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The Factorisation of Chemical Graphs and Their Polynomials: A Polynomial Division Approach

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Recent advances in computational methods allow the Characteristic and Acyclic Polynomials of a Chemical Graph to be calculated easily. A consequence of this is that checking for a zero-value remainder after computer assisted polynomial division is sometimes the simplest way of testing suspected factors of a chemical graph. The technique is simple enough to apply on a routine basis when characteristic or acyclic polynomials need to be solved. Among appropriate choices for test are linear polyenes and rings, because their roots are already independently available in closed form and they do occur as factors in a significant number of structures. Examination of an arbitrary set of structures showed that the acyclic polynomials of non-cyclic structures tend to be the most easily factorisable, followed by characteristic polynomials of cyclic structures and (least easily factorisable) the acyclic polynomials of the same cyclic structures.

INTRODUCTION

One can now evaluate characteristic polynomials (CPs) quite simply in either their classical form of powers of X:

$$X^n + a_{n-1} X^{n-1} + a_{n-2} X^{n-2} + \ldots + a_0$$

or as a linear combination of the characteristic polynomials of the linear polyenes:

$$L_n + b_{n-1} L_{n-1} + b_{b-1} L_{n-2} + \ldots + b_0$$

(Here L_n = the CP of a conjugated linear polyene of n carbon atoms and a and b are coefficients).

In the past this had often been extremely tedious for systems of any size.[1–5] The method of counting subgraphs, for example, is elegant in concept, but unwieldy in practice.[5–10] However, following recent work, and given only modest computer assistance, calculation is quite straightforward for many systems.[11–15] The acyclic Polynomial too can be evaluated without much difficulty by using a recurrence relationship.[16,17]

Subspectrality (where two or more structures have a factor, and consequently some eigenvalues, in common) has been shown to occur quite often, but it is remarkable how complicated it can sometimes be to factorise a structure by applying decomposition rules to a graph or Hückel matrix.[18,21]

The division of one polynomial by another is laborious to do by hand, but with a little computer help it becomes quite a trivial task. Now that the polynomials are easily accessible therefore, polynomial division can sometimes provide a much simpler way of confirming the existence of a suspected factor.

DISCUSSION

Polynomials are notoriously difficult to solve satisfactorily for the general case, and even within the quite circumscribed range used for chemical purposes, care is needed to avoid errors building up. For this reason it is an advantage to split a polynomial into ones of lower order if this can be done accurately. The zeros of a characteristic polynomial can often, of course, be obtained with a more reliable accuracy by diagonalisation of the corresponding adjacency matrix, but this alternative treatment is not generally available for the acyclic polynomial, because usually it does not represent a 'chemically real' structure.

The zeros of a very few classes of characteristic or acycllic polynomial are available in analytic form in terms of trigonometric functions without recourse to direct solution (e. g. the CP of a linear polyene or a monocycle[19]).

It has long been recognised that common integer roots (0, $\pm$ 1, $\pm$ 2) can usefully be extracted by division, and in the 'deflation' procedure dominant roots of a polynomial which have been found by successive approximation, and which are usually irrational, are removed by division. Unfortunately this process of division by the polynomial $(X - k)$ when k is irrational is itself likely to introduce errors because the remainder will never be zero; only an approximation to zero.

Suppose though that the (known) spectrum of some polynomial $P(i)$ is a subset of the roots of the larger polynomial $P(n)$. Then, even if the set of i roots are all inexact, the coefficients of $P(i)$ are exact*, and because $P(i)$ is a factor it will divide exactly into $P(n)$ to leave a polynomial of order $n - i$.

Conversely, if some unsolved polynomial $P(n)$ is divided by $P(i)$ and a remainder of zero is found, then $P(i)$ must be a factor; its roots are perhaps already known; and the quotient is an exact* representation of the reduced polynomial containing the remaining $n - i$ roots.

Similarly if some graph $G(n)$ is suspected of having some subgraph $G'(i)$ as a factor, then this suspicion can be quickly tested by evaluating the two characteristic polynomials and checking by division.

This division procedure does not provide any means of deducing factors, and in that sense it is an empirical »blindsearch« method, but with a modern general-purpose computer it does enable any suspected factors to be tested rapidly. Such a procedure is complementary to methods which split symmetrical graphs into weighted subgraphs. What it does is to ensure that simple factors (or any others if suspected) are found quickly if they occur.

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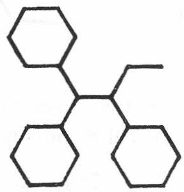
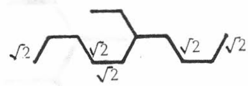
* Exact in this context means a real number which can be completely expressed by a finite decimal representation which is within the accuracy being worked with. It is necessary but not sufficient that such a number be rational, and for unweighted systems such numbers will be integers.

SOME EXAMPLES

(A) 

This was among the structures chosen by McLelland[20] to demonstrate a very neat method of decomposition by the exploitation of local symmetry Application of his rules yields the factors L_2, L_2, R_6 and (R_6 = CP of a six membered ring; benzene).



A third, and graphically less obvious, factor L_2 may be extracted by using the Heilbronner decomposition rules.[21]

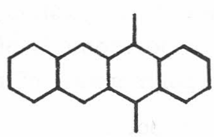
Using to polynomial division approach, the CP of (A) evaluates to

$$L_{22} - 3L_{20} - 2L_{18} - 6L_{16} + 15L_{14} + 17L_{12} + 29L_{10} - 9L_8 - 22L_6 - 50L_4 - 27L_2 - 19$$

and this factorises successively to give

$$R_6 . (L_{16} - 3L_{14} - 2L_{12} - 4L_{10} + 9L_8 + 13L_6)$$
$$= R_6 . L_2 . (L_{14} - 4L_{12} + L_{10} - L_8 + 9L_6 + 5L_4 + 6L_2 + 1)$$
$$= R_6 . L_2 . L_2 . (L_{12} - 5L_{10} + 5L_8 - L_6 + 5L_4 + L_2)$$
$$= R_6 . L_2 . L_2 . L_2 . (L_{10} - 6L_8 + 10L_6 - 5L_4 + 6).$$

An advantage of this method is that with a suitable computer program it can be a purely mechanical process, having once typed in the connectional information for an adjacency matrix of (A).

(B) 

The spectrum of this structure contains the roots of L_6, yet this example of subspectrality could not be explained on the basis of the symmetry properties of the graph, although Randić offered an explanation using a sum rule.[18,22]

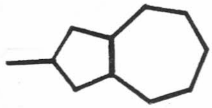
By division; if the C. P. of (B) is evaluated as

$$L_{20} - 4L_{18} - 2L_{16} - L_{14} + 17L_{12} + 26L_{10} + 44L_8 + 41L_6 + 48L_4 + 28L_2 + 18$$

then a routine search will quickly yield the factors

$$L_6 . L_2 . (L_{12} - 6L_{10} + 7L_8 + 11L_4 - 2L_2 + 9).$$

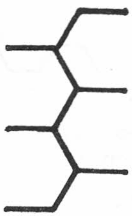
(C)



This is one of the rather few non-alternant structures found where both the characteristic and the acyclic polynomials factorise:

$$\begin{aligned}\text{Characteristic polynomial: } & L_{11} - 2L_9 - 2L_7 + 2L_6 + 4L_4 - L_3 - 3L_1 - 2\\ & = L_1 . (L_2 - 2) . (L_8 - 2L_6 - 2L_4 + 2L_3 - L_2 + 4L_1 + 1)\\ \text{Acyclic Polynomial: } & L_{11} - 2L_9 - 2L_7 - L_3 - L_1\\ & = L_1 . L_2 . (L_8 - 4L_6 + 4L_4 - L_2 - 3).\end{aligned}$$

(D)



(D) is a typical acyclic structure whose characteristic/acyclic polynomial, $L_{12} - 4L_8 - 7L_6 - 4L_4 + 1$, contains a simple factor which can quickly be discovered by a routine search yielding the more amenable expression

$L_6 \cdot (L_6 - L_4 - 4L_2 - 3)$.

In the course of testing this method, an arbitrary set of 65 acyclic and 57 cyclic structures was examined, and the results are summarised in Table I. This gives some idea of the extent to which roots recurr, and how often polynomials are factorisable. The actual figures shown are of limited significance because they depend on the selection of structures made, but they suggest that there is a general tendency for ease of factorisation to follow the order

(characteristic/acyclic polynomials of acyclic structures) >
> (characteristic polynomials of polycyclic structures) >
> (acyclic polynomials of polycyclic structures)

Acyclic polynomials of polycyclic structures are the least amenable to this approach, but even here a significant proportion of them do have factors (though most often L_2), so that a routine search when it is simple is worthwhile. Any help with root evaluation for acyclic polynomials is even more important than for characteristic polynomials, because there is as yet no alternative treatment via matrix diagonalisation, unless one invokes a matrix with irrational or complex elements.[23]

DISCUSSION OF THE METHOD

Mathematically, the procedure for polynomial division is elementary. When the polynomial $L_m + aL_m \cdot \ldots$ is tested as a possible factor of $L_n + xL_n \cdot \ldots$ then the first term in the quotient is L_{n-m}. The product $L_{n-m} \cdot (L_m + aL_m \cdot \ldots)$

TABLE I

Some Results of Analysis of Polynomial Roots and Factors for an Arbitrary Set of Structures

	Polynomials of non-cyclic structures	Characteristic polynomials of cyclic structures	Acyclic polynomials structures
Total number of structures in set	65	57	57
Total number of roots	644	638	638
Number of zero roots	82	14	12
Number of multiple non-zero roots	4	33	0
Number of remaining roots	558	591	626
Frequency distribution within this figure;			
number of occurrences: 1	296	333	544
2	28	34	24
3	22	17	2
4	4	5	2
5	4	3	
6	2	4	
8	2		
10		2	2
13	2		
14		1	
20		1	
25	2		
26		1	
Number of structures with no factors found	5	29	36
Number for which L_1 was the only factor extracted*	16	4	7
Number with other simple factors	44 (68%)	24 (42%)	14 (25%)

* The number in this group is shown because these are trivial results; inspection of a polynomial in its classical form of powers of X immediately shows whether L_1 factor(s) are present, and removal through division by X is elementary.

is reduced to a liner expression by use of the rule $L_i \cdot L_j\ [i > j] = L_{i+j} + L_{i+j-2} + \ldots + L_{i-j}$ and subtracted from $L_n + xL_n \cdot \ldots$ to give an expression of order n'. This procedure is repeated in accordance with classical long division until the the numerator is of lower order than the denominator. If at this stage terms from the polynomial $L_n + xL_n \cdot \ldots$ remain, then $L_m + aL_m \cdot \ldots$ is not a factor and the attempt is abandoned. If on the other hand there is no remainder then it is a factor, and it is tested again on the reduced polynomial before moving on to try another factor on the reduced, quotient, polynomial. A polynomial can be conveniently stored and manipulated as an array of its coefficients.

The listing for an implementation of this routine in North-Star or IMB-PC Basic can be obtained from the author. The characteristic and acyclic polynomials were evaluated from the adjacency or the Hückel matrix by methods which have been described.[11–17]

CONCLUSION

Characteristic polynomials are now easily accessible, and consequently computer assisted polynomial division often provides a convenient way of testing suspected factors of a chemical graph. The technique is simple enough to apply on a routine basis when characteristic or acyclic polynomials need to be solved.

FOOTNOTE

After submission of this paper the author's attention was drawn to two recent papers discussing the factorisation of CPs which were presented at the Sanibel Symposium (Florida, March 1985), and which approach the problem from a different standpoint.[24,25]

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REFERENCES

1. F. Harary, C. King, A. Mowshowitz, and R. C. Read, *Bull. London Math. Soc.* **3** (1971) 321.
2. N. Trinajstić, *Chemical Graph Theory,* CRC Press, Boca Raton, Florida (1983).
3. D. Cvetković, M. Doob, and H. Sachs, *Spectra of Graphs — Theory and Application,* Deutscher Verlag der Wissenschaften, East Berlin 1979; Academic Press, London 1980.
4. K. Kawasaki, K. Mizutani, and H. Hosoya, *Tables of Non-Adjacent Numbers, Characteristic Poynomials and Topological Indices,* Nat. Sci. Report Ochanomizu University, Japan, 1971.
5. J. V. Knop and N. Trinajstić, *Int. J. Quantum Chemistry* (1980): *Quantum Chemistry Symposium* **14** 503.
6. A. Graovac, I. Gutman, N. Trinajstić, and T. Živković, *Theor. Chim. Acta* **26** (1972) 67.
7. N. Trinajstić, *Croat. Chem. Acta* **49** (1977) 593.
8. A. Graovac, O. E. Polansky, N. Trinajstić, and N. Tyutyulkov, *Z. Naturforsch.* **30a** (1975) 1696—1699.
9. Jun-ichi Aihara, *J. Amer. Chem. Soc.* **98** (1976) 6840; 2750.
10. M. J. Rigby, R. B. Mallion, and A. C. Day, *Chem. Phys. Letters* **51** (1977) 178; **53** (1978) 418.
11. K. Balasubramanian, *Theor. Chim. Acta* **65** (1984) 49.
12. K. Balasubramananian, *J. Computat. Chem.* **5** (1984) 387.
13. E. C. Kirby, *J. Chem. Research* (S) (1984) 4; (M) (1984) 123.
14. E. C. Kirby, *Computers and Chemistry* **9** (1985) 79.
15. E. C. Kirby, *Contribution to the 5th International Symposium on Novel Aromatic Compounds,* University of St. Andrews, Scotland, 15—19 July 1985.
16. B. Mohar and N. Trinajstić, *J. Computat. Chem.* **3** (1982) 28.
17. R. Ramamani and K. Balasubramanian, *J. Computat. Chem.* **6** (1985) 122.
18. S. S. D'Amato, B. M. Gimarc, and N. Trinajstić, *Croat. Chem. Acta* (1981) 54, 1.
19. *Molecular Orbital Theory for Organic Chemists,* A. Streitwieser, Jr., New York and London, John Wiley, 1961.
20. B. J. McClelland, *J. C. S. Faraday Trans.* **II 78** (1982) 911 .
21. E. Heilbronner, *Helv. Chim. Acta* **36** (1953) 170.
22. M. Randić, Personal Communication cited in ref. 18.

23. A. Graovac, D. Kasum, and N. Trinajstić, *Croat. Chem. Acta* **54** (1981) 91.

24. P. Křivka, Ž. Jeričević, and N. Trinajstić, *Int. J. Quant. Chem. Symp.* (1985) in press.

25. M. Randić, B. Baker, and A. F. Kleiner, *Int. J. Quant. Chem.* Symp. (1985) in press. See also ref. 26.

26. M. Randić, *SIAM J. ALG. DISC. METH.* **6** (1985) 145.

SAŽETAK

Faktorizacija kemijskih grafova i njihovih polinoma: Postupak dijeljenja polinoma

E. C. Kirby

Prikazana je faktorizacija kemijskih grafova i njihovih karakterističnih i acikličkih polinoma s pomoću postupka dijeljenja polinoma. Postupak je iskušan na lancima i prstenovima, jer se te strukture često javljaju kao faktori. Proučavanja proizvoljno odabranog skupa grafova pokazala su da se aciklički polinomi necikličkih struktura najlakše faktoriziraju, zatim slijede karakteristični polinomi cikličkih struktura, a najteže se faktoriziraju aciklički polinomi cikličkih struktura.