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Counterexamples to a conjecture of Dias on eigenvalues of chemical graphs

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Abstract

Chemical graphs (simple, connected graphs with maximum degree no greater than three) with eigenvalues $\pm\sqrt{8}$ exist for all orders greater than nine, disproving a conjecture of J.R. Dias that no chemical graph with this pair of eigenvalues exists. In fact, the eigenvalue pair can be achieved with arbitrarily high multiplicity.

1 Introduction

Chemical graphs are defined here as simple, unweighted graphs that are connected and have maximum degree less than or equal to three. They correspond to the carbon skeletons

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of known and potential π-conjugated hydrocarbon molecules, and their adjacency spectra provide models for the energies of the π–molecular orbitals of such systems within the simple Hückel approach.[1] The limitation on vertex degree confines the eigenvalues $\{\lambda_i\}$ of a chemical graph of order n to the range $3 \geq \lambda_i \geq -3$. The integer nature of the coefficients of the characteristic polynomial implies that, for integers p that are not squares, the spectrum of a given chemical graph includes either both $+\sqrt{p}$ and $-\sqrt{p}$ or neither.

Dias[2] noted that examples of chemical graphs with adjacency eigenvalues $\pm\sqrt{1}$, $\pm\sqrt{2}$, $\pm\sqrt{3}$, $\pm\sqrt{4}$, $\pm\sqrt{5}$, $\pm\sqrt{6}$, $\pm\sqrt{7}$, $\pm\sqrt{9}$ are all readily found, and he discussed the structural factors associated with the presence of each of these eigenvalues. However, in his search he found no molecular graph with eigenvalues $\pm\sqrt{8}$, and he made the intriguing conjecture (§6, Ref. 2) that no such graphs exist. As it is easy to find examples of general graphs with these eigenvalues (e.g., the star on nine vertices $K_{1,8}$, with spectrum $\pm\sqrt{8}$, 0^7), this conjecture would appear to imply some specific property of chemical graphs.

However, the present note proves that at least one chemical graph with eigenvalues $\pm\sqrt{8}$ exists for all orders $n \geq 10$, and describes several constructions for infinite series of counterexamples to the conjecture. For brevity, we will call the chemical graphs that have eigenvalues $\pm\sqrt{8}$ simply *octo-graphs.*

2 Results

Chemical graphs of all orders $n \leq 18$ were generated using McKay's program *geng.*[3] Spectra were calculated by Jacobi numerical diagonalisation, with an estimated absolute accuracy of better than 10^{-12}, and filtered for eigenvalues within 10^{-10} of $\sqrt{8}$ in absolute value. Candidates were then checked by computation of characteristic polynomials to make sure that the suspected eigenvalues were indeed exactly $\pm\sqrt{8}$. For $n \leq 17$, no problems with truncation error were encountered; at $n = 18$ two chemical graphs each have a single eigenvalue that coincides with $+\sqrt{8}$ to 10 places of decimals but is not equal to $+\sqrt{8}$. Octo-graphs of order n are labelled $G_{n:q}$ where q tracks their occurrence in the *geng* generation order for all chemical graphs. Table 1 compares the frequencies of surd eigenvalues amongst the small chemical graphs. The final column lists the numbers of graphs with eigenvalues $\pm\sqrt{8}$, the counterexamples to the Dias conjecture. Chemical graphs with eigenvalues $\pm\sqrt{8}$ are relatively uncommon at first, but clearly can be found.

n	N_{chem}	$N(\pm\sqrt{2})$	$N(\pm\sqrt{3})$	$N(\pm\sqrt{5})$	$N(\pm\sqrt{6})$	$N(\pm\sqrt{7})$	$N(\pm\sqrt{8})$
2	1	0	0	0	0	0	0
3	2	1	0	0	0	0	0
4	6	0	1	0	0	0	0
5	10	0	1	0	1	0	0
6	29	1	1	1	0	0	0
7	64	9	1	1	0	1	0
8	194	16	4	1	0	2	0
9	531	34	9	1	2	0	0
10	1733	123	50	6	4	1	1
11	5524	491	147	10	4	3	3
12	19430	1249	361	21	11	6	4
13	69322	3973	1214	58	22	7	15
14	262044	11443	3441	210	48	22	7
15	1016740	45162	10481	508	124	31	12
16	4101318	135426	38122	1315	304	80	38
17	16996157	527339	127087	3513	729	187	69

Table 1: Occurrence of chemical graphs with surd eigenvalues $\pm\sqrt{p}$ $(2 \le p \le 8)$. n is the order of the graph. At each n, N_{chem} is the number of chemical graphs and $N(\pm\sqrt{p})$ is the number of chemical graphs with eigenvalues $\pm\sqrt{p}$. For $n = 18$, 74 of the 72556640 chemical graphs are octo-graphs.

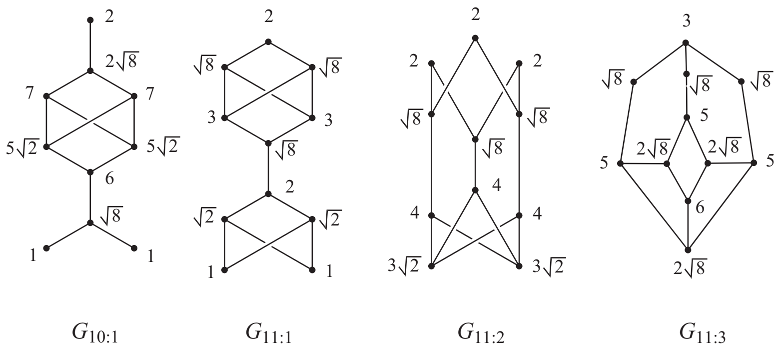

Figure 1: The four smallest octo-graphs. The eigenvectors (unnormalised) for eigenvalue $\sqrt{8}$ are shown; those for eigenvalue $-\sqrt{8}$ follow by reversal of the sign of all surds in the coefficients, or, equivalently for these bipartite graphs, by reversal of signs of coefficients on one of the two partite sets of vertices.

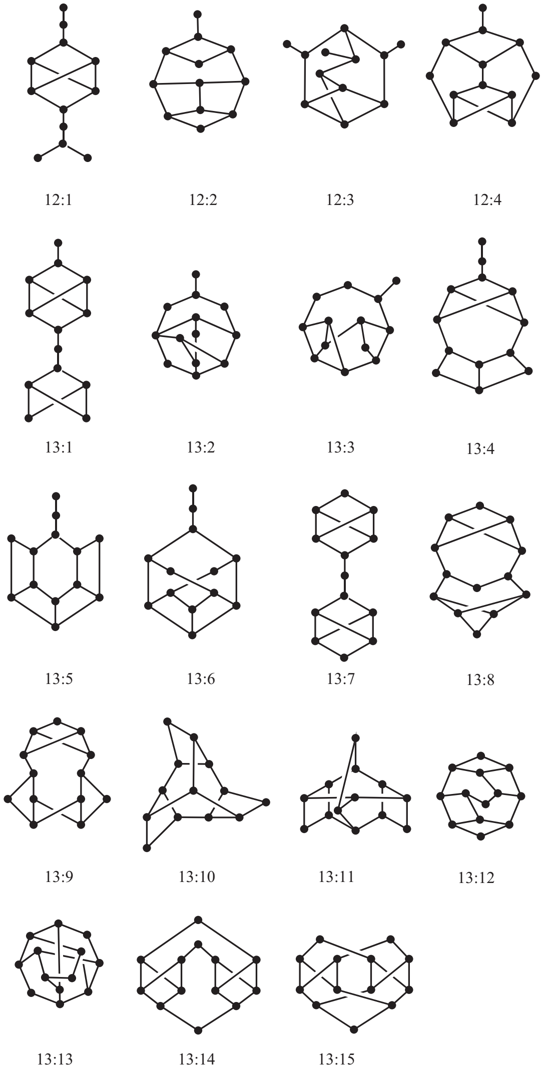

Figure 2: Octo-graphs for $n = 12$ and $n = 13$.

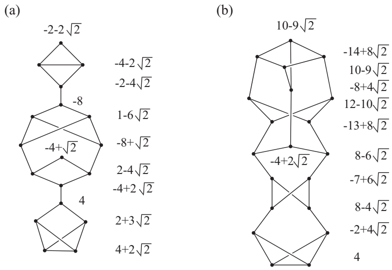

Figure 3: (a) The smallest non-bipartite octo-graph has 18 vertices. (b) the unique 3-regular octo-graph of lowest order has 20 vertices. Eigenvector coefficients for $+\sqrt{8}$ are shown; to obtain those for $-\sqrt{8}$, replace $\sqrt{2}$ by $-\sqrt{2}$ everywhere.

The smallest chemical graph with eigenvalues $\pm\sqrt{8}$ is shown in Figure 1. This graph, $G_{10:1}$, is bipartite, has three vertices of degree one and seven of degree three, has three pairs of duplicate vertices, and has spectrum $\pm\sqrt{8}$, $\pm\sqrt{3}$, ±1, 0^4. The three chemical octo-graphs with 11 vertices, $G_{11:1}$, $G_{11:2}$, and $G_{11:3}$, are also shown in the figure. $G_{11:2}$ is non-planar. All three examples with 11 vertices are bipartite. Figure 2 shows the set of octo-graphs for $n = 12$ and $n = 13$, also all bipartite. The smallest non-bipartite octo-graph is $G_{18:72}$ (Figure 3(left)), with no other non-bipartite octo-graphs on 18 vertices.

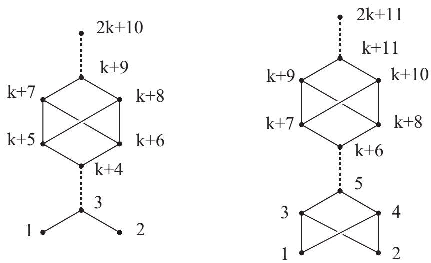

Figure 4: A construction that gives an octo-graph H_n for every order $n > 9$. For even orders $n > 10$ (left), the two dotted edges of $G_{10:1}$ are expanded by insertion of a path of k vertices; for odd orders $n > 11$ (right), the dotted edge of $G_{11:1}$ is expanded by insertion of a path of k vertices and a path of the same length is attached to the vertex of degree two of the six-cycle. The construction produces $G_{12:1}$ from $G_{10:1}$ and $G_{13:1}$ from $G_{11:1}$.

3 An infinite family of octo-graphs

Inspection of the figures suggests the existence of families of octo-graphs. It is easy to show, for example, that an octo-graph H_n exists for all $n \geq 10$, by expanding $G_{10:1}$ and $G_{11:1}$, as indicated in Figure 4.

Theorem 3.1 *For each $n \geq 10$, H_n has simple eigenvalues $\pm\sqrt{8}$.*

Proof. First, let $n = 10 + 2k$ be even, $k \geq 0$. Suppose that $\mathbf{A}$ is an adjacency matrix of H_n. From $\mathbf{A}\mathbf{x} = \sqrt{8}\mathbf{x}$, we have the following system of $n = 2k + 10$ equations:

$$
\begin{array}{lcll}
(1) & x_3 & = & \sqrt{8}\ x_1 \\
(2) & x_3 & = & \sqrt{8}\ x_2 \\
(3) & x_1 + x_2 + x_4 & = & \sqrt{8}\ x_3 \\
\hline
(4) & x_3 + x_5 & = & \sqrt{8}\ x_4 \\
(5) & x_4 + x_6 & = & \sqrt{8}\ x_5 \\
 & \vdots & & \\
(6) & x_{k+2} + x_{k+4} & = & \sqrt{8}\ x_{k+3} \\
\hline
(7) & x_{k+3} + x_{k+5} + x_{k+6} & = & \sqrt{8}\ x_{k+4} \\
(8) & x_{k+4} + x_{k+7} + x_{k+8} & = & \sqrt{8}\ x_{k+5} \\
(9) & x_{k+4} + x_{k+7} + x_{k+8} & = & \sqrt{8}\ x_{k+6} \\
(10) & x_{k+5} + x_{k+6} + x_{k+9} & = & \sqrt{8}\ x_{k+7} \\
(11) & x_{k+5} + x_{k+6} + x_{k+9} & = & \sqrt{8}\ x_{k+8} \\
(12) & x_{k+7} + x_{k+8} + x_{k+10} & = & \sqrt{8}\ x_{k+9} \\
\hline
(13) & x_{k+9} + x_{k+11} & = & \sqrt{8}\ x_{k+10} \\
 & \vdots & & \\
(14) & x_{2k+8} + x_{2k+10} & = & \sqrt{8}\ x_{2k+9} \\
\hline
(15) & x_{2k+9} & = & \sqrt{8}\ x_{2k+10}
\end{array}
$$

Suppose that $x_1 = 1$. From equations (1) – (3) we have

$$x_2 = 1,\ x_3 = \sqrt{8} \text{ and } x_4 = 6.$$

Equations (4)–(6) form a system of recurrence relations

$$x_m + x_{m+2} = \sqrt{8}x_{m+1}, \quad 3 \leq m \leq k+2$$

with $x_3 = \sqrt{8}$ and $x_4 = 6$. The particular solution of this equation is

$$x_m = (\sqrt{2}+1)^{m-2} + (\sqrt{2}-1)^{m-2}.$$

From the equations (8) and (9), and (10) and (11),

$$x_{k+5} = x_{k+6} \text{ and } x_{k+7} = x_{k+8}.$$

Next, from (7) we have

$$x_{k+5} + x_{k+6} = (5\sqrt{2}-7)(\sqrt{2}-1)^k + (5\sqrt{2}+7)(\sqrt{2}+1)^k,$$

and from (8)

$$x_{k+7} + x_{k+8} = (7-5\sqrt{2})(\sqrt{2}-1)^k + (7+5\sqrt{2})(\sqrt{2}+1)^k.$$

Now, from (10),

$$x_{k+9} = (\sqrt{8}-3)(\sqrt{2}-1)^k + (\sqrt{8}+3)(\sqrt{2}+1)^k,$$

and then from (12)

$$x_{k+10} = (\sqrt{2}+1)^{k+1} - (\sqrt{2}-1)^{k+1}.$$

Next, (13) – (14) form another system of recurrence relations, with particular solution

$$x_m = (\sqrt{2}+1)^{2k+11-m} - (\sqrt{2}-1)^{2k+11-m}, \quad k+1 \leq m \leq 2k+9.$$

Finally, from (14) we have $x_{2k+10} = 2$. This solution satisfies the equation (15), so we have found an eigenvector corresponding to $\sqrt{8}$. Thus, graph H_n has $\sqrt{8}$ as an eigenvalue, for n even.

The eigenvalue equations are similar for n odd, and are solved by the same approach. The solution is

$$\begin{aligned}
&x_1 = x_2 = 1, \quad x_3 = x_4 = \sqrt{2},\\
&x_{m+5} = (\sqrt{2}+1)^m + (\sqrt{2}-1)^m, \quad 0 \le m \le k+1,\\
&x_{k+7} = x_{k+8} = \tfrac{1}{2}\left((3+\sqrt{8})(\sqrt{2}+1)^k + (3-\sqrt{8})(\sqrt{2}-1)^k\right),\\
&x_{k+9} = x_{k+10} = \tfrac{1}{2}\left((3+\sqrt{8})(\sqrt{2}+1)^k - (3-\sqrt{8})(\sqrt{2}-1)^k\right),\\
&x_{k+11+m} = (\sqrt{2}+1)^{k+1-m} - (\sqrt{2}-1)^{k+1-m}, \quad 0 \le m \le k,
\end{aligned}$$

and $\mathbf{x} = (x_1, \ldots, x_{2k+11})^T$ is the eigenvector corresponding to the eigenvalue $\sqrt{8}$. As the eigenvector $\mathbf{x}$ is uniquely determined in both cases, we conclude that $\sqrt{8}$ is a simple eigenvalue of H_n, for each $n \ge 10$. Further, as H_n is bipartite, $-\sqrt{8}$ is also a simple eigenvalue of H_n. □

4 Other constructions

Larger octo-graphs can also be produced from any parent octo-graph that has leaves, as illustrated for $G_{10:1}$ in Figure 5(a). Start with two copies of the parent, and join them by a subdivided edge connecting two univalent vertices, one in each copy that carry coefficients of the same magnitude in the $\sqrt{8}$ eigenvector. Decorate the copies with the original eigenvector for $\sqrt{8}$, multiplied by a factor $(-1)^N$ for the N^{th} copy, and placing coefficient zero on the inserted cut vertex. It is easy to check that this decoration is an eigenvector with eigenvalue $\sqrt{8}$ in the new graph. An eigenvector for $-\sqrt{8}$ follows as usual for a bipartite graph by flipping the signs on one of the two partite sets. If the parent octo-graph has multiple leaves, as does $G_{10:1}$, the construction can be extended to give chains and cycles of any desired length. The linker can be expanded to make a fused-triangle bridge (Figure 5(b)) and this allows construction of cyclic oligomers in which all vertices are of degree three. Other 3-regular octo-graphs exist: the smallest is a graph on 20 vertices (Figure 3(b)) and two more are found on 22 vertices.

Repeated use of the same univalent vertex as a base for the fused-triangle bridge leads to a construction of $4k$-cycles of copies of a parent leaf-bearing octo-graph. The $4k$ copies of the parent are linked via the chosen leaf vertex into a cycle of length $4k$ and scale

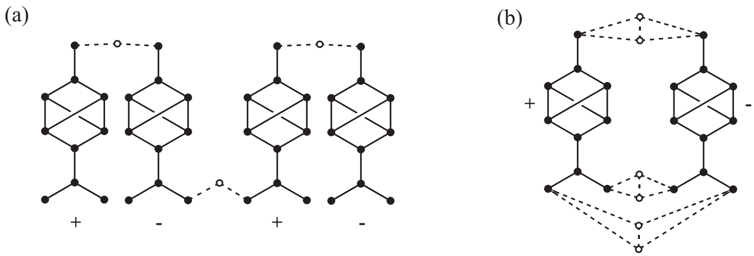

Figure 5: Construction of chemical graphs with eigenvalues $\pm\sqrt{8}$ from copies of $G_{10:1}$ or of any octo-graph that has multiple leaves, as (a) chains and cycles and (b) 3-regular completions. The dotted bridges link vertices that carry coefficients of equal magnitude in the original eigenvector. The repeat units carry copies of the original eigenvector modulated by alternation of sign between units. Vertices marked with a white-filled circle all bear zero coefficient in the eigenvector on the new graph.

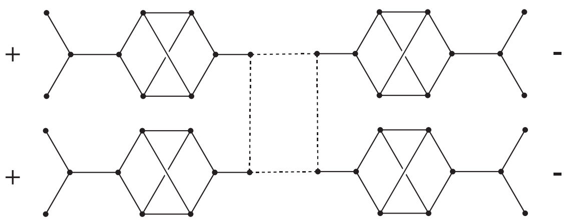

Figure 6: Construction of an octo-graph from $4k$ copies of an octo-graph parent that has a leaf. Copies of the local eigenvector (all with either $\sqrt{8}$ or $-\sqrt{8}$ eigenvalue) are taken with signs $(+,+,-,-,+,+,-,-,+,+,-,-,\dots)$ and $(-,+,+,-,-,+,+,-,-,+,+,-,\dots)$, or equivalently with weights $(+,0,-,0,+,0,-,0,+,0,-,0,\dots)$ and $(0,+,0,-,0,+,0,-,0,+,0,-,\dots)$, to give two independent eigenvectors on the new graph.

factors are assigned to the copies of the local eigenvector (see Figure 6). The composite graph has two eigenvalues $\sqrt{8}$ and two eigenvalues $-\sqrt{8}$, resulting from the independent choices of scale factors $+,+,-,-,+,+,-,-,\dots$ and $-,+,+,-,-,+,+,-,\dots$. Also, the composite graph has more leaves, so it can be used in the same manner to get a graph in which both $\sqrt{8}$ and $-\sqrt{8}$ have multiplicity 4. Repeating this process gives a graph that has eigenvalues $\pm\sqrt{8}$ with multiplicity 2^k, for every $k \geq 1$.

References

[1] I. Gutman, O. E. Polansky, *Mathematical concepts in organic chemistry*, Springer-Verlag: Berlin 1986.

[2] J. R. Dias, Structural origin of specific eigenvalues in chemical graphs of planar molecules *Molec. Phys.* **85** (1995), 1043–1060.

[3] B. D. McKay, *geng* is part of the gtools utilities associated with the graph isomorphism-automorphism software nauty, the manual for which is available at http://cs.anu.edu.au/∼bdm/nauty.