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VALENCE ISOMERS FOR CHEMICAL TREES

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Abstract

The concept of a degree partition matrix, an element of which is the number of graph theoretic 4-trees having a specified point degree partition, is discussed and the availability of data in this format is announced. Comments are also made about symmetry numbers which are derived from the automorphism group of a tree and the role these numbers play in relating degree partition classes to valence classes of chemical trees.

1. Introduction

We have recently obtained and displayed in a particularly convenient format, the number of 4-trees in a specified degree partition class [1]. This was done for a reasonably extensive set of classes and for five types of trees: 4-trees which are rooted at points of degree 1, 2, 3, or 4, and unrooted (free) 4-trees.

Chemical interpretations of such trees are well known. For example, they can be viewed as the carbon skeletons of monosubstituted

alkanes and alkanes respectively [2 and references therein]. In other contexts these 4-trees can be viewed as skeletons of more general chemical trees. In particular, this is the case in polymer chemistry where the detailed structure of a chemical unit can be dispensed with and the unit depicted simply as a point (see [3] and [4]). (Note that here the degree of a point need not be bounded by 4.) Furthermore, the degree partition classes obtained can be interpreted as a refinement of constitutional isomerism classes to constitutional valence isomerism classes, i.e., in the case of alkanes the skeletons are classified according to the numbers of primary, secondary, tertiary, and quaternary carbons. Thus, it seems worthwhile to announce the availability of this data and to give a brief description of our investigations along these lines.

2. Degree partition matrices

A 4-tree is a graph theoretic tree whose every point has degree no greater than 4. A 4-tree having n points, of which p, s, t, and q are of degree 1, 2, 3, and 4 respectively, is said to be in the degree partition or valence class (n; p,s,t,q). In view of the relations

$$p + s + t + q = n$$

$$p + 2s + 3t + 4q = 2(n - 1)$$

any three of the numbers n, p, s, t, and q determine, for a given 4-tree or class, the remaining two values. We have chosen n, t, and q as our parameters. Thus, when n, t, and q are specified we have

$$p = 2 + t + 2q$$

$$s = n - 2 - 2t - 3q \tag{2.1}$$

For a given value of n, we define the degree partition matrix M(n) as the $(t^* + 1)x(q^* + 1)$ matrix shown below, where M_{ntq} is the number of elements in the valence class (n; p,s,t,q) and t^* and q^* are respectively the largest values of t and q such that the $(t + 1)$ row and $(q + 1)$ column of M(n) each have a nonzero entry.

$M(n) =$

n	0	1	2	...	q^*
0					
1					
2					
3			M_{ntq}		
⋮					
t^*					

The entries in the matrices M(n) are the coefficients of counting series which were derived using a relatively straightforward application of the 3-variable form of Pólya's Theorem. The technical problem was that of obtaining an efficient computer program which would generate the explicit values of these coefficients. We are interested in finding a computer algorithm, if such exists, which would substantially lower the computation time used.

The data in [1] consists of the following tables:

Table R_1. Degree partition matrices for rooted 4-trees having n points and root degree 1 with $2 \leq n \leq 27$.

Table R_2. Degree partition matrices for rooted 4-trees having n points and root degree 2 with $3 \leq n \leq 27$.

Table R_3. Degree partition matrices for rooted 4-trees having n points and root degree 3 with $4 \leq n \leq 26$.

Table R_4. Degree partition matrices for rooted 4-trees having n points and root degree 4 with $5 \leq n \leq 25$.

Table F. Degree partition matrices for free 4-trees having n points with $1 \leq n \leq 25$.

Table N. Numbers of 4-trees of a specified type.

As an illustration we display here the degree partition matrix for free 4-trees (alkanes) on 25 points (see Figure 1).

Currently, in work with P. Brown and M. Schiano, we are analyzing distributions of various types of 4-trees by (i) obtaining descriptive observations for the explicit numerical data we have generated and (ii) seeking asymptotic formulas which are valid for large values of n.

3. Discussion

It is important to note that degree partition matrices provide only a first approximation to the distribution of the associated chemical trees. This approximation assumes that all trees are equally likely to occur and, in general, this does not adequately describe the distribution of a specified class of chemical trees. It is postulated that in a random mixture of isomers, each isomer occurs in inverse proportion to a symmetry number associated with that isomer ([4] and

25	0	1	2	3	4	5	6	7
0	1	108	3059	22913	54440	42310	9741	463
1	48	4330	69428	299742	394990	153328	13539	89
2	1335	62845	565819	1362042	929736	154337	3218	0
3	16597	426820	2135031	2728439	859118	44621	0	0
4	107168	1506770	4055704	2524028	295683	1933	0	0
5	379274	2878649	3916775	1017639	26983	0	0	0
6	758629	2978091	1831225	145329	0	0	0	0
7	856310	1604291	360507	3483	0	0	0	0
8	530211	408151	20483	0	0	0	0	0
9	167708	39054	0	0	0	0	0	0
10	23368	672	0	0	0	0	0	0
11	983	0	0	0	0	0	0	0

FIGURE 1. Valence isomers for the alkanes with 25 carbons

[5]). Examples of symmetry numbers are the orders of various groups which can be associated with a chemical graph. One such group is G, the (graph theoretic) automorphism group of the chemical graph being considered. Although G may be readily determined for an individual graph, one often is working with a class of graphs for which G is not the same for each graph in the class. Thus, either one uses an average value of $|G|$ (the order of G) for the given class or, as was done in [5], one introduces a symmetry number which is uniquely related to a specified class of graphs. In particular it was suggested in [5] that, if n, the number of carbons, is large, then the elements of the group of a tree representing an alkane consist predominantly of peripheral permutations, i.e., those which permute the hydrogens while leaving the carbons fixed. This suggests the use of $2^s 6^p$ in place of $|G|$, where s and p are as defined in Section 2. As an application, this symmetry number was used to obtain a good statistical estimate of the radius of convergence for the alkane isomers counting series. For further discussion of the uses of G see [5 and references therein]. With respect to large trees of bounded degree > 4, the asymptotic analysis of points by degree and orbit size developed in [6] is expected to be quite useful in the study of both the distributions of polymer trees and the automorphism groups of these trees.

In the context of our work we note that the reciprocal of the symmetry number $2^s 6^p$ can conveniently be used as a statistical weight for degree partition classes. This is so because each tree in a given

class has the same symmetry number, i.e., if a 4-tree T is in class (n; p,s,t,q), then by (2.1)

$$2^s 6^p = 2^n 9(3/2)^t (9/2)^q$$

Therefore, a weighted degree partition matrix obtained from the matrix M(n) with entries M_{ntq} is the matrix W(n) with entries M_{ntq}/S_{ntq}, where $S_{ntq} = 2^n 9(3/2)^t (9/2)^q$.

Although S_{ntq} was originally intended as a symmetry number for large values of n, it is nevertheless the order of a subgroup of G and as such, with possible modifications, it may be of interest to seek statistical weighting applications of it for chemical 4-trees having relatively small values of n. Toward this end S_{ntq} need not necessarily be thought of as an approximation to $|G|$ but can possibly be thought of as a weight which takes into account the physical distinction between the entities represented by the points of the skeleton (e.g., the centres noted in [4]) and those represented by the terminal points of the chemical tree.

In conclusion we note that symmetry numbers are the source of only one type of statistical weighting. Clearly, other considerations play a role in the probabilistic existence of chemical species. For example, there are the spacial and energetic requirements discussed in [2] and [7]. We expect to incorporate these ideas into the theory of molecular distributions.

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