The Permanental Polynomial

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This study identifies properties and uses of the permanental polynomial of adjacency matrixes of unweighted chemical graphs. Coefficients and zeroes of the polynomial for several representative structures are provided, and their properties are discussed. A computer program for calculating the permanental polynomial from the adjacency matrix is also described.

INTRODUCTION

The adjacency matrix, **A**, of a chemical graph of n vertexes is simply an $n \times n$ matrix consisting of elements $a_{i,j}$ that are 1 if vertexes i and j define an edge and otherwise are 0.

The characteristic polynomial of this matrix, $P(G,x) = \det(x\mathbf{I} - \mathbf{A})$, where det is the determinant, **I** is the identity matrix of appropriate size, and x is a variable that is not assigned a single numeric value, has been reported frequently and has been used widely.[1] Methods of computing this polynomial were recently reviewed.[2] The permanental polynomial is similarly defined as $P^{\mathrm{per}}(G,x) = \mathrm{per}(x\mathbf{I} - \mathbf{A})$. However, with some exceptions,[3−9] little about this polynomial or its potential applications seems to have been published. This may be due to the difficulty of actually computing the permanent per($x\mathbf{I} - \mathbf{A}$). Many shortcuts exist for computing determinants of matrixes, whereas only a few methods exist for permanents.[10−15] Indeed, there appears to be no published method for computing the entire permanental polynomial, as opposed to just the permanent, which is the last coefficient of the polynomial. One can write an equation such as $P^{\mathrm{per}}(G,x) = \mathrm{per}(x\mathbf{I} - \mathbf{A})$, and ref 8 presents a form involving symbolic partial derivatives, but no scheme has appeared for evaluating these equations within an available time frame.

The permanent of a matrix, **A**, may be expressed as

$$\mathrm{per}(\mathbf{A}) = \sum a_{i,1}a_{j,2}a_{k,3}...a_{x,n} \qquad (1)$$

where n is the order of the matrix and the summation is over all possible products of the elements such that $i, j, k, ..., x$ are all different. Thus, for a general $n \times n$ matrix, the permanent is the sum of $n!$ terms, each of which is the product of n elements. A frequently cited result is that the permanent of an $n \times n$ matrix of all 1's is $n!$. Most of the elements in an adjacency matrix are 0, so most of the terms in the summation are also 0, but any algorithm that computes per(**A**) within a reasonable period of time by evaluating the sum must identify and eliminate these terms without actually computing them. The algorithms in refs 9 and 10 accomplish this by pruning a tree that would ultimately have $n!$ leaves. The algorithm makes its way through the matrix looking for nonzero contributions to the sum. When it encounters a 0 element, it prunes off the entire branch structure that begins with that element (since the product of the elements is 0 if any element is 0), thus eliminating a large number of leaves from consideration. By repeated application of this reduction to an adjacency matrix, even a tree of 50! ($\sim 3 \times 10^{64}$) leaves can be pruned to a size manageable on a desktop computer.

Table 1. Coefficients of Characteristic and Permanental Polynomials of Representative Structures

	benzene		*o*-biphenylene		coronene		C_{20} fullerene	
x	char	per	char	per	char	per	char	per
24					1	1		
23					0	0		
22					−30	30		
21					0	0		
20					387	387	1	1
19					0	0	0	0
18					−2832	2832	−30	30
17					0	0	0	0
16					10359	13059	375	375
15					0	0	−24	−24
14					−39858	39858	−2540	2540
13					0	0	480	−480
12			1	1	82281	82305	10095	10215
11			0	0	0	0	−3760	−3760
10			−14	14	−115272	115512	−23502	25590
9			0	0	0	0	14400	−14880
8			69	73	108192	109128	28905	42145
7			0	0	0	0	−27000	−32280
6	1	1	−154	178	−65864	67592	−11400	48720
5	0	0	0	0	0	0	20000	−39520
4	−6	6	162	214	24432	25872	−6000	38640
3	0	0	0	0	0	0	0	−26400
2	9	9	−72	120	−4896	5328	0	16400
1	0	0	0	0	0	0	0	−6240
0	−4	4	9	25	400	400	0	1392

COMPUTATIONAL METHODS

When the elements of **A** are all integers, as in an adjacency matrix, per(**A**) will also be an integer. Per($x\mathbf{I} - \mathbf{A}$), however, will be a polynomial in x of degree n. This is the permanental polynomial of the chemical graph G for which **A** is the adjacency matrix. All of the elements of $x\mathbf{I} - \mathbf{A}$ are x, 0, or −1. Therefore, all nonzero contributions to the summation in eq 1 will have the form $(-1)^{n-i}x^i$. For even n, they will

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all be x when i is even and $-x$ when i is odd. In the present study, the computer code in ref 10 is modified to take advantage of that fact in computing $P^{per}(G,x)$.

At the heart of this algorithm is the augmented adjacency matrix $\mathbf{AAM} = \mathbf{A} + \mathbf{I}$. Herndon[16] has used the augmented adjacency matrix for canonical labeling of vertexes in chemical graphs and has extended its use to the concept of "most-connected" vertex in a sense that includes extended connectivity.[17] Equations 2−4 show the three relevant matrixes for benzene. The salient points here are that **AAM** and $x\mathbf{I} - \mathbf{A}$ have the same pattern of zero−nonzero entries, and that **AAM** is a 1,0 matrix.

$$\mathbf{A} = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 1 \\ 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 \\ 1 & 0 & 0 & 0 & 1 & 0 \end{bmatrix}$$

$$\mathbf{AAM} = \begin{bmatrix} 1 & -1 & 0 & 0 & 0 & -1 \\ -1 & 1 & -1 & 0 & 0 & 0 \\ 0 & -1 & 1 & -1 & 0 & 0 \\ 0 & 0 & -1 & 1 & -1 & 0 \\ 0 & 0 & 0 & -1 & 1 & -1 \\ -1 & 0 & 0 & 0 & -1 & 1 \end{bmatrix} \qquad (2-4)$$

$$x\mathbf{I} - \mathbf{A} = \begin{bmatrix} x & -1 & 0 & 0 & 0 & -1 \\ -1 & x & -1 & 0 & 0 & 0 \\ 0 & -1 & x & -1 & 0 & 0 \\ 0 & 0 & -1 & x & -1 & 0 \\ 0 & 0 & 0 & -1 & x & -1 \\ -1 & 0 & 0 & 0 & -1 & x \end{bmatrix}$$

The computer code presented in ref 10 finds the permanent of a 1,0 matrix in which all rows and columns have two or three nonzero entries, a property of adjacency matrixes of polycyclic aromatic hydrocarbons (PAHs) and fullerenes. To find the entire permanental polynomial, the code in ref 10 was modified so that it handles matrixes with three or four nonzero entries in each row and column and so that, as it searches through the matrix for nonzero contributions to the sum in eq 1, it keeps a running total of the number of active $a_{i,j}$ for which $i = j$. Finally, when the program finds a nonzero contribution, instead of incrementing a counter in which the permanent is kept, it increments one of $n + 1$ counters selected according to the number of $a_{i,j}$ for which $i = j$. When the program so modified operates on the augmented adjacency matrix, it produces a vector of $n + 1$ integers that are the absolute values of the coefficients of the permanental polynomial of the unaugmented adjacency matrix **A**. As explained above, the negative numbers in $x\mathbf{I} - \mathbf{A}$ can be dealt with because, for even n, even powers of x in the polynomial have positive coefficients and odd powers of x have negative coefficients. The code could be modified slightly to handle odd n. CPU time for computing the permanental polynomial with this code scales approximately as 2^n. With a 233 MHz Pentium II CPU, C_{32} fullerenes take 4.3−4.5 h, and C_{36} fullerenes take 58−74 h. Structures with divalent vertexes will generally compute faster than fullerenes of an equal number of carbons, and the coefficients will be smaller, because their adjacency matrixes contain fewer nonzero elements.

Factors and zeros of the polynomials were calculated with Mathematica using its built-in Factor[] and NSolve[] functions. In all cases, polynomial coefficients were cut and pasted into Mathematica, so there were no transcription errors.

RESULTS AND DISCUSSION

Polynomial Coefficients. In both the characteristic polynomials of even alternants, all the coefficients of odd powers of x are 0, the coefficient of the highest power of x is +1, and the signs on the nonzero coefficients alternate. The permanental polynomials share the first two properties, but all the nonzero coefficients are positive (since they are all coefficients of even powers of x). Kasum et al.[3] pointed out that, for chains, $4n + 2$ cycles, and catacondensed benzenoids, the coefficients of the characteristic and permanental polynomials differ only in sign. Although Kasum et al. did not give any examples, they pointed out that this relationship also extends in general to all bipartite graphs with no $4n$ cycles, e.g., trees with branches. The relationship does not extend to alternants with $4n$ cycles, such as [N]phenylenes and pericondensed benzenoids. Even for *o*-biphenylene ([2]-phenylene), the coefficients of the two polynomials are very different. Table 1 lists characteristic and permanental coefficients for a few representative structures.

Comparing the absolute values of the corresponding characteristic and permanental polynomials is of interest. As noted above, for certain structures, of which benzene is an example in Table 1, the absolute values are identical. For *o*-biphenylene, however, only the first two nonzero values are the same. Since *o*-biphenylene is an alternant structure, the last coefficient of the permanental polynomial is equal to K^2, the square of the Kekulé structure count,[18] whereas, as in general for nonbenzenoid alternants, the last coefficient of the characteristic polynomial is not. For the benzenoid structure coronene, the first six nonzero coefficients of the two polynomials have the same absolute values. It is not known whether this number (six) is the same for all benzenoids. Since coronene is a benzenoid, the last coefficient of the two polynomials is also identical (and equal to K^2). For the unique C_{20} fullerene, the first eight coefficients have the same absolute values. Balasubramanian,[19] adapting work published by Dias,[20] showed that these coefficients for characteristic polynomials of all C_n fullerenes depend only on n. His formulas may also apply to the permanental polynomials, but that has yet to be determined.

For alternant structures, an interesting comparison can be made with a point raised by Cvetković et al.[13] concerning the permanent. If an alternant graph is partitioned into starred and unstarred vertexes in the usual manner, and the starred vertexes are numbered 1 through $n/2$ and the unstarred $n/2 + 1$ through n, the adjacency matrix will have the blocked form

$$\mathbf{A} = \begin{bmatrix} \mathbf{0} & \mathrm{B} \\ \mathbf{B}^{\mathrm{T}} & \mathbf{0} \end{bmatrix} \qquad (5)$$

where $\mathbf{B}^{\mathrm{T}}$ is the transpose of **B** and **0** is an $n/2 \times n/2$ matrix

Table 2. Zeroes of Characteristic and Permanental Polynomials of Representative Structures[a]

benzene		*o*-biphenylene		coronene		C_{20} fullerene	
char	per	char	per	char	per	char	per
±2	±2i	±2.532	±2.153i (2)	±2.675	0.264 ± 0.825i	3	0.402 ± 0.545i
±1 (2)	±i (2)	±1.802	±1.314i (2)	±2.214 (2)	0.207 ± 1.441i	√5 (3)	0.390 ± 0.280i
		±1.347	±0.789i (2)	±1.675 (2)	0.207 ± 1.441i	1 (5)	0.284 ± 0.965i
		±1.247		±1.539	0 ± 2.671i	0 (4)	0.283 ± 2.778i
		±0.897		±1.214	0 ± 2.309i	−2 (4)	0.095 ± 2.596i
		±0.445		±1 (3)	0 ± 2.087i	−√5 (3)	0.0002 ± 2.186i
				±0.539 (2)	0 ± 0827i		−0.008 ± 1.698i
					0 ± 0.390i		−0.334 ± 1.448i
					0 ± 1.000i		−0.384 ± 2.135i
					−0.264 ± 0.825i		−0.729 ± 1.091i
					−0.207 ± 1.441i		
					−0.207 ± 1.441i		

[a] The numbers in parentheses indicate the multiplicity of the roots of the polynomials.

of all 0's. Since, in general, the permanent of a square matrix equals the permanent of its transpose, per(**A**) = [per(**B**)]^2. Therefore, since for an alternant structure per(**A**) = K^2, the square of the Kekulé structure count, it is also true for alternants that K = per(**B**). Thus, for an n-vertex alternant, per(**A**) can be found by evaluating an $n/2 \times n/2$ matrix. The Factor[] function, which factors symbolic polynomials in Mathematica, shows that no similar simplification can apply to the entire permanental polynomial because most permanental polynomials examined in detail so far have no factors smaller than themselves. (That is, factors with all integer coefficients; obviously, any polynomial with roots r_i has factors $x - r_i$.) This property is in sharp contrast to the characteristic polynomials, which typically have several factors. An exception is *o*-biphenylene, for which $x^{12} + 14x^{10} + 73x^8 + 178x^6 + 214x^4 + 120x^2 + 25 = (x^6 + 7x^4 + 12x^2 + 5)^2$. It is obvious, however, that $x^6 + 7x^4 + 12x^2 + 5$ is not the permanental polynomial of any unweighted graph. It is equal to the permanental polynomial of 3,3-dimethylhexane divided by x^2, but this is probably a coincidence. It is not known whether this result is unique to *o*-biphenylene or is a property of some more general class of structures. The permanental polynomials of linear [3]phenylene and [4]-phenylene, however, have no factors.

An entire class of structures for which the permanental polynomial has factors is the non-Kekuléan alternants. For all such structures, per(**A**) = 0 (since by definition $K = 0$). Therefore, the permanental polynomial will be divisible by at least x^2. Several non-Kekuléan alternants were tested where the numbers of starred and unstarred vertexes were not the same, i.e., $s - u \neq 0$, and all these polynomials were divisible by at least x^{s-u}. The matching polynomial shares this property, a fact exploited recently by Dias.[21]

Given this finding for $s - u \neq 0$ alternants, theoretical considerations alone dictate that non-Kekuléan alternants with $s - u = 0$ cannot follow the same pattern. Since per(**A**) = 0, the permanental polynomials of such structures must be divisible by at least x^2 and must have at least two 0 roots. Smaller concealed non-Kekuléan benzenoids with $s - u = 0$ have been enumerated.[22] The smallest one is $C_{38}H_{18}$, and the next smallest are the two $C_{40}H_{20}$, three $C_{42}H_{20}$, and five $C_{42}H_{22}$ isomers. One might presume that the permanental polynomials of all these structures have two and only two 0 roots, but no confirmation seems to have been published.

Zeros. The zeros of all the permanental polynomials examined in the present study have the form $x \pm y$i, where $i^2 = -1$ and $y \neq 0$. By contrast, the zeros of characteristic polynomials of chemical graphs are all real. For *o*-biphenylene, the zeros of the permanental polynomial are all imaginary. This is not generally true for other alternants, but Klein states[23] that it will be true for the class of graphs discussed in ref 2, which includes all catacondensed alternants. Coronene has six pairs of complex zeros and six pairs imaginary. It is not known whether all alternants have some imaginary zeros with no real component. All of the nonalternants studied to date, including several fullerenes to be reported separately, have all zeros complex and none purely imaginary. Table 2 lists the zeros of the characteristic and permanental polynomials for the same four structures whose polynomial coefficients appear in Table 1.

CONCLUSIONS

Computer code was developed for calculating all the coefficients of permanental polynomials of adjacency matrixes. Using this code, the fastest PC-compatible desktop computers currently available (≥500 MHz) should accommodate matrixes as large as 40 × 40. For nonalternant structures and alternant structures containing 4n cycles, the coefficients and zeros of the permanental polynomial are very different from those of the commonly used characteristic polynomial. With the permanental polynomial now open to computation, a great deal of work remains to be done to characterize the relationship of that polynomial to chemical structure and properties.

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