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Comments on characteristic polynomials of chemical graphs

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1. Introduction

In a recent paper, [1] Frame's method [2] has been applied to the evaluation of characteristic polynomials of chemical graphs. In particular the characteristic polynomials of the Petersen graph and of a graph for an isomerisation of the tetragonal pyramidal complexes have been derived in this way. It has been argued in this paper that these characteristic polynomials cannot be easily obtained by other methods.

However, it is well known that chemical graphs describing permutational modes of rearrangements are invariant with respect to groups of very high order [3-6]. These symmetry properties have been used previously to obtain the characteristic polynomials of various chemical graphs of such modes or of their adjacency matrices [3, 4, 7, 8]. Such a symmetry factoring has been widely used for instance in quantum mechanics [9] and in normal mode analysis [10]. More recently, significant results in this domain have been obtained by various authors (see for instance Refs. [11, 12, 13, 14] and work cited therein). In the present note, we first recall some of these results and we discuss their relation to Balasubramanian's paper [1]. It appears in particular that the characteristic polynomial of the Petersen graph had already been obtained in this previous work [8]. We conclude by comparing the advantages of Frame's method to those of the procedure based on the symmetry properties.

2. Trigonal bipyramids

There are five non trivial modes of rearrangements. Their connectivity δ i.e. the degree of the graph, the number of vertices v of each disconnected part are recalled in Table 1. The characteristic polynomials of each disconnected part are also given (for definitions, enumeration of modes of rearrangements, $M(y_i)$ symbols and the corresponding graphs, see Ref. [15] and the original papers cited therein).

3. Octahedra

The number of non trivial modes of rearrangements is four. The corresponding graphs have been discussed extensively in a previous work [16]. The M_i symbols are those of Ref. [4]. The results are shown in Table 2.

Table 1. Characteristic polynomials for modes of isomerisation of the trigonal bipyramid

Modes	δ	v	Characteristic polynomial [7, 8]
$M(y_1)$	3	20	$(\lambda+3)(\lambda-3)(\lambda+2)^4(\lambda-2)^4(\lambda+1)^5(\lambda-1)^5$
$M(y_2)$	6	10	$(\lambda-6)(\lambda-1)^4(\lambda+2)^5$
$M(y_3)$	6	20	$(\lambda+6)(\lambda-6)(\lambda+1)^4(\lambda-1)^4(\lambda+2)^5(\lambda-2)^5$
$M(y_4)$	3	10	$(\lambda-3)(\lambda+2)^4(\lambda-1)^5$
$M(y_5)$	1	2	$(\lambda+1)(\lambda-1)$

Table 2. Characteristic polynomials for modes of isomerisation of the octahedron

Modes	δ	v	Characteristic polynomial [4]
$M(y_2)(M_2)$	1	2	$(\lambda+1)(\lambda-1)$
$M(y_3)(M_1)$	12	30	$(\lambda-12)(\lambda+6)^5(\lambda-2)^9\lambda^{15}$
$M(y_4)(M_3)$	8	30	$(\lambda-8)(\lambda+4)^5(\lambda+2)^9(\lambda-2)^{15}$
$M(y_5)(M_4)$	8	30	$(\lambda-8)(\lambda-2)^5(\lambda-4)^5(\lambda+2)^{19}$

Table 3. Characteristic polynomials for modes of isomerisation of the tetragonal pyramid

Modes	δ	v	Characteristic polynomial [3]
$M(y_2)(M_1)$	1	2	$(\lambda-1)(\lambda+1)$
$M(y_3)(M_2)$	4	30	$(\lambda-4)(\lambda+1)^4(\lambda-2)^{11}(\lambda+2)^5\lambda^5(\lambda+3)^4$
$M(y_4)(M_6)$	4	30	$(\lambda-4)(\lambda+1)^4(\lambda-2)^5(\lambda+2)^{11}\lambda^5(\lambda-3)^4$
$M(y_5)(M_4)$	8	30	$(\lambda-8)(\lambda+2)^9(\lambda-2)^{15}(\lambda+4)^5$
$M(y_6)(M_5)$	8	30	$(\lambda-8)(\lambda+2)^{19}(\lambda-2)^5(\lambda-4)^5$
$M(y_7)(M_3)$	4	6	$(\lambda-4)(\lambda+2)^2\lambda^3$

4. Tetragonal pyramids

In this case there are six non trivial modes of rearrangements. The results are recalled in Table 3. The graphs have been obtained previously [17]. The M_i symbols are those of Ref. [3].

5. Discussion

In each of the above cases, the characteristic polynomial appears in a factorised form since it has been obtained by diagonalising the matrix for the corresponding mode of rearrangement.

In the case of trigonal bipyramids, the cyclic group of order ten has been used to diagonalise the matrix of $M(y_1)$ [7]. The eigenvalues of the other modes of rearrangements have been obtained by using the relations between the mode operators [8]. Hence, Table 1, obtained previously [7, 8], shows the characteristic polynomials for the graphs corresponding to any mode of rearrangement of the trigonal bipyramidal skeleton, including the Petersen graph which corresponds to mode $M(y_4)$ [15].

Table 2 shows similar results for the octahedral skeleton. It has been obtained [4] by using the fact that the adjacency matrices of these graphs are invariant with respect to the full permutation-inversion group $S_6 \otimes (E, J)$.

Finally, we have also recalled the results obtained [3] for tetragonal pyramids in Table 3. Here again the invariance with respect to $S_5 \otimes (E, J)$ has been exploited. The graph of Fig. 3 in Ref. [1] does not correspond to any of the graphs for the isomerization modes listed in Table 3. Indeed the 15 vertices of the former correspond each to an enantiomeric pair $(a, \bar{a})$ whereas the 30 vertices of the latter correspond to an isomer a or $\bar{a}$. The former graph may be constructed by drawing an edge between the vertices $(a, \bar{a})$ and $(b, \bar{b})$ each time the graph corresponding to $M(y_3)$ in Table 3 has an edge from a or $\bar{a}$ to b or $\bar{b}$[1] [17]. By using the fact that the resulting graph (see Fig. 3 of Ref. [1]) is invariant with respect to S_5 [6] it can be shown that its characteristic polynomial is

$$(\lambda - 4)(\lambda + 1)^4(\lambda - 2)^5(\lambda + 2)^5,$$

which is equivalent to Eq. (17) of Ref. [1]. Note that the eigenvalues of this graph are found among those of $M(y_3)$ and $M(y_4)$ [see Table 3].

To conclude, we think that characteristic polynomials of chemical graphs for modes of rearrangements are easy to obtain by using the symmetry properties [3–8] of these graphs. This method has been successfully applied to the cases of trigonal bipyramids, octahedra and tetragonal pyramids. Among the results obtained in this way, the factorised form of the characteristic polynomial of the Petersen graph has been derived previously [8, 19]. Concerning tetragonal pyramids, these previous results include the characteristic polynomials of graphs

[1] One could obtain the same result by starting from the graph corresponding to $M(y_4)$ instead of $M(y_3)$

with 30 vertices related to the graph for tetragonal pyramids discussed recently [1]. This method also has the advantage to yield the eigenfunctions of the adjacency matrices of the discussed graphs.

Of course, for less symmetric graphs, such as the 36-vertices square lattice or the 24-vertices hexagonal lattice [1], the use of the symmetry properties do not lead to direct diagonalization. Hence, Frame's method and the computer-assisted algorithm developed recently [1, 18] are superior in this case.

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