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On a resonance energy model based on expansion in terms of acyclic moments: Exact results

Darko Babic[1], **Ante Graovac**[1], **and Ivan Gutman**[2]

[1] The "Rugjer Bošković" Institute, YU-41001 Zagreb, POB 1016, Yugoslavia
[2] Faculty of Science, University of Kragujevac, POB 60, YU-34000 Kragujevac, Yugoslavia

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Summary. The new concept of the resonance energy in conjugated hydrocarbons introduced by Jiang Y, Zhang H (1989) Theor Chim Acta 75:279 is further developed. This model is based on expansion of the π-electron energy in terms of moments which are also equal to numbers of closed walks in a molecular graph. The reference system is established by counting only acyclic walks, i.e. those tracing only on acyclic subgraphs. Because acyclic walks could be counted only up to some finite length, the energy of the reference system has been evaluated by truncating higher terms in the expansion. In this paper a finite expression for the energy of the same reference system is derived, thus allowing its exact evaluation. The exact values differ significantly from the truncated ones. This difference, as well as the discrepancy between exact results and chemical experience, are discussed.

Key words: Hückel theory – Resonance energy – Acyclic walks – Moments

1. Introduction

Recently a novel approach to evaluating the resonance energy in conjugated systems has been proposed [1, 2]. Generally, the resonance energy (RE) is defined as the difference between the total π-electron energy and the energy of some reference system. RE reflects the effect of cyclic conjugation in a system. In the reference system the influence of cycles has to be suppressed, which can be achieved in a variety of ways.

The use of moments is a convenient means of relating the energy of a molecule to its structural details, e.g., cycles. In a graph-theoretical picture, the j-th moment equals the number of closed walks of the length j. The Topological Resonance Energy (TRE) model [3, 4] can also be expressed in terms of moments which correspond to tree-like walks [5, 6]. In the recently introduced TRE* model [1, 2], the moments of the reference system are obtained by counting only acyclic walks [5], i.e. those walks in the molecular graph whose projections are only acyclic graphs[1]. Because of practical reasons acyclic walks are counted only up to some finite length thus allowing only approximate TRE* values [1, 2]. In the present paper a method for calculating the exact TRE* values is presented. It by-passes the counting of acyclic walks and expresses TRE* in terms of the energies of the molecular graph and its certain subgraphs. The exact values differ from the approximate ones significantly. Moreover, the exact results are in contradiction with the chemical experience.

2. Method

The Hückel π-electron energy for the ground state of an alternant hydrocarbon, E_π, can be written as [7]

$$E_\pi = \sum_{i=1}^{N} |x_i| \tag{1}$$

where x_i are the eigenvalues of the adjacency matrix of a graph representing a given hydrocarbon with N conjugated centers. The function $|x_i|$ is approximated by means of an even polynomial of degree $2L$, viz.

$$|x|_L = \sum_{i=0}^{L} a_i(L)x^{2i}. \tag{2}$$

The coefficients a_i in Eq. (2) are determined by least-squares fitting in an appropriately chosen interval $(-\lambda, +\lambda)$; in [1] the value $\lambda = 3$ was employed. Note that the actual numerical values of the coefficients a_i depend on the parameter L. Substitution of Eq. (2) into Eq. (1) yields

$$(E_\pi)_L = \sum_{i=0}^{L} a_i(L)u_{2i} \tag{3}$$

where u_{2i} denotes the $2i$-th moment

$$u_{2i} = \sum_{j=1}^{N} x_j^{2i}. \tag{4}$$

It is well known [7] that moments reflect the molecular connectivity, i.e. that the j-th moment equals the number of closed walks of the length j. On this basis the expansion in Eq. (3) can be transformed into another form which uses the occurrence numbers of individual molecular fragments instead of moments [1, 2]. In these papers a new way to evaluate RE has been proposed: by excluding all cyclic fragments from the expansion, and taking the resulting value as the energy of the reference system. Here we consider the equivalent expansion in terms of acyclic moments, as has been presented in [5].

The closed walks could be partitioned into either acyclic or cyclic walks according whether the projection of the walk is an acyclic or a cyclic graph,

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[1] The names for the tree-like and acyclic walks are chosen rather inappropriately. The tree-like walks [5] never close the cycle in their "walking", and the projections of the acyclic walks [6] are trees. Reversing the names would be more appropriate, but in the present paper we follow the accepted terminology

respectively. Therefore, the moments and E_π could be partitioned as well

$$u_i = u_i' + u_i'' \tag{5}$$

$$(E_\pi)_L = (E_\pi)_L^{\text{acyclic}} + (E_\pi)_L^{\text{cyclic}} \tag{6}$$

where

$$(E_\pi)_L^{\text{acyclic}} = \sum_{i=0}^{L} a_i(L) u_{2i}' \tag{7a}$$

$$(E_\pi)_L^{\text{cyclic}} = \sum_{i=0}^{L} a_i(L) u_{2i}'' \tag{7b}$$

and u_i' and u_i'' stand for the number of the acyclic and cyclic walks of the length i, respectively.

The above partitioning enables one to define a possible measure of the resonance energy [1, 2, 5]

$$\text{TRE}^* = E_\pi - (E_\pi)^{\text{acyclic}} \tag{8}$$

where the energy of the reference system, $(E_\pi)^{\text{acyclic}}$, is the limiting value of $(E_\pi)_L^{\text{acyclic}}$ for $L \to \infty$. Up to now TRE* has been evaluated only approximately as

$$(\text{TRE}^*)_L = E_\pi - (E_\pi)_L^{\text{acyclic}} \tag{9}$$

mostly up to $L = 6$ [1, 2]. The TRE* values thus obtained resemble the results of the TRE model.

A question has been raised as to whether TRE* could be evaluated exactly [5]. In the following text we describe the method which overrides the infinite summation involved in the definition of TRE*, Eq. (8), and enables one to calculate it in a completely different and exact manner.

Let us begin with some definitions. A graph G is defined as an ordered pair $G = (V, E)$; $V = V(G)$ and $E = E(G)$ are the sets of its vertices and edges, respectively. A subgraph of G is a graph whose vertices and edges belong to subsets of $V(G)$ and $E(G)$, respectively. A subtree of G is a subgraph which is a tree. If a subtree of G contains all vertices of G, then it is called a spanning tree of G, and denoted by T. The intersection graph $H = G_1 \cap G_2 \cap \cdots \cap G_m$ is defined by $V(H) = V(G_1) \cap V(G_2) \cap \cdots \cap V(G_m)$ and $E(H) = E(G_1) \cap E(G_2) \cap \cdots \cap E(G_m)$. In this paper we deal with labeled graphs only; their subgraphs are also appropriately labeled.

Any $(j+1)$-tuple $w = (i_0, i_1, \ldots, i_j)$ of vertices of G such that i_{k-1} and i_k are adjacent, $k = 1, 2, \ldots, j$, is called a walk of length j. Note that a walk may also be viewed as the j-tuple of edges $i_{k-1} - i_k$. A walk in which the first and the last vertex coincide is called a closed walk. We emphasize that the definition of a walk allows backtracking. For each walk w of G, its projection $\bar{w}$ is defined as the subgraph of G having all vertices and edges contained in w, and only those vertices and edges. By $W(G)$ we denote the set of all closed walks which can be generated on a graph G, and by $W^{ac}(G)$ its subset of acyclic walks. $W(T_1, T_2, \ldots, T_n)$ stands for the union of sets $W(T_1), W(T_2), \ldots, W(T_n)$, n = number of spanning trees of G. Thus $W(T_1, T_2, \ldots, T_n)$ is the set of closed walks of all spanning trees.

Examples depicted in Fig. 1 illustrate various types of closed walks; w_1 and w_2 are cyclic walks, while w_3 is an acyclic walk. Note that w_2 does not close any

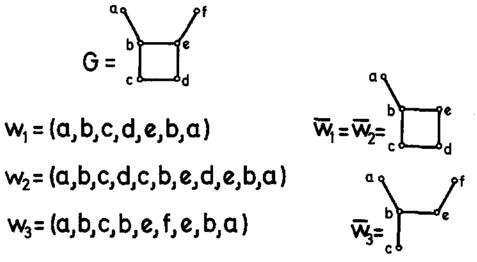


Fig. 1. Examples of closed walks and their projections illustrating the difference between cyclic and acyclic walks

cycle during its "walking", but is classified as cyclic because the criterion is based on the presence (or absence) of cycles in its projection, $\bar{w}$.

In deriving our method for the exact evaluation of TRE*, we recognize that the set of acyclic walks of G is equal to the set of closed walks of its spanning trees.

First, let us show that each acyclic walk of G is contained in the set of all closed walks of some spanning tree T of G. We regard as obvious that $W(T)$ contains w if the projection $\bar{w}$ is the subgraph of T. Since the projection of the acyclic walk is a subtree (by definition), it is sufficient to show that each subtree of G is a subgraph of some spanning tree of G. Let us construct a spanning tree of a connected graph G in the following way. We start from the graph which consists of all vertices of G and only those edges which are present in a given subtree. This means that all vertices which are not in the subtree are isolated. We gradually connect the isolated vertices with the subtree by adding edges from $E(G)$ using exactly one edge per isolated vertex. First we join the subtree with the vertices which are its neighbors in G, then the augmented subtree with its neighbors, and so on. Ultimately, this growth procedure yields a fully connected graph (since otherwise G would not be connected). This graph contains no cycles because the starting graph was acyclic and each new edge has been inserted only between the (growing) subtree and an isolated vertex. Therefore the resulting graph is the spanning tree of G, and it is clear that it can be obtained starting from any subtree of G. This proves the statement that each subtree of G is a subgraph of some spanning tree of G, and consequently that closed walks of spanning trees contain all acyclic walks of G:

$$W^{ac}(G) \subseteq W(T_1, T_2, \ldots, T_n). \tag{10}$$

On the other hand, each closed walk of a spanning tree is equal to some acyclic walk of G. It follows from these facts that (1) the spanning tree is a subgraph of G, and (2) the projection of each closed walk of this spanning tree is a tree. This means that

$$W(T_1, T_2, \ldots, T_n) \subseteq W^{ac}(G). \tag{11}$$

From relations (10) and (11) follows that

$$W^{ac}(G) = W(T_1, T_2, \ldots, T_n). \tag{12}$$

Whence the problem of enumerating the acyclic walks of G is equal to the problem of enumerating the closed walks of all spanning trees of G. This latter task is much easier to solve.

To count the cardinality of $W(T_1, T_2, \ldots, T_n)$ one has to take into account partial overlapping of the sets $W(T_1)$, $W(T_2), \ldots, W(T_n)$. In other words, the same closed walks may be generated on more than one spanning tree. To resolve this problem we prove the following equation:

$$W(T_i) \cap W(T_j) = W(T_i \cap T_j). \tag{13}$$

The intersection graph $T_i \cap T_j$ is the subgraph of both T_i and T_j, therefore all walks of $T_i \cap T_j$ are also the walks of T_i and T_j. Further, equal walks of T_i and T_j have equal projections which must be the subgraph of $T_i \cap T_j$ according to the definition of the intersection of graphs. Hence, all walks which are present in both T_i and T_j are also the walks of their intersection graph. This proves Eq. (13).

The well known inclusion-exclusion principle [8] reads as follows:

$$\begin{aligned}|W(T_1) \cup W(T_2) \cup \cdots \cup W(T_n)| &= \sum_i |W(T_i)| - \sum_{i<j} |W(T_i) \cap W(T_j)| \\ &\quad + \sum_{i<j<k} |W(T_i) \cap W(T_j) \cap W(T_k)| \cdots \\ &\quad - (-1)^n |W(T_1) \cap W(T_2) \cap \cdots \cap W(T_n)|. \end{aligned} \tag{14}$$

We have shown that the left hand side of the above equation equals $|W^{ac}(G)|$. The application of Eq. (13) to its right hand side gives

$$\begin{aligned}|W^{ac}(G)| &= \sum_i |W(T_i)| - \sum_{i<j} |W(T_i \cap T_j)| + \sum_{i<j<k} |W(T_i \cap T_j \cap T_k)| - \cdots \\ &\quad - (-1)^n |W(T_1 \cap T_2 \cap \cdots \cap T_n)|. \end{aligned} \tag{15}$$

The last equation holds for any subset with walks of a given length l, so that we may immediately write

$$\begin{aligned}u_l' &= \sum_i u_l(T_i) - \sum_{i<j} u_l(T_i \cap T_j) + \sum_{i<j<k} u_l(T_i \cap T_j \cap T_k) - \cdots \\ &\quad - (-1)^n u_l(T_1 \cap T_2 \cap \cdots \cap T_n). \end{aligned} \tag{16}$$

By substitution into Eq. (7a), and after some rearrangement, we obtain

$$\begin{aligned}(E_\pi)_L^{\text{acyclic}} &= \sum_i \sum_{l=0}^{L} a_{2l}(L) u_{2l}(T_i) - \sum_{i<j} \sum_{l=0}^{L} a_{2l}(L) u_{2l}(T_i \cap T_j) \\ &\quad + \sum_{i<j<k} \sum_{l=0}^{L} a_{2l}(L) u_{2l}(T_i \cap T_j \cap T_k) - \cdots \\ &\quad - (-1)^n \sum_{l=0}^{L} a_{2l}(L) u_{2l}(T_1 \cap T_2 \cap \cdots \cap T_n). \end{aligned} \tag{17}$$

According to the starting assumption about the relation between E_π and the graph moments, we finally arrive at the desired expression:

$$\begin{aligned}(E_\pi)^{\text{acyclic}} &= \sum_{i=1}^{n} E_\pi(T_i) - \sum_{\substack{i,j=1 \\ (i<j)}}^{n} E_\pi(T_i \cap T_j) + \sum_{\substack{i,j,k=1 \\ (i<j<k)}}^{n} E_\pi(T_i \cap T_j \cap T_k) - \cdots \\ &\quad - (-1)^n E_\pi(T_1 \cap T_2 \cap \cdots \cap T_n). \end{aligned} \tag{18}$$

Each term on the right hand side represents the E_π of a certain acyclic subgraph of G. If this subgraph consists of more components, its energy is equal to the sum of energies of the components.

3. Results

Although applying Eq. (18) to the calculation of E_π^{acyclic} seems to be straightforward, this is not the case. This is because the number of subgraphs which have to be generated and whose spectra are to be evaluated is equal to 2^n. This is a forbiddingly large number even for molecules of moderate size. For instance, naphthalene has 35 spanning trees implying that over 3.4×10^{10} subgraphs have to be taken into account.

Fortunately, it is possible to reduce this number substantially by exploiting the fact that the same component may appear in intersections with opposite signs. As a consequence, numerous terms in Eq. (18) will cancel out making the calculation of E_π^{acyclic} a feasible task. This is illustrated by the example given in Fig. 2. A comprehensive analysis reveals a formula which enables us to predict

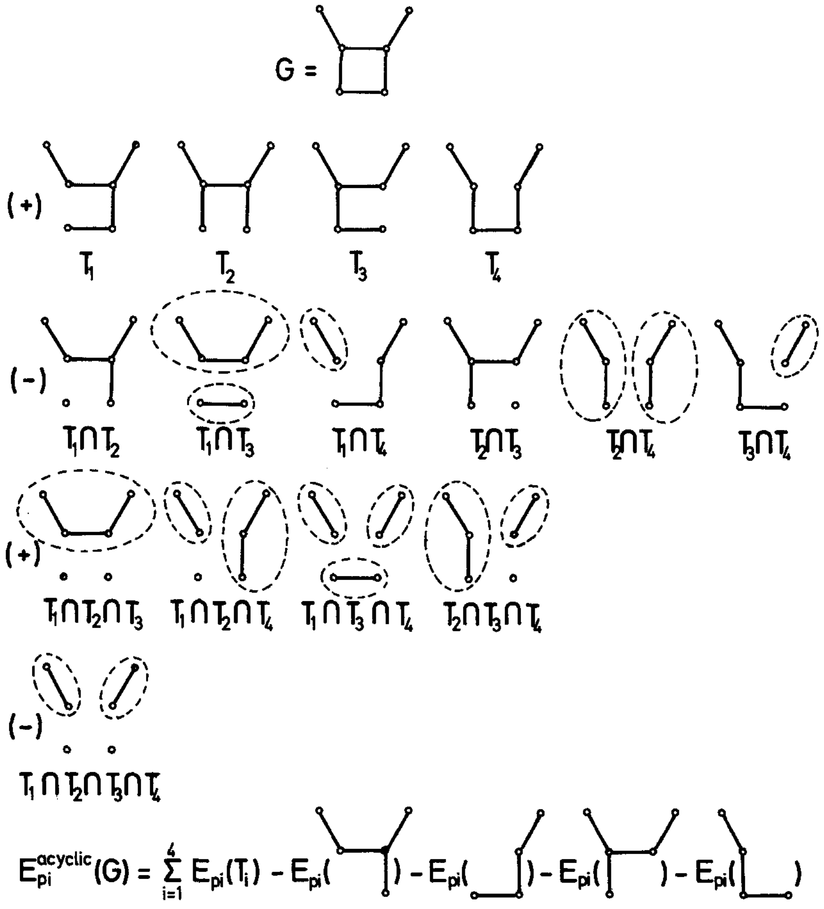
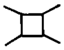
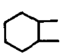
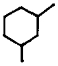
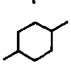
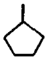
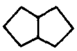
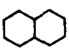
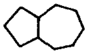


Fig. 2. Acyclic subgraphs for the example graph G being included in the evaluation of the energy of the reference system. The sign at the beginning of each row stands for the sign with which E_π of the subgraphs depicted in the row enter into the summation of Eq. (18). The components whose contributions cancel out are encircled. The final expression for $E_\pi^{\mathrm{acyclic}}(G)$ contains only terms which remained after cancellation

Table 1. Resonance energies per electron of some conjugated molecules calculated by exact and approximative formulas for TRE*, and by TRE model

Molecule	TREPE*	$(\text{TREPE*})_{L=6}$[a]	TREPE[b]
	−0.030	−0.046	−0.027
	−0.009	0.006	0.009
	−0.190	0.069	0.046
	0.006	0.017	0.007
	0.009	−0.027	0.012
	0.006	0.018	−0.031
	0.022	0.016	0.003
	−0.374	−0.019	−0.027
	−0.403	0.042	0.039
	−0.298	0.013	0.015

[a] Ref. 1
[b] Ref. 6

which molecular fragments will survive in Eq. (18), and to determine coefficients which multiply their E_π contributions. Thus, instead of using Eq. (18), one generates molecular fragments and multiplies their E_π by an appropriate coefficient. Due to the lengthy proof of the method, its details will be communicated in a separate publication.

By means of this shortcut we were able to calculate the TRE* values of the molecules listed in Table 1. For annulenes the method renders an especially simple formula:

$$E_\pi^{\text{acyclic}}(C_N) = N[E_\pi(P_N) - E_\pi(P_{N-1})]$$

where C_N and P_N denote the circuit and the path, respectively, with N vertices. The topological resonance energies per π-electron in the TRE* model, TREPE*, for C_N, $N = 3$–18 are depicted graphically in Fig. 3.

We first call attention to the differences between the exact and approximate values of TREPE* listed in Table 1. One is forced to conclude that for $L = 6$ the approximate values reproduce the exact ones poorly. In fact, $(\text{TREPE*})_{L=6}$ shows better agreement with the TREPE values than with the exact ones. This seems to be a consequence of the fact that the moments corresponding to acyclic and tree-like walks start to differ when the walk length equals either the size of the smallest even membered cycle, or the double size of the smallest odd

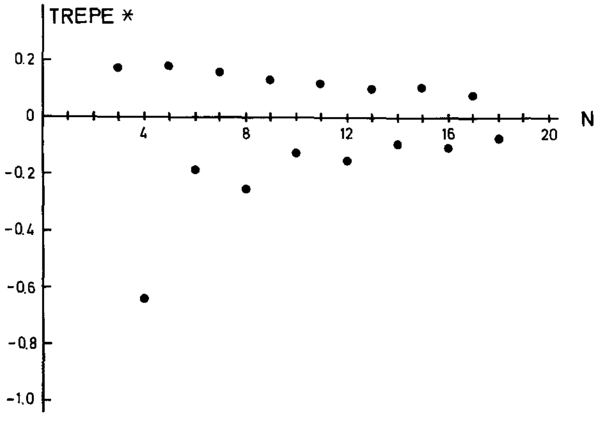


Fig. 3. TREPE* values for annulenes plotted against the ring size N

membered cycle, whichever is less. The difference is small for lower moments and increases for higher moments, but this is compensated by a simultaneous decrease [1] of their weights, $a_{2i}(L)$ in Eq. (7a).

One might expect that by letting L go to infinity a valuable estimation of RE could be achieved; note that the positive values of RE correspond to stabilization, while the negative ones indicate the destabilizing effect of cyclic conjugation. From Table 1 one immediately sees that benzene, naphthalene and azulene, which are known for their stability and aromatic character, have large negative TREPE* values. A similar contradiction may be seen in Fig. 3, which shows that $4n+2$ rings have negative TREPE* values, while for all odd membered rings they are positive. This is contrary to the widely confirmed $4n+2$ rule [9]. Recent results by Shaik et al. [10] bring in a qualitatively different picture of a delocalization in which a dominant role is played by σ-electrons. It has been shown there that π-electrons are equally reluctant to achieve delocalization, irrespective of the ring size, while the σ-framework exhibits a reasonably strong tendency towards symmetric geometry, thus favoring delocalization. From this viewpoint the exact TRE* values would seem reasonable and are in even better agreement with modern theories of resonance than the older concepts. However, this agreement could also be a mathematical artifact, and more extensive study is needed.

It is interesting to note that the two models, TRE and TRE*, start from similar ideas. The TRE model excludes all cyclic components from the set of Sachs graphs, thus giving the coefficients of matching polynomial whose zeros represent the energy levels of the reference system [3, 4]. The TRE* model, as was mentioned earlier, excludes all cyclic subgraphs in the expansion of E_π. At the first glance these two approaches seem to be equally reasonable and it is not clear *a priori* which of them should render better agreement with chemical facts. The present analysis shows that for certain, hitherto concealed, mathematical reasons, the TRE* model gives unexpected results for larger values of the parameter L. The invalid results of the TRE* model point out the sensitivity of the calculated RE on the way of accounting for the effects of cyclic conjugation and also put some more weight on the earlier TRE approach [3, 4].

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