Journal of Mathematical Chemistry 15 (1994) 261–271

An algorithmic approach to the number of spanning trees in Buckminsterfullerene*

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Received 18 December 1992; revised 14 October 1993

The algorithm of John and Sachs (1990), based on the theorem of Gutman, Mallion and Essam (1983), is applied to give an independent count of the number of spanning trees in the recently synthesised sixty-carbon-atom cluster Buckminsterfullerene (icosahedral C_{60}, footballene, soccerballene, etc.). If the original "Matrix-Tree" theorem is used to solve this problem, a 59×59 determinant needs to be evaluated; the method of Gutman et al. reduces this requirement to the development of a 31×31 determinant; the John–Sachs algorithm further reduces this problem to the computation of an 11×11 determinant. The "complexity" of Buckminsterfullerene is confirmed to be

$$2^{25} \times 3^4 \times 5^3 \times 11^5 \times 19^3,$$

which is of the order of 3.75×10^{20}. Attention is redirected to the observation that *any specified one* of these numerous spanning trees could be selected as the starting point if a standard calculation were to be made of the relative π-electron "ring-current" intensities extant in icosahedral C_{60}.

1. Introduction

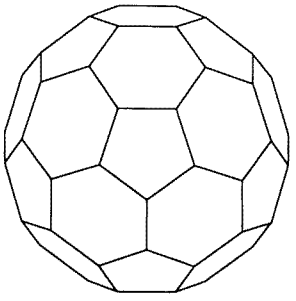
Counting the spanning trees in an electrical network (or, more generally, a graph) is an old problem that goes back to Kirchhoff in 1847 [1] – see also refs. [2] and [3] for a historical account of this subject. Some years ago, one of us (R.B.M.), with Gutman and Essam [2], invoked use of the inner dual of a given network/graph, together with the generalised characteristic polynomial [4] of that inner dual, in order to simplify the problem of spanning-tree enumeration in a general, planar graph. The other of the present authors (P.J.), with Sachs [5], later devel-

* Dedicated to Professor Horst Sachs, on the occasion of his 65th birthday.

oped an algorithmic approach to the 1983 theorem of Gutman et al. [2]; this algorithm is described in detail in ref. [5]. In the meantime, it was pointed out [6] that this theorem [2] (and, consequently, the algorithm devised in connection with it [5]) also holds true when the planar graph in question is embedded on the surface of a sphere. In 1983, when the method of Gutman et al. was originally proposed [2], the prospect of its application to a graph embedded in this way was of only academic interest, because the main use of the theorem was for counting the spanning trees in graphs that represent conjugated-hydrocarbon molecules [2]. However, since the diagnosis [7] of Buckminsterfullerene (also since known as icosahedral C_{60}, soccerballene, footballene, etc. – see fig. 1) in 1985, an opportunity to apply this theorem to a molecular graph just so embedded arises quite naturally [6]. Furthermore, as the *concept* of spanning trees is encountered when calculating so-called "ring-current" effects in conjugated molecules [8–14], consideration of the spanning trees latent within the Buckminsterfullerene molecular graph would be relevant to a proper theoretical treatment of the ^{13}C-NMR spectrum of that species [13–15], if such could be obtained – for, until recently, this spectrum was, itself, hypothetical. The remarkable synthesis of Buckminsterfullerene in macroscopic quantities, announced in 1990 by Krätschmer et al. [16], has, however, enabled this goal instantly to be realised, in the form of the ^{13}C-NMR spectrum of icosahedral C_{60} published immediately afterwards [17,18]. These recent experimental developments of the last few years could therefore be said to make an immediate application of Gutman et al.'s 1983 theorem [2] to Buckminsterfullerene especially timely [3]. Accordingly, in this communication, we choose to adopt the algorithmic version [5] of that theorem [2], referred to earlier, in order to confirm [3] the number of spanning trees in icosahedral C_{60}.

2. Application of the algorithm of Sachs and John to the molecular graph of Buckminsterfullerene

For brevity, we give only the essential details here. For a full description of the algorithm being used, the reader is referred to ref. [5]; for a definition of any graph-



I

Fig. 1. Three-dimensional perspective view of the molecular graph (*I*) of Buckminsterfullerene (Icosahedral C_{60}).

theoretical terms not specifically explained, ref. [4], for example, may profitably be consulted.

Let G be a labelled graph. A *spanning tree* of G is a tree of G which covers all the vertices of G. Denote by $t(G)$ the number of all spanning trees; ($t(G)$ is also called the "complexity" of G). Let I denote the graph of icosahedral C_{60} (Buckminsterfullerene, soccerballene, footballene, etc. – see fig. 1) and let F be an embedding of I (drawn with D_{5h} symmetry) in the plane, effected in such a way that F has no edge cuts. (F is thus, in essence, the Schlegel diagram of C_{60}, also illustrated in refs. [19] and [3]). F divides the plane into 31 finite regions $R_f, f = 1, 2, \ldots, 31$,and one infinite region (see fig. 2). Let $B_f = B(R_f)$ denote the boundary of the finite region R_f, and let $l_f = l(B_f)$ stand for its length; (in the case of the Buckminsterfullerene molecular graph, l_f will always be either 5 or 6). The inner dual $D = D(F)$ of F is the dual of F without the vertex that corresponds to the infinite region of F; (i.e., it is the dual of F with what is sometimes called the "infinite-face vertex" – and all edges incident upon it – deleted). Note that D has the vertex set $V(D) = \{v_1, v_2, \ldots, v_{31}\}$, where v_f is in 1-1 correspondence with the finite region R_f. A representation of D – with D_{5h} symmetry – is given in fig. 3; in that figure, vertices of the inner dual that lie within a five-membered ring in the embedding, F (fig. 2), of the original molecular graph, I (fig. 1), are denoted by filled circles, and those vertices of the inner dual that lie within a six-membered ring in F are depicted as open circles. Let

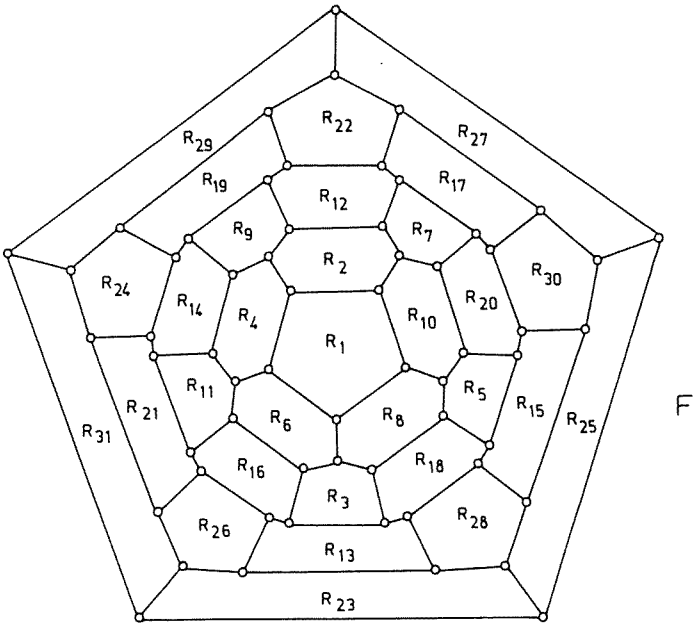


Fig. 2. Embedding (F) of the Buckminsterfullerene molecular graph (I) in the plane, effected in such a way that F has no edge cuts. This "Schlegel Diagram", F, of I, drawn with D_{5h} symmetry, depicts the division of the plane into 31 finite regions $R_f, f = 1, 2, \ldots, 31$, and one infinite region.

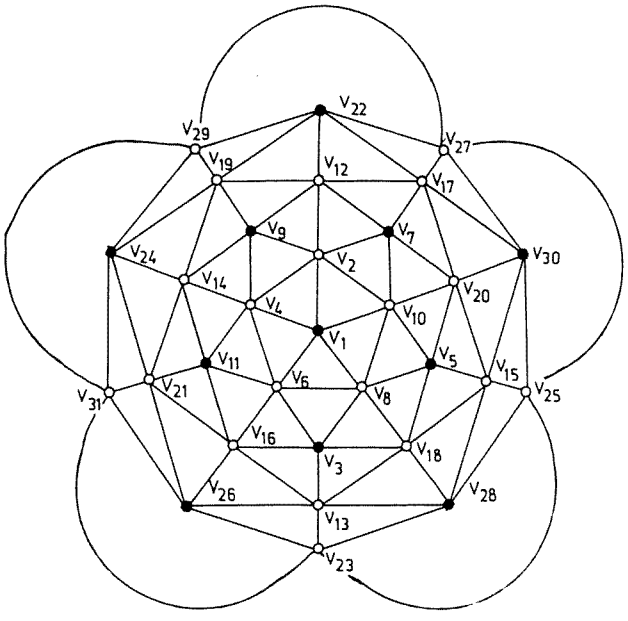


Fig. 3. The inner dual, D $(= D(F))$, of F, drawn with D_{5h} symmetry. This is the dual of F with the "infinite-face" vertex – and all edges incident upon it – suppressed. The vertices of D are $v_f, f = 1, 2, \ldots, 31$. Vertices of D that lie within a five-membered ring in the embedding, F, of I are denoted by filled circles; those vertices of D that lie within a six-membered ring in F are depicted as open circles.

$A = A(D)$ be the (0, 1)-adjacency matrix of the inner dual, and define also the matrix $W = (w_{fi}), i = 1, 2, \ldots, 31$, with

$$w_{fi} = \begin{cases} l_f & \text{if } f = i, \\ 0 & \text{if } f \neq i, \end{cases}$$

as the vertex-weight matrix of D. Note that l_f is the weight of vertex $v_f, f = 1, 2, \ldots, 31$.

According to the theorem of Gutman et al. [2],

$$t(F) = \det(W - A). \tag{1}$$

We are now in a position to explain in detail an application to icosahedral C_{60} of the algorithm given in ref. [5].

With the vertices of D labelled as in fig. 3, we define two (non-disjoint) subsets of $V(D)$,

$$V^s(D) = \{v_1, v_2, v_3, \ldots, v_{11}\} \quad \text{and}$$

$$V_s(D) = \{v_1, v_{22}, v_{23}, \ldots, v_{31}\},$$

as sets of what we shall call [5], respectively, *source points* and *sink points*, of D. The elements of both sets are connected by pairwise-disjoint "linear segments" [5],

arranged in a "star-shape" [5] and covering all vertices of $V(D)$. These "star segments", $S_k, k = 1, 2, \ldots, 11$, in D reduce to a single point in the case of $k = 1$ and, for $k = 2, 3, \ldots, 11$, they connect source point s^k (defined to be equal to v_k), of a given star segment S_k, with sink point s_k (defined to be equal to v_{20+k}) of that same star segment, as drawn in fig. 4. In that figure, "source" vertices are shown as large, open circles, "sink" vertices as small, filled circles, and vertices that are neither "source" nor "sink" ones are represented simply as the points of intersection of two or more edges of D. In what follows, therefore, the points $s^1, s^2, \ldots, s^{11}$ will be referred to as the "source vertices of D". As prescribed in the algorithm devised in ref. [5], every star segment S_k of D is now extended beyond its sink point s_k by connecting s_k with an additional, so-called "virtual" [5], vertex s_k^*; let the path S_k^* denote the star segment S_k prolonged in this way by extension as far as its "virtual" vertex, s_k^*. Finally, direct all paths *from* "source" *to* "sink"; D is thereby transformed into a diagram (presented as fig. 5) that we shall call D^*. In fig. 5, "source" vertices are shown as large, open circles, "sink" points are depicted as small, filled circles, and "virtual" vertices are denoted by small, open circles; all the other vertices (not classified as "source", "sink" or "virtual") are just represented as points of intersection of two or more edges of D^*. (The reader is alerted here to the unfortunate possibility of confusion that could arise as a result of our use of this "asterisk" notation. This is because the basis of the present collaborative paper

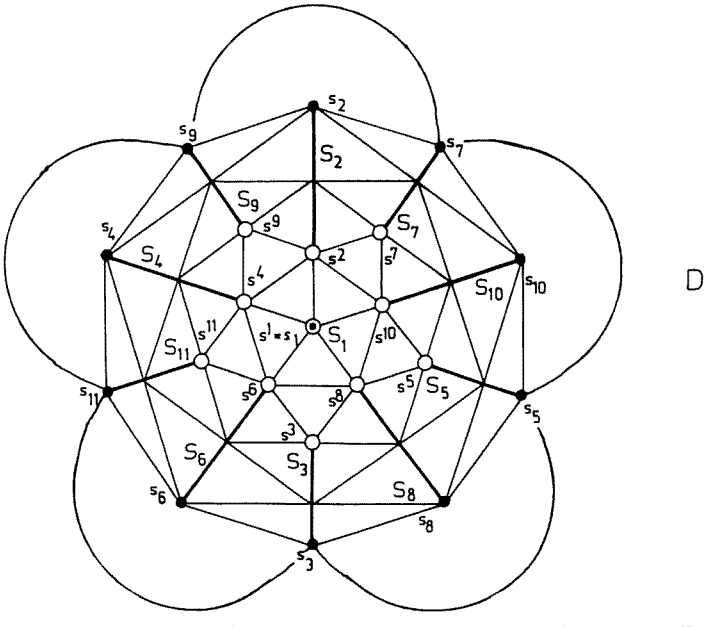


Fig. 4. "Star segments" S_k, in D, which, for each k ($k = 2, 3, \ldots, 11$), connect "source points" s^k ($:= v_k$) with their respective "sink points" s_k ($:= v_{20+k}$); when $k = 1$, this segment reduces to a single point. "Source" vertices are shown as large, open circles, "sink" vertices as small, filled circles, and vertices that are neither "source" nor "sink" ones are represented simply as the points of intersection of two or more edges of D.

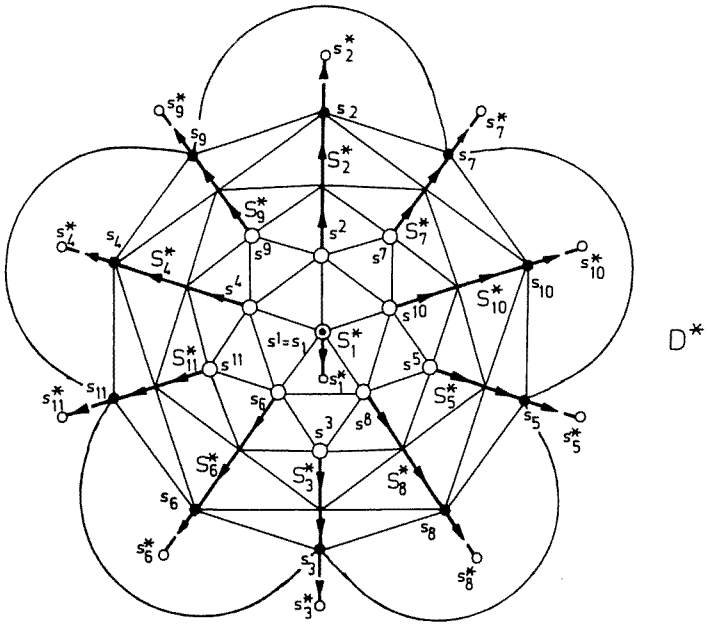


Fig. 5. The diagram referred to as "D^*", in which every "star segment" S_k of D (fig. 4) is extended beyond its "sink point" s_k by connecting s_k with an additional "virtual" vertex s_k^*. S_k^* is the "star segment" S_k so extended, and all paths are directed *from* "source" *to* "sink". "Source" vertices are shown as large, open circles, "sink" points are depicted as small, filled circles, "virtual" vertices are denoted by small, open circles, and all other vertices (not classified as "source", "sink" or "virtual") are just represented as points of intersection of two or more edges of D^*.

from Canterbury and Ilmenau is to make appeal to the results contained in two of our respective earlier works, prepared independently of each other – the 1983 theorem of Gutman, Mallion and Essam [2] and the 1990 algorithm of John and Sachs [5]. Gutman et al. [2] used "G^*" to denote the inner dual of a graph G, of which the complete ("geometric") dual would, in their terminology, be called "G^+". In the current analysis, *we* are using the notation introduced by John and Sachs [5] and described in detail, above. Consequently, the adoption of the superscripts "$*$" and "$+$" in some of the symbolism invoked here does, regrettably, have *no* connection with the way in which they were used by Gutman et al. in ref. [2] – even though the present paper *is* very much based on the *results* of that latter work!)

Now let v be a vertex (which is not a source point) of D^* lying on path S_k^*, say. Vertex v has a unique immediate predecessor on S_k^* which we denote by v^+; let $N(v^+)$ be the set of all neighbours of v^+ in D^*, and denote by $N^+(v)$, defined as being equal to $N(v^+) - \{v\}$, the set of those neighbours of v^+ in D^* that are distinct from v. To every vertex v of D^* we may assign a vector

$$\boldsymbol{c}(v) = (c_1(v)\ c_2(v)\ c_3(v) \ldots c_{11}(v))^{\mathrm{T}}$$

by means of the following recursive procedure:

(i) For each source vertex, s^k, $k = 1, 2, \ldots, 11$, consider forming the vector

$$\boldsymbol{c}(s^k) = (\delta_{1k}\ \delta_{2k}\ \delta_{3k} \ldots \delta_{11k})^{\mathrm{T}}$$

where

$$\delta_{lk} = \begin{cases} 1 & \text{if } l = k, \\ 0 & \text{if } l \neq k \end{cases}$$

($l = 1, 2, \ldots, 11$).

When a given vertex has been thus encountered, and its associated vector has been formed in this way, we shall refer to that vertex as having been "marked". ("Marking" a vertex z may be thought of as a process in which the vector $\boldsymbol{c}(z)$ is written down beside the vertex z; this is, of course, to be considered as only figurative and in most cases it is in fact more practical to arrange the vector list in a tabular form, as we shall do presently in the current application of this algorithm).

(ii) Let v be a vertex of D^* not so far encountered and "marked" as described above, and suppose that v^+ and all vertices of $N^+(v)$ have already been dealt with ("marked") and that v^+ has weight $w(v^+)$; now mark v and put

$$\boldsymbol{c}(v) = w(v^+)\boldsymbol{c}(v^+) - \sum_{v' \in N^+(v)} \boldsymbol{c}(v') .$$

By running through all the vertices of D^* from the centre outwards, it is straightforward successively to calculate, in this way, all the required vectors $\boldsymbol{c}(v)$ (which are uniquely determined).

Finally, form the matrix

$$\begin{aligned} \boldsymbol{C}^*(D) &= (\boldsymbol{c}(s_1^*)\ \boldsymbol{c}(s_2^*)\ \boldsymbol{c}(s_3^*) \ldots \boldsymbol{c}(s_{11}^*)) \\ &= [c_l(s_k^*)]; \quad l = 1, 2, \ldots, 11, \\ &\qquad\qquad k = 1, 2, \ldots, 11 . \end{aligned}$$

The matrix $\boldsymbol{C}^*(D)$ that results from an application of the above recursive scheme to icosahedral C_{60} is presented in table 1.

By appeal to theorem 6 of ref. [5], we may finish this process by concluding that

$$\begin{aligned} t(F) &= \det \boldsymbol{C}^*(D) \quad (D = D(F)) \\ &= \text{the complexity of icosahedral } C_{60} . \end{aligned} \tag{2}$$

3. Numerical calculations

Calculating the number of spanning trees in Buckminsterfullerene by the algorithmic approach [5] adopted here thus amounts to evaluating the determinant of the (11×11) matrix $\boldsymbol{C}^*(D)$, the individual elements of which are displayed in the

Table 1
The matrix $C^*(D) = [c_l(s_k^*)]$.

k	l										
	1	2	3	4	5	6	7	8	9	10	11
1	5	−1	0	−1	0	−1	0	−1	0	−1	0
2	−121	415	−2	79	−30	−17	−178	−17	−178	79	−30
3	154	−4	415	140	79	−484	−17	−484	−17	140	79
4	−121	79	−30	415	−2	79	−30	−17	−178	−17	−178
5	154	140	79	−4	415	140	79	−484	−17	−484	−17
6	−121	−17	−178	79	−30	415	−2	79	−30	−17	−178
7	154	−484	−17	140	79	−4	415	140	79	−484	−17
8	−121	−17	−178	−17	−178	79	−30	415	−2	79	−30
9	154	−484	−17	−484	−17	140	79	−4	415	140	79
10	−121	79	−30	−17	−178	−17	−178	79	−30	415	−2
11	154	140	79	−484	−17	−484	−17	140	79	−4	415

table. The advantages of the present algorithmic procedure [5] are thus manifest, for application [3] of the original theorem of Gutman et al. [2] to this same problem requires [3] finding the determinant of a (31 × 31) matrix – and, if the standard "matrix-tree" theorem [4] had been applied in order to count the number of spanning trees in icosahedral C_{60}, the value of a (59 × 59) determinant would have to have been calculated. Even so, a difficulty that *is* still encountered when computing the determinant of the matrix $C^*(D)$ shown in table 1 – and one that is also met with when the original, unmodified theorem of Gutman et al. [2] is applied directly to the Buckminsterfullerene molecular graph [3] – is that the complexity in question is an *integer* of the order of 10^{20}, the value of which is required *precisely*. This necessitates display of a number of significant figures which is outside the range of most large computers, and is certainly beyond that of the computers to which the present authors had access in this work. This difficulty is essentially just a computational (though by no means trivial) problem, the resolution of which has been fully described elsewhere [3] – several mathematical and computational devices need to be invoked, including the use of modulo arithmetic and the storage of numbers as arrays [3], and knowledge is, furthermore, required of the approximate order-of-magnitude of the quantity being calculated [3]. The result is

$$\det(C^*(D)) = t(F) = \text{the complexity of icosahedral } C_{60}$$
$$= 375\,291\,866\,373\,898\,816\,000\,,$$

which, factorised as powers of prime numbers, is

$$2^{25} \times 3^4 \times 5^3 \times 11^5 \times 19^3\,.$$

4. Concluding remarks

By way of conclusion, it may in passing be mentioned that (as has been emphasised before [2,3,9–11,20–22]) *any desired one* of these approximately 3.75×10^{20} spanning trees extant within the molecular graph of Buckminsterfullerene may be selected as a starting point for effecting a calculation of the molecule's relative π-electron "ring-current" intensities by an application of the now-classic method due to McWeeny [8–12,20–23]. In that approach, knowledge is assumed of the standard ("field-free") basis atomic-orbitals – i.e., the orbitals as they would be in the absence of any magnetic field – and then a clever unitary transformation [8–12] is performed on the field-influenced orbitals in such a way that all the perturbation brought about by the presence of an applied, external, magnetic field is concentrated into *just one* bond in *each* of the *rings* (in the chemical sense of that term) contained within the conjugated molecule under study. These latter (called by McWeeny [8] "circuit–completing bonds") are precisely the bonds that are in 1-1 correspondence with those edges which, if added to an appropriate spanning-tree of the molecular graph in question, would cause that original parent molecular graph to be reconstituted [11]. The relevance that the *concept* of spanning trees, discussed here, has to "ring-current" calculations is thus manifest.

The unitary transformation originally put forward by McWeeny [8] may be applied if the spanning tree selected is "unbranched" (i.e., if it represents a Hamiltonian path through the parent molecular graph in question [11]); otherwise, if the chosen spanning-tree is "branched" (i.e., if it does *not* represent a Hamiltonian path through the parent molecular graph [11]), a modified (and more general) unitary transformation, devised more than a decade later by Gayoso and Boucekkine [10], must be invoked. As has been pointed out previously [8–12,20–22], because the final, relative "ring-current" intensities evaluated by the McWeeny method are invariant to the choice of the particular spanning-tree on which the calculation is based, there are necessarily many more relationships between the bond orders and the self- and mutual *imaginary* bond–bond polarisabilities (molecular-orbital indices that arise in the McWeeny formalism [8–12,20–23]) than there are among the bond orders and the corresponding *real* bond–bond polarisabilities, originally introduced, more than 10 years before McWeeny's [8] work, by Coulson and Longuet-Higgins [24]. It has been noted [3] that there are 4095 imaginary bond–bond polarisabilities ($^{90}C_2$ "mutual" ones, and 90 "self" ones), as well as 90 bond orders, associated with the 90 carbon–carbon bonds of icosahedral C_{60}, and that – because of symmetry and the constraints on these quantities arising from the invariance of calculated relative "ring-current" intensities to the choice of which spanning tree is adopted for their computation – only a very small proportion of these 4185 numerical entities will, in practice, actually be *distinct*.

A further chemical implication of the complexity of a graph representing a molecule lies in the area of chemical nomenclature. Any notation for a given molecule and its derivatives involves selecting what amounts to a spanning tree of the mole-

cule in order to label its vertices and then produce the required linear notation [25,26]. The complexity is a measure of how easy or difficult it will be to identify and compare derivatives, on such an indexing scheme.

The main thrust of this work, however, has been to illustrate a specific application, to a molecule of currently very wide chemical interest, of a particular determinant-reduction algorithm [5]. If the original "Matrix-Tree" theorem [4] had been used to count the spanning trees in icosahedral C_{60}, a co-factor of a (60×60) matrix would have been needed; if the method of Gutman et al. [2] is applied in its original form, it is possible [3] to solve the problem by evaluating a (31×31) determinant, to a minimum of 21 significant figures. This may be done by invoking some devices in modulo arithmetic [3], or – by use of recently available commercial programs such as Mathematica – directly [27]. In the work described here, we have applied a simple and easily handled algorithm to reduce even this 31st-order determinant to one of (11×11). Because of the exceptionally high symmetry possessed by icosahedral C_{60}, it is possible to use the five-fold symmetry inherent within our (11×11) determinant (see the table) in order to factorise it into the product of two (2×2) determinants, both squared, and one (3×3). The hand-calculated result, in terms of powers of prime numbers, agrees with the one given here. P. Pollak (a colleague of R.B.M.) has also confirmed the quoted result "by hand", by capitalising [28] on this same symmetry as displayed by the (60×60) matrix that features in an application of the original "Matrix-Tree" theorem [4] to C_{60}.

Acknowledgements

R.B.M. thanks his colleague Mr. P. Pollak, M.A., of the King's School, Canterbury, and his former pupil Mr. T.J.N. Brown, O.K.S. (also once of the King's School, and now of St. John's College, Oxford) for their kind and invaluable help with computation of the determinant shown in table 1, by the methods described in ref. [3].

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