Proc. Indian Acad. Sci. (*Chem. Sci.*), Vol. 112, No. 1, February 2000, pp. 27–33

Characteristic polynomials of linear polyacenes and their subspectrality

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MS received 11 May 1999; revised 24 August 1999

Abstract. Coefficients of characteristic polynomials (CP) of linear polyacenes (LP) have been shown to be obtainable from Pascal's triangle by using a graph factorisation and squaring technique. Strong subspectrality existing among the members of the linear polyacene series has been shown from the derivation of the CP's. Thus it has been shown that the entire eigenspectrum of an n-ring LP is included in that of $(2n + 1)$-ring LP. Correspondence between the eigenspectra of linear chains and LP's is brought out by a recently developed vertex-alternation and squaring algorithm.

Keywords. Characteristic polynomials; linear polyacenes; Pascal's triangle; subspectrality.

1. Introduction

Although a closed formula for the eigenspectra of linear polyacene (LP) graphs is known[1], no such formula for their characteristic polynomials (CP) exists in the literature. On the other hand, search for a hierarchical structure of the CP coefficients of graphs has been of interest for a long time. For example, Randic[2] showed the use of Young diagrams and traces of adjacency matrices of graphs for determination of their CP coefficients. El-Basil[3] showed how Fibonacci relations and Lucas sequences can be used to generate CPs of a family of graphs starting from smaller ones. Generation of CP coefficients of reciprocal graphs[4] from Pascal's triangle has recently been shown[5]. This triangle, in its symmetric and anti-symmetric forms, has been shown[6] to be of use in the enumeration of $s, p, d, f, \ldots$ orbitals of the H-atom in D-dimensional hyperspace. The object of the present paper is to show how the CP coefficients of linear polyacene (LP) graphs are related to Pascal's triangle (PT). Subspectrality in the series of LPs will also be explained.

2. Experimental

2.1 *Construction of CP of a general LP by graph factorization*

The graph of a general n-ring linear polyacene, $(LP)_n$, can be factorised as shown in figure 1 by McClelland's method of mirror plane fragmentation[7,8]. We now define a function

*For correspondence

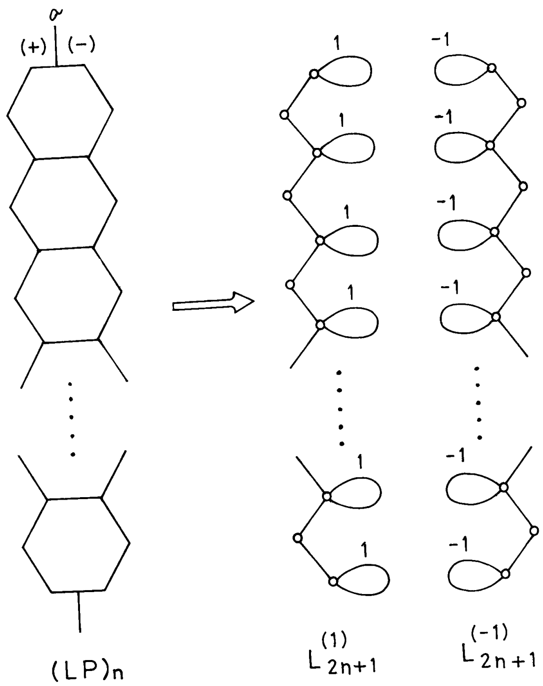

Figure 1. Mirror plane fragmentation of a linear polyacene.

$$F_i(x) = (x - h)x(x - h)x \text{ ... to } i \text{ factors}, \tag{1}$$

where i is an odd integer. The linear chain $L_n^{(h)}$ having successively alternating vertex weights h, 0, h, 0, ..., can be easily shown to have the CP,

$$P(L_n^{(h)}; x) = \sum_{k=0}^{[n/2]} (-1)^k \; {}^{n-k}C_k F_{n-2k}, \tag{2}$$

where $[n/2]$ is the largest integer not greater than $n/2$. The mirror plane fragments of $(\mathrm{LP})_n$, where n may be both odd and even, are chains of the above type with $(2n + 1)$ vertices. The value of h is +1 for the left hand and –1 for the right hand fragment. We denote these by $L^{(1)}{}_{2n+1}$ and $L^{(-1)}{}_{2n+1}$ respectively. Consequently, the CP of $(\mathrm{LP})_n$ is given by,

$$P((\mathrm{LP})_n; x) = P(L^{(1)}{}_{2n+1}; x)P(L^{(-1)}{}_{2n+1}; x), \tag{3}$$

where

$$P(L_{2n+1}^{(1)}; x) = \sum_{k=0}^{[(n+1)/2]} (-1)^k \; {}^{2n+1-k}C_k F_{2n+1-2k}^{+}, \tag{4}$$

$$P(L^{(-1)}_{2n+1}; x) = \sum_{k=0}^{[(n+1)/2]} (-1)^k \; {}^{2n+1-k}C_k F_{2n+1-2k}, \quad (5)$$

$$F^{+}_{2n+1-2k} = (x-1)x(x-1) \ldots \text{ to } 2n+1-2k \text{ factors}, \quad (6)$$

and

$$F^{-}_{2n+1-2k} = (x+1)x(x+1) \ldots \text{ to } 2n+1-2k \text{ factors}. \quad (7)$$

Some examples are given in table 1. It can now be noted that the coefficient of F^{+}_{1}, F^{+}_{2}, ... in the left hand fragments and F^{-}_{1}, F^{-}_{2}, ... in the right hand ones in the CP of $(\mathrm{LP})_n$ are numbers appearing in Pascal's triangle as shown in figure 2. The required numbers are enclosed in parentheses. The parallel arrows contain the coefficients of the F_i's as indicated in figure 2.

3. Subspectrality in the series of linear polyacenes

Each $F_{2n+1-2k}$ contains an odd number of factors and in the expansion (4), all the terms of $P(L^{(1)}_{2n+1}, x)$ have a common factor $(x - 1)$; similarly $(x + 1)$ is a common factor of $P(L^{(-1)}_{2n+1}, x)$. This explains the occurrence of ± 1 as two eigenvalues common to all $(\mathrm{LP})_n$. Successive mirror plane fragmentation also brings out an interesting feature about the eigenspectra of $(\mathrm{LP})_n$s – the eigenspectrum of $(\mathrm{LP})_n$ is entirely contained in that of $(\mathrm{LP})_{2n+1}$ i.e.,

$$\{e(\mathrm{LP})_n\} \subset \{e(\mathrm{LP})_{2n+1}\}. \quad (8)$$

Thus the eigenspectra of benzene, naphthalene, anthracene, are contained in those of anthracene, pentacene, heptacene respectively. The reason for this is obvious from the scheme shown in figure 3. For verification of this feature some $(\mathrm{LP})_n$ eigenspectra, collected from Coulson's compilation of HMO eigenvalues [1], are shown in table 2.

A number of graphs are said to be 'strongly subspectral' if they have many eigenvalues in common. The strong subspectrality among the $(\mathrm{LP})_n$ graphs just demonstrated brings out an example of 'accidental degeneracy'. Thus anthracene has two pairs of eigenvalues with two-fold degeneracy viz. $(\pm 1, \pm 1)$ and $(\pm 1{\cdot}4142, \pm 1{\cdot}4142)$ although it belongs to the abelian D_{2h} point group and is, therefore not expected to possess

Table 1. Characteristic polynomials of some linear polyacenes in terms of linear chains.

n	CP of each linear fragment*
1	$F_3 - 2F_1$
2	$F_5 - 4F_3 + 3F_1$
3	$F_7 - 6F_5 + 10F_3 - 4F_1$
4	$F_9 - 8F_7 + 21F_5 - 20F_3 + 5F_1$
5	$F_{11} - 10F_9 + 36F_7 - 56F_5 + 35F_3 - 6F_1$

* '+' and '–' signs as superscripts of *F* have been omitted for convenience; they should be used adequately for the appropriate fragments

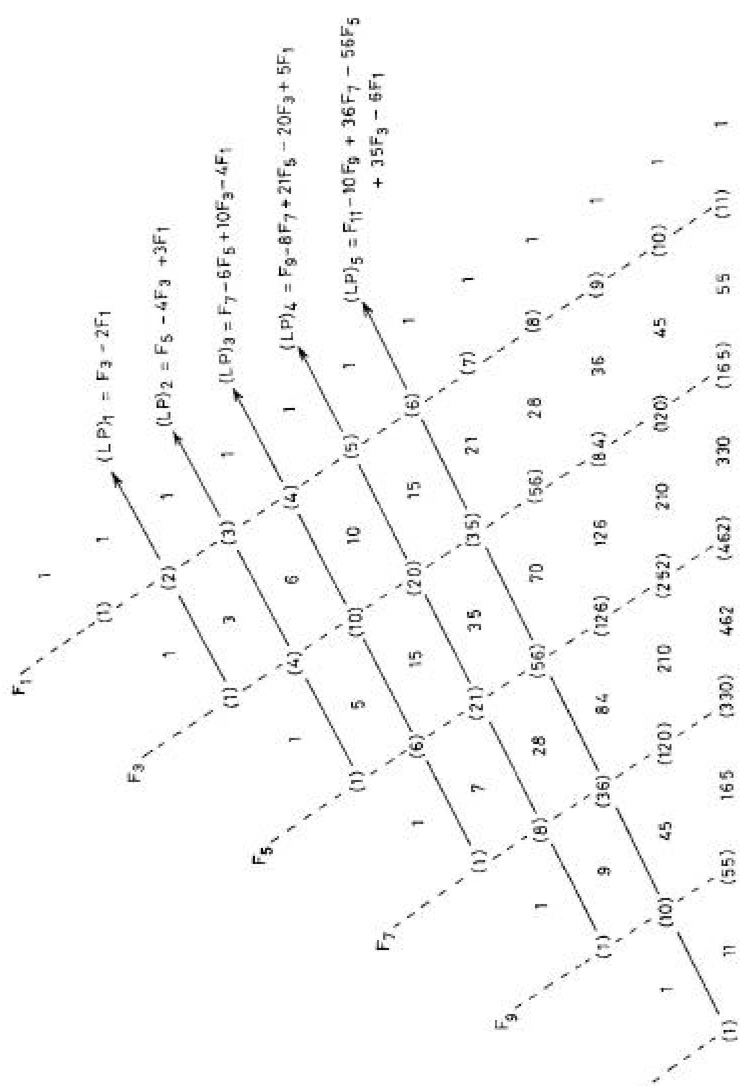

Figure 2. Characteristic polynomials of the '+' and '–' fragments of the linear polyacenes and Pascal' s Triangle.

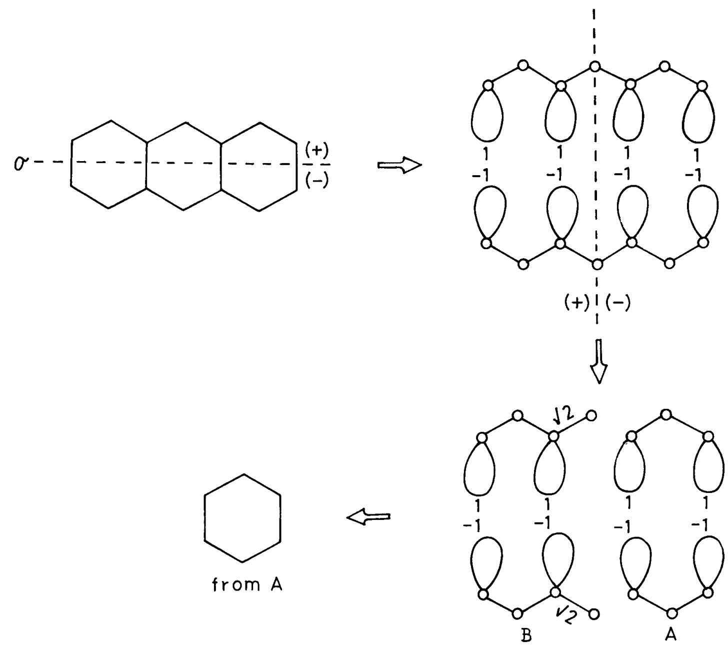

Figure 3. Subspectrality of benzene and anthracene.

Table 2. Eigenvalues of n-ring linear polyacenes (other than the common ±1).

n	Eigenvalues
1	± 2, ± 1
2	± 2·3028, ± 1·6180, ± 1·3028, ± 0·618
3	± 2·4142, ± 2, ± 1·4142, ± 1·4142, ± 0·4142, ± 1
4	± 2·4667, ± 2·1935, ± 1·7775, ± 1·4667, ± 1·2950, ± 1·1935, ± 0·7775, ± 0·2950
5	± 2·4955, ± 2·3028, ± 2, ± 1·6180, ± 1·4955, ± 1·3028, ± 1·2197, ±1, ± 0·6180, ± 0·2197

degenerate eigenvalues. Considered from the view-point of D_{2h} symmetry operations only, this degeneracy seems to be 'accidental'. However, anthracene has a bipartite graph and if 'colour pairing symmetry'[9] is coupled with D_{2h} symmetries, then probably the roots of the observed degeneracy can be revealed. This however requires a separate and detailed analysis and will be dealt with in a future communication.

4. Correspondence between the eigenspectra of $(LP)_n$ and linear chain (L_n)

To determine this correspondence, a recently developed vertex-alternation and squaring scheme[10] has been utilised which is outlined below.

Let L_n (alt) be a linear chain with n vertices of weights alternating as $h, -h, h, -h, \ldots$, the edge-weights being arbitrary. After maximal starring of the vertices, if the starred vertices are labelled first as 1, 2, 3, ... r and the unstarred ones as $r+1, r+2, \ldots n$ then it can be shown[10] that the square of the adjacency matrix $\mathbf{A}$ of L_n (alt) is block-factored as

$$\mathbf{A}^2 = \begin{bmatrix} \mathbf{B}_1 & \mathbf{0} \\ \mathbf{0} & \mathbf{B}_2 \end{bmatrix},$$

and that each block is the adjacency matrix of a smaller linear chain whose vertex and edge-weights can be calculated by the following steps.

(1) Draw a linear chain L^* by taking only the starred vertices labelled 1, 2, 3, ... r. Similarly, draw a separate chain L^0 by taking only the unstarred vertices.
(2) The edge-weight between the vertices i and j in L^* (or L^0) is the product of the edge-weights in going from i to j in the original graph, L_n (alt).
(3) The weight of the vertex i in L^* (or L^0) is the sum of the square of the vertex-weight at i and the squares of the weights of the edges incident to i in L_n (alt).

Under this scheme $\mathbf{B}_1$ and $\mathbf{B}_2$ are found to be the adjacency matrices of L^* and L^0 respectively. This is illustrated in figure 4.

The right hand mirror-plane fragment of $(\mathrm{LP})_n$ graph is a linear chain with successive vertex-weights –1, 0, –1, 0, ... Now, if each vertex weight is increased by 0·5, which amounts to a diagonal shifting of the corresponding adjacency matrix, the resulting chain has the desired vertex-weight pattern, –0·5, 0·5, –0·5, 0·5, ... After maximal starring of this chain and following the steps (1)–(3), the block $\mathbf{B}_2$, which corresponds to the unstarred vertices, is found to be a linear chain of n vertices each carrying a weight of 2·25. The entire scheme is shown in figure 4. A further diagonal shifting by –2·25 converts this into a simple linear chain, L_n .Utilising this and the fact that $(\mathrm{LP})_n$ is an alternant system, we can trace back from the bottom of figure 4 to arrive at $4n$ eigenvalues of $(\mathrm{LP})_n$ in the analytic form,

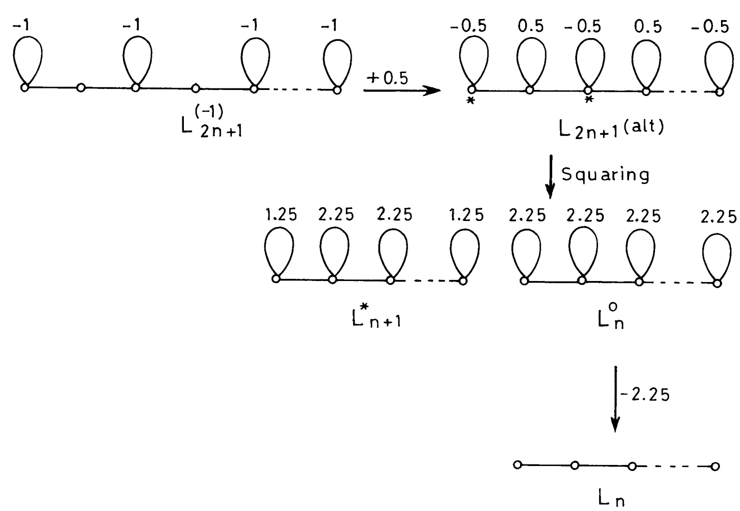

Figure 4. Correlation of the eigenspectrum of the right hand mirror-plane fragment of $(\mathrm{LP})_n$ with that of L_n.

$$\{e(LP)_n\} = \pm [-0{\cdot}5 \pm [2{\cdot}25 + e_j(L_n)]^{1/2}], \quad (9)$$

where $e_j(L_n)$, $j = 1$ to n, is the set of n eigenvalues of L_n. Thus, apart from the eigenvalues ± 1, the entire eigenspectrum of the $(LP)_n$ has a one-to-one correspondence with that of L_n.

Acknowledgement

The authors are thankful to the learned referees for their valuable comments. Financial support by the University Grants Commission, New Delhi is gratefully acknowledged.

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