On Acyclic Polynomials of $[N]$-Heteroannulenes

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It is known that the acyclic polynomial of a graph has real roots. However, it is of some interest to give a direct, graph-theoretical proof. Such a proof is given for heteroannulene graphs.

Acyclic polynomial is essential quantity in the topological theory of aromaticity$^{1-3}$. It may be defined in several ways$^4$. Here we will use the definition based on the Sach formula$^5$,

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

with

$$a_n^a(G) = \sum_{s \in S_n^a} (-1)^{c(s)}$$

where $G$ stands for Hückel graph$^6$ with $N$ vertices, $s$, the Sachs graph with $n$ vertices, is a member of $S_n^a$ set consisting of only $K_2$ graphs$^7$, while $c(s)$ is the number of $K_2$ components, respectively.

In the early work$^{1-3}$ there was no proof given that the zeros of the acyclic polynomial are always real. This result is needed in order to ensure the meaningful topological resonance energies$^{1-3,9}$. Several chemical papers were published in 1979 considering the problem$^{10-12}$. However, this recent interest in the acyclic polynomial has revealed that it was independently discovered in mathematics$^{13}$, physics$^{14-17}$, besides being rediscovered in chemistry by Aihara$^{18}$. Altogether the acyclic polynomial was discovered, as far as we know, at least five times; authors being unaware of the previous works. In addition, various authors proposed and used different names for $P^a(G; x)$, such as acyclic polynomial$^{1-3,9}$, reference polynomial$^{16,12,14}$, and matching polynomial$^{11,14}$, respectively.

In our early work we conjectured that the acyclic polynomial of a given structure has real roots; the conjecture being based on the numerical work$^{10}$. However, the proof was shown to be true by several authors, e.g., most recently by Godsil and Gutman$^{11}$. However, the proof, that was given by these authors and others, is obtained using the reasoning of mathematical induction. Therefore, we know that the acyclic polynomials of all graphs have real roots, and, consequently, that the topological resonance energies of conjugated systems are real. However, we feel that it is of some interest to give more direct, graph-theoretical proof. Some initial work is already carried out$^{10-12,20,21}$. 

Note
For example, several »acyclic« graphs are known (Figure 1). »Acyclic« graph \( G_{ac} \), corresponding to a graph \( G \), is defined as the graph whose characteristic polynomial \( P(G_{ac}; x) \) equals the acyclic polynomial \( P_{ac}(G; x) \) of \( G \).

![Figure 1. Examples of »acyclic« graphs \( G_{ac} \) and the corresponding parent graphs \( G \).](image)

In we could construct »acyclic« graph for every structure, then the problem of proving that the zeros of \( P_{ac}(G; x) \) are always real would not exist. In this case we will be able to set up the corresponding adjacency matrix, which is a Hermitian matrix, and the roots of the acyclic polynomial would be immediately proved real. However, this is not the case; »acyclic« graphs are available only for a few simple structures.

Another approach is also based on a construction of a Hermitian matrix but the original molecular skeleton is retained and the complex weights of the form \( e^{±ia} \) are associated with edges\(^{18,19,30} \). Unfortunately, until now the method is applicable to monocyclic\(^{10,12} \) and some bicyclic\(^{20} \) hydrocarbon systems.

In the present note we wish to extend the later approach to the vertex- and edge-weighted graphs, \( G_{vw} \), which pictorially represent heteroconjugated molecules\(^{22,23} \). Only heteroannulene graphs will be treated here. A vertex- and edge-weighted graph is a graph in which vertices and edges of different »type« are weighted, and their »weights« are identified by parameters \( h \) and \( k \) for heteroatoms and heterobonds, respectively. Vertex weight \( h \) is diagrammatically represented by a loop. In Figure 2 we give as an example the graphical representation of pyrrole.

![Figure 2. Vertex- and edge-weighted graph of pyrrole.](image)
In our approach the undirected molecular graph $G$ has to be replaced by the corresponding directed graph $\overrightarrow{G}$, namely each edge from $G$ has to be represented by two oppositely directed lines. Moreover, a weight $e^{ia}$ should be associated with the line $i \rightarrow j$ and its complex conjugate weight $e^{-ia}$ should be associated with the line $j \rightarrow i$. In such a way »graphs« $\overrightarrow{G}$ described by a Hermitian matrix is obtained and it is clear that its characteristic polynomial $P(\overrightarrow{G}; x)$ has real roots. Because the edge contributions from $G$ and $\overrightarrow{G}$ ($e^{ia} \cdot e^{-ia} = 1$) are the same, it is evident that $P^{rr}(G; x)$ and $P(\overrightarrow{G}; x)$ could differ only in contributions originating from cycles. In the case of $[N]$-annulene, represented by the graph $C_N$, cycle enters only through the last coefficient:

$$P(C_N; x) = P^{rr}(C_N; x) + a_{N}^{cyclic}(\overrightarrow{G})$$

(3)

where:

$$a_{N}^{cyclic}(\overrightarrow{G}) = (-1)^{\epsilon} [e^{iNa} + e^{-iNa}] = -2 \cos Na$$

(4)

Therefore, for:

$$\alpha = \frac{\pi}{2N}$$

(5)

the $a_{N}^{cyclic}(\overrightarrow{G})$ coefficient vanishes thus giving

$$P(C_N; x) = P^{rr}(C_N; x)$$

(6)

Now, we go a step further and consider the vertex-weighted graph $G_{vw}$.

Our procedure gives,

$$P(\overrightarrow{G_{vw}}; x) = P^{rr}(\overrightarrow{G_{vw}}; x) + a_{\overrightarrow{G_{vw}}}^{cyclic}$$

(7)

where,

$$a_{\overrightarrow{G_{vw}}}^{cyclic} = -2 \cos 5\alpha$$

and for: $5\alpha = \frac{\pi}{2}$ one obtains,

$$P(\overrightarrow{G_{vw}}; x) = P(\overrightarrow{G_{vw}}; x)$$

(8)

independently on loop $h$. 


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Let us now consider the vertex- and edge-weighted graph $G_{\text{vEw}}$ corresponding to 5-membered ring,

![Diagram of a 5-membered ring with vertex and edge weights]

The relation between $P(G_{\text{vEw}}; x)$ and $\overrightarrow{P}(G_{\text{vEw}}; x)$ is given as before by,

$$P(G_{\text{vEw}}; x) = P(G_{\text{vEw}}; x) + a_{\text{cyclic}}(G_{\text{vEw}})$$  \hspace{1cm} (9)

where

$$a_{\text{cyclic}}(G_{\text{vEw}}) = (-1)^{k} [k \cdot e^{i\alpha} + k \cdot e^{-i\alpha}] = -2k^2 \cos 5\alpha$$  \hspace{1cm} (10)

For $5\alpha = \pi/2$ we obtain again,

$$P(G_{\text{vEw}}; x) = P_{\text{c}}(G_{\text{vEw}}; x)$$  \hspace{1cm} (11)

The conclusion is that the relation (11) is independent on the values for parameters $h$ and $k$, respectively.

This procedure extends along the same line for $[N]$-heteroannulenes,

![Diagram of a heteroannulene with vertex and edge weights]

thus giving,

$$P(G_{\text{vEw}}; x) = P_{\text{c}}(G_{\text{vEw}}; x) + a_{\text{cyclic}}(G_{\text{vEw}})$$  \hspace{1cm} (12)

where

$$a_{\text{cyclic}}(G_{\text{vEw}}) = (-1)^{N} \prod_{i=1}^{N} k_{1} k_{2} \ldots k_{N} e^{i\alpha} e^{-i\alpha} = -2 \cos \frac{Na}{2} \prod_{i=1}^{N} k_{i}$$  \hspace{1cm} (13)

and for $Na = \frac{\pi}{2}$, one obtains as before

$$P(G_{\text{vEw}}; x) = P_{\text{c}}(G_{\text{vEw}}; x)$$  \hspace{1cm} (14)
The above result does not depend on the number and values of parameters \( h \) and \( k \).

Therefore, the acyclic polynomial of \([N]\)-heteroannulene has real roots. Moreover both for \([N]\)-annulenes and \([N]\)-heteroannulenes the acyclic polynomial equals the characteristic polynomial of a Hermitian matrix for the unique choice:

\[
N\alpha = -\frac{\pi}{2}
\]

The procedure described here although attractive from the graph theoretical point of view should be understood as a rather limited. Namely, the procedure could be generalized to polycyclic hetero-systems only under very restrictive conditions on symmetry of the systems studied.

REFERENCES


SAŽETAK

O acikličkim polinomima \([N]\)-heteroanulena

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