}\ x^{N\,-\,n\,(s)}$$

according to eqs. (7),

$$P^{ac}\,(G, x) = \sum_{s\in S^{ac}} (-1)^{c\,(s)}\ x^{N\,-\,n\,(s)} \tag{8}$$

which will be presented also in the form

$$Pac\ (G) = \sum_{n=0}^{N} a_n^{ac}\ x^{N-n} \qquad (9)$$

Let the roots of $P(G)$ be $x_1, x_2, \ldots, x_N$ ($x_i \geqslant x_j$ if $i < j$), and these numbers comprise the spectrum of the graph G. Then the roots of $P^{ac}(G, x)$, x_1^{ac}, $x_2^{ac}, \ldots, x_N^{ac}$ ($x_i^{ac} \geqslant x_j^{ac}$ if $i < j$) will form the »acyclic spectrum« of the graph G. The chemical meaning of the above introduced notions is evident from the following statement.

Proposition 1

If the total π-electron energy fulfills the relation

$$E_\pi = \sum_{j=1}^{N} |x_j| \qquad (10)$$

the reference structure energy of eq. (5) is

$$E_\pi \left(\begin{smallmatrix} \text{reference} \\ \text{structure} \end{smallmatrix}\right) = \sum_{j=1}^{N} |x_j^{ac}| \qquad (11)$$

The proof of this proposition is simple. Namely, the Coulson formula (4) is just an integral representation for the sum of the absolute values of the roots of a polynomial[16-18]. Eq. (4) describes such a sum for $P(G, x)$, while eq. (5) is the analogous expression for $P^{ac}(G, x)$.

In the general case, instead of (10),

$$E_\pi = \sum_{j=1}^{N} g_j x_j$$

where g_j is the occupancy number of the j'th MO. In agreement with the above discussion, eq. (11) can also be generalized as

$$E_\pi \left(\begin{smallmatrix} \text{reference} \\ \text{structure} \end{smallmatrix}\right) = \sum_{j=1}^{N} g_j x_j^{ac}$$

which finally yields

$$TRE = \sum_{j=1}^{N} g_j (x_j - x_j^{ac}) \qquad (12)$$

If G is an acyclic graph,

$$a_n^{ac} \equiv a_n \qquad (13a)$$

$$P^{ac}\ (G, x) \equiv P\ (G, x) \qquad (13b)$$

$$x_j^{ac} \equiv x_j \qquad (13c)$$

and consequently,

$$TRE \left(\begin{smallmatrix} \text{acyclic} \\ \text{polyene} \end{smallmatrix}\right) \equiv 0$$

THE ACYCLIC CHARACTERISTIC POLYNOMIALS FOR MOLECULAR GRAPHS
OF CONJUGATED HYDROCARBONS

Conjugated hydrocarbons are presented by graphs without loops and weighted edges[19,20]. Therefore Sachs graphs from S^{ac} are composed entirely from complete graphs of degree one***. Proposition 2 follows now from eqs. (8) and (9).

Proposition 2

$$a_n^{ac} = \begin{cases} (-1)^{n/2} \, b_{n/2} & \text{for } n = \text{even} \\ 0 & \text{for } n = \text{odd} \end{cases}$$

where $b_j = b_j(G)$ is the number of different choices of j nonincident edges from the graph G. ($b_0 = 1$ by definition.) It seems worth mentioning that for acyclic graphs (cf. eq. (13a)) this proposition has been independently discovered by various researchers[21-24].

Let e be an arbitrary edge of the graph G and $G-e$ denote the graph obtained by deletion of this edge from G. Let further $G-(e)$ denote the graph obtained by deletion of the edge e and its two incident vertices from G. The numbers b_j have the following important property.

Proposition 3

$$b_j(G) = b_j(G-e) + b_{j-1}(G-(e))$$

Proof. — Among the $b_j(G)$ choices of j nonincident edges from G, there are $b_j(G-e)$ such choices which do not contain the edge e and $b_{j-1}(G-(e))$ choices which contain the edge e.

Propositions 2 and 3 give together with eq. (9) the following corrolary.

Proposition 4

$$P^{ac}(G, x) = P^{ac}(G-e, x) - P^{ac}(G-(e), x) \tag{14}$$

This equation has been proved for acyclic graphs (cf. eq. (13b)) many years ago by Heilbronner[25] and was recently independently derived[24]. Hosoya has obtained the Proposition 4 in a different, but equivalent form[22].

Proposition 4 presents a very simple graphical procedure for evaluating the P^{ac}'s for polycyclic graphs. In fact, eq. (14) enables one to relate P^{ac} of a polycyclic graph with the acyclic characteristic polynomials of acyclic graphs. For these latter graphs, on the other hand, eq. (13b) is applicable. As an example let us calculate the P^{ac} of biphenylene. L_n will denote the characteristic polynomial of the chain with n vertices.

*** These graphs contain two vertices joined by an edge.

Now

$$P^{ac}\left(\text{[structure]}\right) = P^{ac}\left(\text{[structure]}\right) - P^{ac}\left(\text{[structure]}\right)$$

$$= L_{12} - L_{10}$$

$$P^{ac}\left(\text{[structure]}\right) = L_4 L_6$$

$$P^{ac}\left(\text{[structure]}\right) = L_4 P^{ac}\left(\text{[structure]}\right) = L_4(L_6 - L_4)$$

Finally,

$$P^{ac}\left(\text{[structure]}\right) = L_{12} - L_{10} - 2L_4 L_6 + (L_4)^2$$

$$= x^{12} - 14x^{10} + 71x^8 - 162x^6 + 164x^4 - 60x^2 + 5$$

The roots of this polynomial can be obtained by standard computer routines. Note that the polynomials L_n can be easily evaluated using the well known[25] recurrence relation

$$L_n = x L_{n-1} - L_{n-2}$$

$$L_0 = 1, \; L_1 = x$$

As another example we consider the P^{ac} of an N-membered cycle, C_N, which is, of course, the graph representation of annulenes. Since for an arbitrary edge e, $C_N - e$ and $C_N - (e)$ are identical with chains of N and $N-2$ vertices, respectively,

$$Pac \; (C_N) = L_N - L_{N-2} \tag{15}$$

It is known[24] that

$$L_n = \frac{\sin (n+1) t}{\sin t}$$

for $x = 2 \cos t$. Therefore from (15),
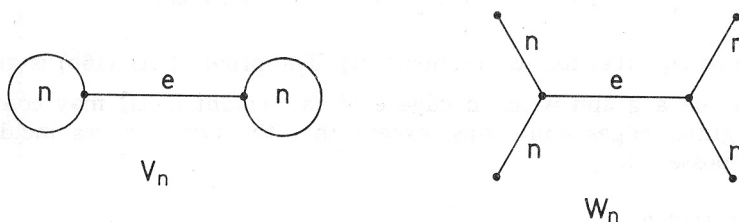
$$Pac \; (C_N) = 2 \cos Nt$$

The acyclic spectrum of C_N is now simply obtained from $Nt = \pi/2 + j\pi$:

$$x_j^{ac} = 2 \cos \frac{(2j-1)\pi}{2N}, \qquad j = 1, 2, \ldots, N$$

and for neutral annulenes

$$E_\pi \left(\begin{array}{c} \text{reference} \\ \text{structure} \end{array} \right) = \begin{cases} 2 \, \text{cosec} \, (\pi/2\,N) & \text{if } N = \text{even} \\ 2 \, \text{cotg} \, (\pi/2\,N) & \text{if } N = \text{odd} \end{cases}$$

As the third example, we consider the bicyclic system V_n, containing two n-membered cycles joined by an edge e.

Now,

$$P^{ac} \, (V_n) = [P^{ac} \, (C_n)]^2 - (L_{n-1})^2 = (L_n - L_{n-2})^2 - (L_{n-1})^2$$

On the other hand, the characteristic polynomial of the graph W_n (with $4n-2$ vertices)* is according to eq. (14)

$$P \, (W_n) = (L_{2n-1})^2 - (L_{n-1})^4 = (L_{n-1})^2 \, [(L_n - L_{n-2})^2 - (L_{n-1})^2]$$

and hence one obtains an amusing relation

$$TRE \, (V_n) = E_\pi \, (V_n) - E_\pi \, (W_n) + 2 \, E_\pi \, (L_{n-1})$$

Using eq. (14), P^{ac}'s for a large number of molecular topologies have been calculated, together with the corresponding acyclic spectra and TRE values. These will be reported elsewhere[26].

THE ACYCLIC CHARACTERISTIC POLYNOMIALS FOR GRAPHS OF HETEROCONJUGATED MOLECULES

In the graph theoretical representation of conjugated molecules, a hetero-atom is presented by a loop of the weight h attached to the vertex corresponding to the heteroatom[27,28]. The edges incident on such a vertex have the weight k. Therefore, Propositions 2—4 are no more valid and P^{ac} cannot be calculated by a simple recipe described in the previous section. Fortunately, the following two relations enable one to express the P^{ac}'s of weighted graphs with loops in terms of graphs without loops and weighted edges.

Let us consider a graph G_h with a loop of weight h attached to the vertex v. G_h may contain also other loops or weighted edges. Let G and $G-v$ be obtained from G_h by deleting the loop at the vertex v and by deleting the vertex v, respectively.

Proposition 5

$$P \, (G_h, x) = P \, (G, x) - h \, P \, (G - v, x) \qquad (16a)$$

$$P^{ac} \, (G_h, x) = P^{ac} \, (G, x) - h \, P^{ac} \, (G - v, x)$$

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* This graph is obtained by joining the central vertices of two chains with $2n-1$ vertices.

Proof. — Let S be the set of all Sachs graphs of the graph G_h. The Sachs graphs from S either contain the loop h or not. Let the former comprise a subset S_h, while the latter a subset S_-. Of course, $S_h \cup S_- = S$. On the other hand,

$$\sum_{s \in S_h} (-1)^{c(s)} \, 2^{r(s)} \, x^{N-n(s)} = -h \, P(G-v, x)$$

$$\sum_{s \in S_-} (-1)^{c(s)} \, 2^{r(s)} \, x^{N-n(s)} = P(G, x)$$

out of which eq. (16a) follows immediately. The proof of eq. (16b) is analogous.

Let G_k be a graph with an edge e of the weight k. G_k may contain also other weighted edges and loops, except that the two vertices incident to e must not possess loops.
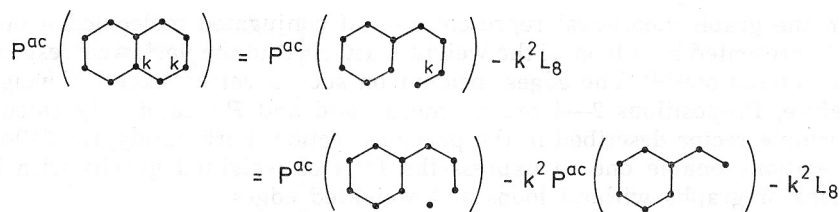
Proposition 6

$$P^{ac}(G_k, x) = P^{ac}(G - e, x) - k^2 P^{ac}(G - (e), x)$$

Proof — is analogous to that of Proposition 3.

Propositions 5 and 6 present a relatively simple procedure for the calculation of P^{ac}'s for graphs representing heteroconjugated systems. The graph of a quinoline-like molecule may serve as an illustration. Application of Proposition 5 gives
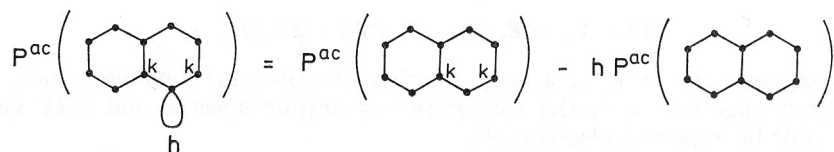
while from Proposition 6,

Hence, the problem is reduced to obtaining of P^{ac}'s of simple graphs. Finally,

$$= L_1 L_9 - L_1 L_3 L_4 - k^2 (2 L_8 - L_2 L_4) - h(L_9 - L_3 L_4)$$
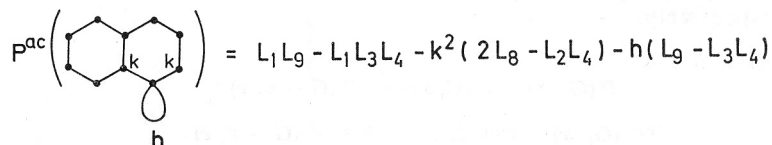
Numerical work on the TRE's of heterocyclic compounds will be reported elsewhere[26].

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SAŽETAK

Teorija grafova i molekularne orbitale. XVIII. O topološkoj rezonancijskoj energiji

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Pokazano je kako se topološka rezonancijska energija, *TRE,* može praktički izračunati. Definiran je aciklički karakteristični polinom, P^{ac}, i aciklički spektar grafa, a također je diskutirana i njihova bliska veza s *TRE.* Prikazana je grafička metoda, koja omogućuje na vrlo jednostavan i elegantan način određivanje P^{ac} i za jednostavne i za složene molekularne grafove.

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