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Some methods for counting the spanning trees in labelled molecular graphs, examined in relation to certain fullerenes

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Abstract

The number of spanning trees in a molecular graph (its 'complexity') has been of recent interest and, in this paper, various methods are applied to calculate the complexities of graphs that represent the fullerenes — as exemplified by the molecules C_{60} and C_{70}, and the notional structures C_{60} (known as 'handballene') and C_{120} ('Archimedene'). These graphs are large, regular and highly symmetrical and the methods chosen address the computational difficulties and advantages presented by these features. The methods discussed are of general applicability when the graph under study has at least one of these properties. One of the methods needs only 'pencil-and-paper' working when applied to the two C_{60} structures, C_{70} and the dual of C_{120}. For C_{120}, the evaluation of the (real) determinant of the (complex) matrices that arise was carried out on a personal computer.

1. Introduction

The spanning trees of a molecular graph are of chemical interest in areas ranging from the magnetic properties of conjugated systems [49–51] to concepts arising in chemical nomenclature [24]. There has been some recent activity aimed at counting the number of spanning trees in a labelled molecular graph (i.e., finding its 'complexity') [27, 61, 35, 36, 9, 57, 64] and, in this paper, we review the several methods that are available. We apply some of them to find the complexities of certain graphs representative of the family of carbon clusters now becoming known as the fullerenes [42–48, 67, 66, 54, 20, 3–5].

We have chosen the molecule C_{60}, structure (I) of Fig. 1 (the prototype of the series — Buckminsterfullerene, also known as soccerballene, footballene, truncated

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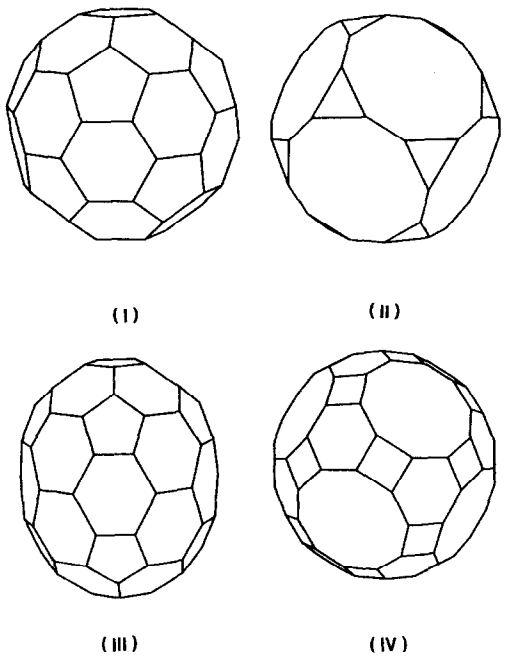

Fig. 1. Depictions of three-dimensional models of the carbon-atom connectivity of the four C_n carbon-clusters ('fullerenes') studied: C_{60} (Buckminsterfullerene) (I) (an extant molecule), C_{60} ('hand' form) (II) (a hypothetical structure), C_{70} (III) (extant), and C_{120} ('Archimedene') (hypothetical). Each vertex should be taken to represent a carbon atom, each edge a chemical bond between two such carbon atoms.

icosahedral C_{60}, etc.) and the recently characterised [56] C_{70} (III), as well as the notional structures [30, 22, 65] C_{60} (II) (truncated dodecahedral C_{60} [30, 65], dubbed 'handballene' [22, 65, 4, 5]) and [30, 22] C_{120} (IV) (truncated icosidodecahedral-, or great rhombicosidodecahedral C_{120}, also called 'Archimedene' [30, 22, 4, 5]). These graphs are large, regular and highly symmetrical, and the methods we have chosen address the computational difficulties and advantages presented by these features. The approaches that we discuss are of general applicability when the graph under study has at least one of these properties. One of the methods that we describe needs only 'pencil-and-paper' working when applied to the two C_{60} structures, C_{70} and the dual of C_{120}. For C_{120}, the evaluation of the (real) determinant of the (complex) matrices that arise was carried out on a personal computer.

The lay-out of the paper is as follows: Since we have been unable to find all the relevant results conveniently and simply brought together elsewhere, in one place, we take the opportunity in Sections 2 and 3 to present, in a uniform notation, a review of the various ways in which the Matrix Tree Theorem [41, 7, 8, 11–17, 29, 68, 21, 32, 37, 59, 49, 50, 62, 27, 33, 58, 26, 60] may be expressed (Section 2), with emphasis (Section 3) on the simplifications that arise when the graphs in question are regular. Section 4 examines the advantages of a device that is available only if the graph is planar. In Section 5 we describe in some detail an approach — briefly referred to above — that

we have found useful for highly symmetric graphs (which many fullerene graphs are). The final sections, Sections 6–8, are devoted to applying these various methods to find the complexities of the representative fullerene graphs (I)–(IV) (Fig. 1), and to assessing the computational advantages and drawbacks of the several approaches considered.

2. The Matrix Tree Theorem

Let $\mathbf{D} = (d_{ij})$ be an $(n \times n)$ diagonal matrix associated with a given labelled graph, G, such that d_{ii} is the degree (valence) of the ith vertex of G and $d_{ij} = 0$, whenever $i \neq j$. Let $\mathbf{A} = (a_{ij})$ be the standard $(n \times n)$ adjacency-matrix of G, i.e., the matrix for which

$$a_{ij} = \begin{cases} 1 \text{ if the vertices labelled } i \text{ and } j \text{ in } G \text{ are joined by an edge in } G, \\ 0 \text{ otherwise,} \end{cases}$$

Now define a matrix $\mathbf{K}$ by

$$\mathbf{K} = \mathbf{D} - \mathbf{A}.$$

$\mathbf{K}$ is occasionally referred to as the Kirchhoff matrix [49, 50] of G, but it is also known as the Laplacian matrix [58, 57, 69] (of G) while, in electrical contexts, it is also sometimes called the admittance matrix [17]. From its definition, $\mathbf{K}$ is symmetrical about its leading diagonal, and each row and each column of it adds to zero; it is, therefore, a singular, equi-cofactorial matrix [7, 23], each of its n cofactors of dimension $(n-1) \times (n-1)$ having the same value — say, v.

The classic *Matrix Tree Theorem* may then be stated as follows: If $t(G)$ denote the number of spanning trees in G (i.e., its complexity), then

$$t(G) = v. \tag{1}$$

3. Other forms of the Matrix Tree Theorem

3.1. The complexity of a graph in terms of the characteristic polynomial of its Laplacian matrix

Define $\mathbf{K} = \mathbf{D} - \mathbf{A}$, as before, and let $K(x) = \det(\mathbf{Ix} - \mathbf{D} + \mathbf{A})$ be the characteristic polynomial of $\mathbf{K}$. Then

$$K(x) = \sum_{j=0}^{n} (-1)^j s_j x^{n-j},$$

where the coefficient s_j is equal to the sum of all those $j \times j$ minors of $\det(\mathbf{K})$ whose principal diagonals contain only diagonal elements of $\mathbf{K}$ [2] (and $s_0 = 1$).

Taking $j = n - 1$ and bearing in mind that, by the Matrix Tree Theorem, any $(n-1)\times(n-1)$ cofactor of **K** (and, in particular, each of the n diagonal minors of that size) is equal to the complexity, $t(G)$, of the graph, we obtain

$$t(G) = \frac{1}{n}(s_{n-1}). \tag{2}$$

Since **K** is singular, $s_n = 0$. Therefore,

$$s_{n-1} = (-1)^{n-1}\left(\frac{K(x)}{x}\right)\Bigg|_{x=0}$$

and we may write

$$t(G) = (-1)^{n-1}\frac{1}{n}\left(\frac{K(x)}{x}\right)\Bigg|_{x=0} \tag{3}$$

or

$$t(G) = (-1)^{n-1}\frac{1}{n}(K'(0)). \tag{4}$$

Alternatively, s_j can be taken as the sum of the products of the zeros of $K(x)$, the eigenvalues of **K**, taken j at a time. Setting $j = n - 1$ and remembering that one of the eigenvalues of the singular matrix **K** is 0, we obtain [17,21]

$$t(G) = \frac{1}{n}(s_{n-1})$$

$$= \frac{1}{n}\Pi\, x_k, \tag{5}$$

where the product is taken over the other $(n-1)$ eigenvalues of **K** (denoted $\{x_k\}$). We note that, as $t(G) \neq 0$, none of these is equal to 0: we may say that the product is taken over the non-zero eigenvalues of **K**.

3.2. The complexity of a regular graph in terms of the characteristic polynomial of its adjacency matrix

Define **A** as before and let $P(\lambda) = \det(\mathbf{I}\lambda - \mathbf{A})$ be the characteristic polynomial of **A**. Let r denote the degree of a regular graph, i.e., the common degree of its vertices. We observe the convention that the variable in the Laplacian polynomial is x and in the adjacency polynomial it is λ. We have

$$K(x) = \det(\mathbf{I}x - \mathbf{D} + \mathbf{A}) = \det(\mathbf{I}x - \mathbf{I}r + \mathbf{A})$$

$$= \det(\mathbf{I}(x - r) + \mathbf{A}) = (-1)^n \det(\mathbf{I}(r - x) - \mathbf{A}).$$

Comparing the last of these expressions with $P(\lambda) = \det(\mathbf{I}\lambda - \mathbf{A})$, we obtain the identity

$$P(\lambda) = (-1)^n K(r - \lambda).$$

Eqs. (3) and (4) may therefore be put in the form [17, 32]

$$t(G) = \frac{1}{n}\left(\frac{P(\lambda)}{\lambda - r}\right)\Bigg|_{\lambda = r} \tag{6}$$

and

$$t(G) = \frac{1}{n}(P'(r)). \tag{7}$$

To recast Eq. (5), we obtain from the same identity the relations

$$r - \lambda_j = x_j, \quad j = 1, 2, \ldots, n,$$

among the zeros of $K(x)$ and $P(\lambda)$, or, equally well, among the eigenvalues of $\mathbf{K}$ and $\mathbf{A}$, provided that the suffixes are assigned suitably. In passing, we note that the simple eigenvalue 0 of $\mathbf{K}$ implies that there is a simple eigenvalue r of $\mathbf{A}$ — a well-known result for a graph of degree r [16, 23, 53, 70–73]. Formula (5) now becomes [11, 22]

$$t(G) = \frac{1}{n}\Pi(r - \lambda_k), \tag{8}$$

where the product is taken over the eigenvalues $\{\lambda_k\}$ ($(n-1)$ of them) that are not equal to r.

3.3. *An adaptation of the results of the preceding section to non-regular graphs*

The addition of loops to a graph produces another of the same complexity. It is possible to add loops to a graph in such a way that the modified graph is regular. The formulae of the preceding subsection then apply to it; and its complexity, and thus also the complexity of the original graph, may be calculated from them. This is part of the concept of 'row-regularisation', introduced by Waller [70–72].

Let N be a number whose value will be discussed later. Define

$$\mathbf{A}^{\rho} = N\mathbf{I} - \mathbf{K}.$$

If N is an integer not less than the greatest d_{ii}, then $\mathbf{A}^{\rho}$ can be interpreted as the adjacency matrix of a graph modified — or 'regularised', as explained — $(N - d_{ii})$ loops having been added to vertex i. The degree of this modified graph is N and the formulae of Section 3.2 apply. Waller [70–72] sets $N = (n-1)$, Wilson [73] sets $N = \max d_{ii}$ [49].

If we leave the value of N undecided, we can still construct $P^{\rho}(\lambda) = \det(\lambda\mathbf{I} - \mathbf{A}^{\rho})$, though this will not, in general, be the characteristic polynomial of the adjacency matrix of an (unweighted) graph, merely of the matrix $\mathbf{A}^{\rho}$. However,

$$\begin{aligned} P^{\rho}(\lambda) = \det(\lambda\mathbf{I} - \mathbf{A}^{\rho}) &= \det(\lambda\mathbf{I} - N\mathbf{I} + \mathbf{K}) \\ &= (-1)^n \det((N - \lambda)\mathbf{I} - \mathbf{K}) \\ &= (-1)^n K(N - \lambda). \end{aligned}$$

$P^{\rho}(\lambda)$ is, therefore, $(-1)^n$ times the Laplacian characteristic polynomial of the original graph, with a change of variable from x to $(N - \lambda)$. There is thus no constraint on the value of N — unless a pictorial interpretation in terms of unweighted graphs is desired for an essentially algebraic manoeuvre.

4. Methods applicable to planar graphs only

Planar graphs (only) have the general property that the complexity of a graph is equal to the complexity of its dual [6]. Accordingly, any general method can be applied to the dual, with advantage if it is smaller (and, perhaps, regular). This was an idea developed by one of the present authors and Gutman and Essam [27].

In formulating and applying their theorem, Gutman et al. [27] considered a judiciously chosen cofactor of the Laplacian matrix appropriate to the complete ('geometric') dual of G — a cofactor which is, in effect, the determinant of a matrix that, itself, is a modification of the Laplacian matrix describing a graph called the 'inner dual' of G. This inner dual is obtained from the complete ('geometric') dual by deleting the so-called 'infinite-face' vertex [27], and all the edges incident upon it. The spanning-tree counting-theorem of Gutman et al. [27] then states that

$$t(G) = \det(\mathbf{B}^* - \mathbf{A}^*),$$

where $\mathbf{A}^*$ is an adjacency matrix of the inner dual and $\mathbf{B}^*$ is a diagonal matrix with elements $b_1, b_2, \ldots, b_{n^*}$, where b_i is the number of edges in the boundary of the face of G that is in 1–1 correspondence with the vertex labelled i in the inner dual (which, in total, has n^* vertices). This method, though frequently offering a major short-cut [27], does, however, apply only to *planar* graphs [27, 61, 39, 40] — which category does, of course, include the molecular graph of, for example, Buckminsterfullerene (I) and, indeed, such graphs of *all* the fullerenes. C_{60} (I) is undoubtedly *geometrically* non-planar, but, since its vertices are disposed over the surface of a sphere, its molecular graph *is*, in the *graph-theoretical* sense of the word, planar [61, 9]. Some of the present authors have already applied the theorem of Gutman et al. [27] to C_{60} (I) [9], while John and Sachs have developed an algorithmic version of it [35, 36], which has also subsequently been used to confirm the previously established [9] spanning-tree count of C_{60} (I) [34].

5. Methods for graphs with much symmetry

In two papers of comprehensive scope, Davidson [19] and Byers Brown [10] have used group-theoretical methods to determine the characteristic polynomials of symmetrical graphs. Not surprisingly, these methods show to best advantage when there is much symmetry. With remarkable anticipation, Davidson [19] crowned his exposition — published in 1981, four years before the announcement of C_{60}'s diagnosis [47], and aptly described by Byers Brown [10] as a '*tour de force*' — with a calculation of the eigenvalues of the graph representing Buckminsterfullerene! Other approaches capitalising on symmetry (including one [31] that has been applied [20] to C_{60}) have used procedures that decompose a larger ('composite' [18]) graph into smaller component-subgraphs [31, 55, 38, 28, 18, 20].

Our treatment (which we developed before these earlier papers came to our attention) is mathematically much more elementary and does not rely on the availability of character tables or on the use of any other aspects of formal group-theory [19, 10], nor does it make explicit appeal to any graph-splitting algorithms [31, 55, 38, 28, 18]. The underlying ideas are closer to Davidson's [19] than to those contained in the other papers we have mentioned that make use of symmetry [31, 55, 38, 28, 18, 10, 20].

In this section, we therefore describe in some detail how to use the symmetry of a graph to find the characteristic polynomial of its adjacency matrix as the product of factors of relatively low degree. The complexity of the graphs that are considered here, which are all regular, may be calculated as in Section 3.2. For graphs that are not regular a modification leading to the Laplacian characteristic polynomial is available; it is briefly described at the end of this section. Alternatively, one of the 'regularisation' procedures of Section 3.3 can be employed as a first step. One feature of the approach is that no special software is needed. In fact, only a hand-held calculator (albeit programmable) was used to obtain the results for the four graphs ((I)–(IV) of Fig. 1) considered in this paper. The factors of the characteristic polynomial so obtained are *intrinsically* related to (one aspect of) the graph's symmetry, and so they may perhaps be of independent interest; the eigenvectors are also available, as a by-product. This method for calculating eigenvalues was, in essence, used in our recent study of hexagonal species embedded on a torus [39]. The general isomorphism between determinants and graphs (weighted, directed and looped) should be borne in mind in this approach because some quantities or expressions that arise as determinants can conveniently be evaluated by the Sachsian method [64, 25, 1, 63].

Suppose that **T** is an automorphism of the graph which expresses one of its symmetries, i.e., which leaves connections between the vertices invariant. It is possible to select a basis for the eigenvectors of the graph so that each vector in it is invariant, up to multiplication by a non-zero constant, under **T**. Consider a particular vertex, say V_0, and apply **T** repeatedly. The vertex will pass through a succession of positions, $V_1, V_2, \ldots, V_{k-1}$, till V_k coincides with V_0. If $\mathbf{T}^k$ is not the identity, further applications of **T**, up to its period, will repeat this cycle; it is clear that k must be a factor, proper or

not, of the period of **T**. If the elements $a_0, a_1, \ldots, a_{k-1}$ of an eigenvector selected as above correspond to the vertices $V_0, V_1, \ldots, V_{k-1}$, then they must take the form

$$a_i = a\omega_A^i, \quad (i = 0, 1, \ldots, k-1)$$

for some a (possibly zero), with ω_A one of the kth roots of 1, real or complex. If these elements do not constitute the whole eigenvector we select a new vertex and perform a similar tour. Eventually, the eigenvector ($\mathbf{v}$, say) will be expressed in the form

$$\mathbf{v} = (a, a\omega_A, a\omega_A^2, \ldots, a\omega_A^{k-1}, b, b\omega_B, \ldots, c, c\omega_C, \ldots)^{\mathrm{T}}.$$

By allowing the various roots of 1 to assume all their possible values (in general, subject to certain conditions of consistency, described later), we construct the form of all the eigenvectors of the basis and from that proceed to the determination of the characteristic polynomial of the graph.

By way of illustration, let us apply what has been sketched out so far to the graph of C_{70} (III). The automorphism **T** chosen may be described as rotation through 72° ($= 2\pi/5$) about a 'North–South' axis, followed by a reflection in the plane of the 'Equator' — see structure (III), of Fig. 1, which shows the molecule metrically. It is clear that its period is 10. Sixty of the 70 vertices are arranged in six sets of 10, the remaining 10 in two sets of five. The Schlegel diagram shown in Fig. 2 indicates the 70 elements of an eigenvector alongside the corresponding vertices, by use of an abbreviated version of the notation described above. ω_A, ω_B, ω_C, ω_D, ω_E, and ω_F are all equal to ω, a 10th root of 1; ω_P and ω_Q are both equal to Ω, a 5th root of 1.

Now we return to the general case. The eigenvalue λ belonging to the eigenvector $\mathbf{v}$ obeys $\lambda\mathbf{v} = \mathbf{A}\mathbf{v}$, where $\mathbf{A}$ is the $(n \times n)$ adjacency matrix of the graph. Of the n scalar equations so represented, k will take the form

$$\lambda a\omega_A^i = \sum h\omega_H^t, \quad (i = 0, 1, \ldots, k-1),$$

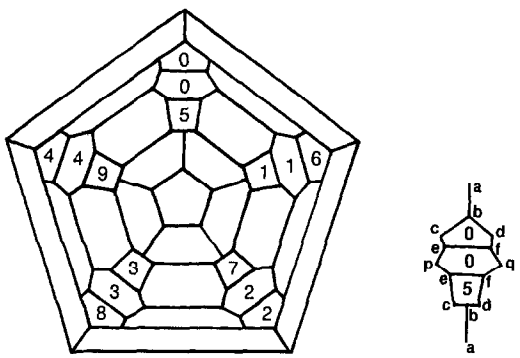

Fig. 2. A C_{70} eigenvector. To identify any element, refer to the small diagram for its 'type' ($a, b, \ldots, f, p, q$) and to the numbers for its suffix (or, equivalently, for the power of ω or of Ω). The numbers in the pentagons apply to $a, b, \ldots, f$ and those in the hexagons apply to p and q.

where the sum is taken over the vertices connected to V_i. If all the ω_H are equal to ω_A, then these k equations are not independent, each being simply a multiple of that corresponding to $i = 0$. If the ω's are not all equal, the equations will not be consistent unless certain relations hold good: these are the conditions of consistency mentioned earlier. When they are satisfied, the k equations are again simply multiples of the $i = 0$ one. Continuing in this way, we reduce the original n equations to just one for each subset of vertices related by T. We now exclude zero vectors in the usual way by requiring $\det(\lambda\mathbf{I} - \mathbf{M})$ to be 0, where $\mathbf{M}$ is the matrix of the residual set of equations, just described, and $\mathbf{I}$ is the appropriate unit matrix. If we do not solve for λ but instead evaluate the determinant in terms of it (Sachs' method [64, 25, 1, 63] is convenient for this in the C_{70} case) we obtain one factor of the characteristic polynomial from each new permitted combination of the various ω's. The complete characteristic polynomial is thus built up in factor form.

Apply the foregoing to the graph of C_{70}, referring to Fig. 2 as required. Four equations contain only ω (and not p, q or Ω) and so are part of the reduced set as they stand. They are

$$\begin{aligned}
\lambda a &= (\omega^4 + \omega^6)a + b \\
\lambda b &= a + c + d \\
\lambda c &= b + \omega^4 d + e \\
\lambda d &= b + \omega^6 c + f
\end{aligned}$$

The remaining four are typified by

$$\begin{aligned}
\lambda e &= c + f + p \\
\lambda f &= d + e + q \\
\lambda p &= (1 + \omega^5)\,e + \Omega^4 q \\
\lambda q &= (1 + \omega^5)\,f + \Omega p
\end{aligned}$$

and all the equations of this type are mutually consistent if and only if $(\omega - \Omega)p = 0$, $(\omega - \Omega)q = 0$, $(\omega - \Omega)(1 + \omega^5)e = 0$, $(\omega - \Omega)(1 + \omega^5)f = 0$. If $\omega = \Omega$, then each must have one of the values $\cos(\frac{2\pi}{5}t) + \mathrm{i}\sin(\frac{2\pi}{5}t)$ for $t = 0, 1, 2, 3, 4$. Since the matrix $\mathbf{M}$ is (8×8), this supplies $5 \times 8 = 40$ of the 70 degrees of the characteristic polynomial. If $p = 0$, $q = 0$, then either $e = 0$, $f = 0$ or $(1 + \omega^5) = 0$. The former leads to $a = b = c = d = 0$ and so is not admissible. The latter requires $\omega = \cos(\frac{\pi}{5} + \frac{2\pi}{5}t) + \mathrm{i}\sin(\frac{\pi}{5} + \frac{2\pi}{5}t)$ for $t = 0, 1, 2, 3, 4$. The matrix $\mathbf{M}$ is now only (6×6) and so $5 \times 6 = 30$ of the 70 degrees, all that remain, are supplied.

The two determinants $\det(\lambda\mathbf{I} - \mathbf{M})$ are conveniently evaluated by drawing up the related looped and weighted directed graphs and using Sachs' method [64, 25, 1, 63]. The factors of degree 8 are

$$\begin{aligned}
&\lambda^8 - k\lambda^7 - 12\lambda^6 + 10k\lambda^5 + (k^2 - 3k + 41)\lambda^4 + (3k^2 - 26k - 2)\lambda^3 \\
&\quad - (6k^2 - 12k + 44)\lambda^2 - (5k^2 - 19k - 2)\lambda - (2k^3 - 7k^2 + 5k - 10),
\end{aligned}$$

where $k = 2\cos(\frac{2\pi}{5}t)$ for $t = 0, 1, 2, 3, 4$.

When $t = 0$, the expression can be written as

$$(\lambda - 3)(\lambda + 1)(\lambda^2 - 2)(\lambda^2 - 2\lambda - 1)(\lambda^2 + 2\lambda - 2),$$

showing the factor $(\lambda - 3)$ which must be identified to calculate the complexity by the formula

$$\frac{1}{70}\left(\frac{P(\lambda)}{(\lambda - 3)}\right)\Bigg|_{\lambda=3},$$

where $P(\lambda)$ is, in this case, the characteristic polynomial of the molecular graph of C_{70} (III).

The factors of degree 6 are

$$\lambda^6 + k\lambda^5 - 7\lambda^4 - 5k\lambda^3 + (k^2 + k + 10)\lambda^2 + (k^2 + 5k - 2)\lambda - (k^2 + 3k + 2),$$

where $k = 2\cos(\frac{\pi}{5} + \frac{2\pi}{5}t)$ for $t = 0, 1, 2, 3, 4$.

The numerical stage of the calculation is made more convenient by the observation that all the factors must take the form $(u + v\sqrt{5})$, where u and v are rational numbers and the surds (if $v \neq 0$) must appear in conjugate pairs. Those occurring in the factors of degree 8 are $1125 \pm 323\sqrt{5}$, those in the factors of degree 6 are $325 \pm 70\sqrt{5}$.

The complexities of the three other graphs among those considered (structures (I)–(IV) shown in Fig. 1) were also calculated by this method. The reader may find that picking labour-saving automorphisms has some interest.

To adapt the method to graphs that are not regular we may proceed as described till the stage of evaluating the determinants by Sachs' method [64, 25, 1, 63] is reached. From $(\mathbf{I}\lambda - \mathbf{M})$ we now construct $(\mathbf{I}x - \mathbf{D} + \mathbf{M})$ where $\mathbf{D}$ is the diagonal matrix showing the original degrees of the vertices concerned (as defined in Section 2). This is done by modifying the weights of the loops and changing the signs of the edge-weightings. We can now find the characteristic polynomial of the Laplacian matrix of the graph (or just the term in x) and thence the complexity as the absolute value of the coefficient of x divided by the number of vertices (as per Eqs. (2) and (3) in Section 3). This adaptation is useful when the smaller but non-regular dual of a planar graph is used to calculate its complexity — i.e., when the method of this section is combined with the key idea of Gutman et al. [27] (Section 4). For example, for Buckminsterfullerene (I), the calculations involve only graphs with 3 or 4 vertices, and, for Archimedene (IV), only graphs of 6 or 7 vertices.

6. Calculations

In calculating the complexities of the representative fullerenes (I)–(IV), we have used the following methods of computation.

Method A. This is based on the ideas of Section 3 (Eq. (6)). The required characteristic polynomials of the appropriate adjacency matrices were obtained by (i) taking the

available [4, 5, 48] four-decimal-place eigenvalues and finding the polynomials (irreducible over the integers) of which they are the approximate zeros, and (ii) using these to reconstitute the characteristic polynomial, $P(\lambda)$, of the graph in question, factorised over the integers. Attention paid to the multiplicities of the various zeros greatly facilitates this reconstitution. It should be noted that some care was needed over this: the published values of Balasubramanian and Liu [4, 5] contained errors [52, 3] but Liu's thesis [48] — kindly supplied to us by Professor Balasubramanian [3] — reports more-accurate data. The polynomials deduced by this process (conveniently presented for computation of $(P(\lambda)/(\lambda - 3))|_{\lambda=3}$), are the following.

C_{60}(I) Buckminsterfullerene:

$$(\lambda - 3)(\lambda + 2)^4(\lambda - 1)^9(\lambda^2 + 3\lambda + 1)^3(\lambda^2 + \lambda - 4)^4$$

$$(\lambda^2 + \lambda - 1)^5(\lambda^2 - \lambda - 3)^5(\lambda^4 - 3\lambda^3 - 2\lambda^2 + 7\lambda + 1)^3.$$

C_{60}(II) ('hand' form):

$$(\lambda - 3)\lambda^{10}(\lambda + 2)^{11}(\lambda^2 - \lambda - 1)^4(\lambda^2 - \lambda - 3)^4$$

$$(\lambda^2 - \lambda - 4)^5(\lambda^4 - 2\lambda^3 - 5\lambda^2 + 6\lambda + 4)^3.$$

C_{120} (IV) ('Archimedene):

$$(\lambda - 3)(\lambda + 3)(\lambda - 1)^6(\lambda + 1)^6(\lambda^4 - 4\lambda^3 + \lambda^2 + 6\lambda + 1)^3$$

$$(\lambda^4 + 4\lambda^3 + \lambda^2 - 6\lambda + 1)^3(\lambda^4 - 6\lambda^2 + 2\lambda + 2)^4(\lambda^4 - 6\lambda^2 - 2\lambda + 2)^4$$

$$(\lambda^5 + 3\lambda^4 - 3\lambda^3 - 11\lambda^2 - \lambda + 3)^5(\lambda^5 - 3\lambda^4 - 3\lambda^3 + 11\lambda^2 - \lambda - 3)^5.$$

It may be noted that C_{120} (IV) has a bipartite molecular graph — this is what in chemical jargon is called an 'alternant hydrocarbon' [53] — since it has no odd-membered fundamental circuits (in chemical terminology: it has no odd-membered rings). Since, in addition, the graph of C_{120} has an even number of vertices, the characteristic polynomial of the adjacency matrix of (IV) is an *even* function [53], as found when, in the above, factors of like multiplicity are combined together. Thus, the characteristic polynomial of C_{120} (IV) just stated may also be written:

$$(\lambda^2 - 9)(\lambda^2 - 1)^6(\lambda^8 - 14\lambda^6 + 51\lambda^4 - 34\lambda^2 + 1)^3$$

$$(\lambda^8 - 12\lambda^6 + 40\lambda^4 - 28\lambda^2 + 4)^4(\lambda^{10} - 15\lambda^8 + 73\lambda^6 - 133\lambda^4 + 67\lambda^2 - 9)^5.$$

Method B. This was the device of Gutman et al. [27], described in Section 4, applicable because the fullerenes do have planar molecular graphs. Modular arithmetic was invoked in order precisely to evaluate the resulting 21-digit complexity on a personal computer and without special software — as described by Brown et al. in [9]. This method was used only for C_{60} (Buckminsterfullerene) (I).

Method C. This again exploits the theorem of Gutman et al. [27] (Section 4), but the exact complexities were evaluated directly on a NeXT workstation, by means of versions 2.0, 2.1 and 2.2 of the software Mathematica [74].

Method D. Like Method B, this procedure was applied only to C_{60} (Buckminsterfullerene) (I). It consists of using the algorithmic version of the Gutman–Mallion–Essam approach [27], devised by John and Sachs [35, 36]. For C_{60} (Buckminsterfullerene) (I), this algorithm reduces the size of the determinant to be evaluated from (31×31) to (11×11) — as fully described in [34].

Method E. This is the scheme described in Section 5, appropriate for highly symmetric graphs. All four species (I)–(IV) of Fig. 1 were treated by this method.

7. Results

(a) C_{60} *(I) Buckminsterfullerene*: Methods A–E all confirm the complexity as

375 291 866 372 898 816 000,

or, as a product of powers of prime numbers,

$$2^{25} \times 3^4 \times 5^3 \times 11^5 \times 19^3 \ (\approx 3.75 \times 10^{20}).$$

This value, computed by Methods B and D, has been reported previously, in Refs [9] and [34], respectively. Trinajstić and co-workers have also recently confirmed it, on two occasions [57, 69], by Method A — they used Eq. (5). It should be noted that although the complexity of C_{60} (I) expressed as powers of prime numbers given in [34] agrees with the above, there is a mis-print in the 21-digit number claimed in [34] to be its equivalent; the 12th figure of this integer should be '2' (as here, and as in [9, 57, 69]), rather than the '3' unintentionally alleged in [34].

(b) C_{60} *(II) ('hand' form)*. Methods A, C and E give the complexity as

4 982 259 375 000 000 000,

which is equal to

$$2^9 \times 3^{13} \times 5^{14} \ (\approx 4.98 \times 10^{18}).$$

(c) C_{70}*(III)*. By Methods C and E, we obtain for the complexity

1 136 544 737 068 261 950 000 000,

which is

$$2^7 \times 3^1 \times 5^8 \times 11^2 \times 13^1 \times 59^2 \times 37199^2$$

i.e., approximately 1.14×10^{24}.

(d) C_{120} *(IV) ('Archimedene')*. Methods A, C and E give the complexity as

21 789 262 703 685 125 511 464 767 107 171 876 864 000,

which, as a product of powers of prime numbers, is

$$2^{31} \times 3^{15} \times 5^{3} \times 7^{4} \times 17^{5} \times 23^{4} \times 181^{3}$$

or, approximately, 2.18×10^{40}.

8. Conclusions and assessment

The several methods discussed have their own respective benefits and snags. Method A is very convenient if, as in the case of (I), (II) and (IV), characteristic polynomials or eigenvalues of **K** or **A** are easily obtainable. Procedures based directly on the Matrix Tree Theorem (Section 2 — Eq. (1)) generally require appropriate software and suitable machines for the input and evaluation of determinants that are not only large in dimension — at least (59×59), for application of the Matrix Tree Theorem to either C_{60} structure — but are also large in value (ca. 3.75×10^{20} for C_{60} (I)). The latter problem may be overcome by taking advantage of modular arithmetic, as in Method B, a generally applicable method, if the calculations involve only integers; knowledge of an upper bound for the result is, however, a prerequisite. The difficulties caused by the large dimensions of the determinants under study may partly be obviated for planar graphs (as in Methods B, C and D) by capitalising on the theorem of Gutman et al. ([27], Section 4) which makes use of the inner dual — but all the disadvantages already stated still apply if the dual itself is also large. (For C_{120} (IV), use of the inner dual would lead to the evaluation of a (61×61) determinant instead of a (119×119) one.) Method D [34] can further reduce the determinant size — e.g., for C_{60} (I) from (31×31) by Methods B and C down to (11×11) [34] — although the algorithm involved does require some considerable practice and skill for its successful application (see, for example, Ref. [34]).

The approach that we found suitable for those not having access to special software and/or large computers, and one of only two methods among Methods A–E that we have tested on each of the species (I)–(IV), is Method E. It must, however, be emphasised that a great deal of symmetry is necessary if the reduction in determinant size is to be of value. Although (or, maybe, because) it has the rustic attraction of being, in favourable cases, a 'pencil-and-paper' scheme, Method E — at least in our hands — tended to attract careless errors when a Sachsian evaluation [64, 25, 1, 63] was involved. Checking is therefore essential.

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Matrix Tree Theorem, in the mathematical and electronics literature, of which, previously, we had been unaware.

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