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Chemical Graph Theory. III[1]. On the Permanental Polynomial

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The permanental polynomial of a graph is presented. It is shown how it could be constructed by means of the Sachs formula. The recursion relations for calculation of the permanental polynomials of chains (linear polyenes) and cycles (annulenes) are given. The properties of the coefficients of the permanental polynomial are discussed. The connection between the characteristic and permanental polynomials is described.

The *permanent* of the adjacency matrix, per *A*, is only occasionally employed in chemical research.[2–5] The corresponding *permanental polynomial* so far has not been utilized in chemistry. The permanent of the adjacency matrix possesses convenient properties[6–8] for its use in chemistry, e. g. in the enumeration of Kekulé structures.[2] These data are needed, for example, in the Herndon structure-resonance theory[9] or in the Randić theory of conjugated circuits.[10] Here we wish to review some properties of permanents and, in the light of the recent interest in the graph-theoretical polynomials of chemical (molecular) graphs,[1,11] to discuss the permanental polynomial, to investigate its properties, and to demonstrate its relationship to the structure of (conjugated) molecules. In addition, the connection between the permanental polynomial and the characteristic polynomial will be discussed.

1.1 *Definition*

The permanent of the adjacency matrix $A = [a_{ij}]$, $i, j = 1, 2, \ldots, N$, is defined by[8,12]

$$\text{per } A = \sum_{\sigma} a_{1\sigma(1)} \cdot a_{2\sigma(2)} \cdot \ldots a_{N\sigma(N)} \tag{1}$$

where the summation extends over the N! permutations of the integers $\sigma(1)$, $\sigma(2), \ldots, \sigma(N)$.

The adjacency matrix of a graph *G* with N vertices, $A(G) \equiv A$, is the square $N \times N$ matrix in which $a_{ij} = 1$, if a vertex *i* is adjacent to a vertex *j*, $a_{ij} = 0$ otherwise.[13] Thus, the adjacency matrix *A* is a symmetric binary matrix with zero entries along the main diagonal. The polynomial $\det |xI - A| = 0$, where *I* is the unit matrix, is called the characteristic polynomial of a graph G.

Let us denote by $A(i_1, i_2, \ldots, i_k \mid j_1, j_2, \ldots, j_k)$, $i_1 < i_2 < \ldots < i_k \leqslant N$, $j_1 < j_2 < \ldots < j_k \leqslant N$, a matrix which is generated from *A* by the removal of rows $i_1, i_2, \ldots, i_k$ and columns $j_1, j_2, \ldots, j_k$, respectively. Then, the property of the permanent of A equivalent to the Laplace expansion of a determinant is given by

$$\text{per } A = \sum_{j=1}^{N} a_{ij} \text{ per } A\,(i|j) \text{ for every } i \in \{1, 2, \ldots, N\} \tag{2}$$

The polynomial per $|xI - A| = 0$ will be called the permanental polynomial of a graph G. We will show later the close relationship that exists between the characteristic polynomial and the permanental polynomial of G, in some special cases, and how in such a case one graph-theoretical structure may be converted into the other.

1.2 *Lemma*[8]

Let the elements a_{ij} of A be continuous functions of some real variable x. Then the derivative of the permanent of A is

$$(\text{per } A)' = \sum_{i=1}^{N} \text{per} \begin{bmatrix} a_{11} & \cdots & a_{1N} \\ \vdots & & \vdots \\ a'_{i1} & \cdots & a_{iN} \\ \vdots & & \vdots \\ a_{N1} & \cdots & a_{NN} \end{bmatrix} \tag{3}$$

Proof

The derivation of per A produces (making use of definition (1))

$$(\text{per } A)' = \sum_{\sigma} (a'_{1\sigma(1)} \cdot a_{2\sigma(2)} \cdot \ldots \cdot a_{N\sigma(N)} + a_{1\sigma(1)} \cdot a'_{2\sigma(2)} \cdot \ldots \; a_{N\sigma(N)} + \ldots + a_{1\sigma(1)} \cdot a_{2\sigma(2)} \cdot \ldots \cdot a'_{N\sigma(N)}) \tag{4}$$

After the appropriate permutation of the elements in (4) is carried out, the relationship (3) is obtained and thus the Lemma is proved.

1.3. *Lemma*[8]

Let the matrix A be a matrix with the constant coefficients. Then,

$$\text{per } |xI - A| = \sum_{k=0}^{N} c_k x^{N-k} \tag{5}$$

where

$$c_0 = 1 \tag{6}$$

and

$$c_k = (-1)^k \sum \text{per } A\,(i_1, \ldots, i_{N-k} | i_1, \ldots, i_{N-k}) \tag{7}$$

The summation in (7) is over all the ordered $(N\text{-}k)$-tuples $(i_1, \ldots, i_{N-k})$ and $i_1 < i_2 < \ldots < i_{N-k} \leqslant N$.

Proof

Let

$$\text{per } |xI - A| = x^N + c_1 x^{N-1} + c_2 x^{N-2} + \ldots + c_N \tag{8}$$

Then,

$$c_N = \text{per } |xI - A|\,|_{x=0} = \text{per } |-A| = (-1)^N \text{ per } A \tag{9}$$

$$c_{N-1} = (\text{per } |xI - A|\,|_{x=0})' =$$

$$\left(\sum_{i=1}^{N} \text{per} \begin{vmatrix} x-a_{11} & \cdots\cdots\cdots & \cdots\cdots\cdots & -a_{1N} & \\ \vdots & & \vdots & \vdots & \\ 0 & \cdots\cdots\cdots & 1 \cdots\cdots\cdots & 0 & \text{the } i\text{-th row} \\ \vdots & & \vdots & \vdots & \\ -a_{N1} & \cdots\cdots\cdots & \cdots\cdots\cdots & x-a_{NN} & \end{vmatrix} \right)_{x=0} \quad \text{(the } i\text{-th column)} \tag{10}$$

By using (1) and substituting $x = 0$ in (10) we obtain

$$c_{N-1} = (-1)^{N-1} \sum_{i} \text{per}\, \mathbf{A}\, (i \,|\, i) \tag{11}$$

$$c_{N-2} = (\text{per}\, |\, xI - A \,|)'\, |'_{x=0} = (\sum_{i_1} \text{per}\, |\, xI - A \,|\, (i_1 \,|\, i_1))'\, |_{x=0}$$

$$= (\sum_{i_1<i_2} \text{per}\, |\, xI - A \,|\, (i_1 i_2 \,|\, i_1 i_2))\, |_{x=0} = (-1)^{N-2} \sum_{i_1<i_2} \text{per}\, \mathbf{A}\, (i_1 i_2 \,|\, i_1 i_2) \tag{12}$$

Following the analogous reasoning for other coefficients, one can set the master expression for a given coefficient as follows,

$$c_{N-t} = (-1)^{N-t} \sum_{i_1<i_2<\ldots<i_t} \text{per}\, A\, (i_1 i_2 \ldots i_t \,|\, i_1 i_2 \ldots i_t) \tag{13}$$

or

$$c_k = (-1)^k \sum_{i_1<i_2<\ldots<i_{N-k}} \text{per}\, A\, (i_1 i_2 \ldots i_{N-k} \,|\, i_1 i_2 \ldots i_{N-k}) \tag{14}$$

1.4 *Definition*

Let G be a graph with N vertices,

$$V(G) = \{v_1, v_2 \ldots, v_N\} \tag{15}$$

A Sachs graph[14] (mutation graph[15], sesquivalent graph[8]) G' is a subgraph of G whose components are regular graphs of degree 1 and/or 2, i. e. K_2 and C_m ($m = 3, 4, 5, \ldots, N$) graphs. K_2 is a regular graph of degree 1, i. e. ○——○, whilst C_m are regular graphs of degree 2, i. e. cycles.

1.5 *Proposition*

The permanent of the adjacency matrix A may be given in terms of the Sachs graphs, so

$$\text{per}\, A = \sum 2^{c(G')} \tag{16}$$

where the summation is over all Sachs graphs G' for which $V(G) = V(G')$, i. e. G' are in this case spanning subgraphs while $c(G')$ is the number of cycles in G'.

Proof

The proof is analogous to the proof for det A given by Harary.[16]

1.6 *Proposition*[17]

Let G be a graph with N vertices and A be its adjacency matrix, then

$$\text{per}\, |\, xI - A \,| = \sum_{k=0}^{N} c_k x^{N-k} \tag{17}$$

where

$$c_0 = 1 \tag{18}$$

and

$$c_k = (-1)^k \Sigma 2^{c(G')} \tag{19}$$

The summation in (19) is over all Sachs graphs G' with k vertices.

Proof

Σ per $A(i_1, \ldots, i_{N-k} \mid i_1, \ldots, i_{N-k})$ is the sum of all permanents of the submatrices obtained by removing the rows and columns $i_1, \ldots, i_{N-k}$ from A. These submatrices are really the adjacency matrices of the corresponding subgraphs with k vertices generated from G. Every Sachs graph G' with k vertices is contained in one of these subgraphs and by applying the proposition 1.5 to each of the submatrices the following results are obtained.

1.7 *Corollary*

(*i*) $c_1 = 0$ (20a)

(*ii*) c_2 = the number of edges in G (20b)

(*iii*) $-c_3$ = twice the number of C_3 cycles in G (20c)

(*iv*) For bipartite (bichromatic) graphs $c_N = K^2$ (20d)

where K is the number of 1-factors (Kekulé structures) in G (conjugated molecule).

A bipartite graph G is a graph whose vertex-set $V(G)$ can be partitioned into two subsets $V_0(G)$ and $V_*(G)$ such that every edge of G joins $V_0(G)$ with $V_*(G)$. In chemistry the alternant structures[18] can be depicted by the bipartite graphs.

Proof

(*i*) Since per $A(i_1, \ldots, i_{N-1} \mid i_1, \ldots, i_{N-1})$ equals the diagonal element of A, which by definition is zero, c_1 is also zero.

$$\text{per } A\ (i_1, \ldots, i_{N-1} \mid i_1, \ldots, i_{N-1}) = 0 = c_1 \tag{21}$$

(*ii*) per $A(i_1, \ldots, i_{N-2} \mid i, \ldots, i_{N-2})$ differs from zero only if it is of the form.

$$\text{per } A\ (i_1, \ldots, i_{N-2} \mid i_1, \ldots, i_{N-2}) = \text{per}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} = 1 \tag{22}$$

The submatrix in (22) corresponds to the adjacency matrix of an individual edge in G. Thus, the c_2 coefficients are equal to the number of these submatrices, which in turn is equal to the number of edges in G.

(*iii*) There exist only three kinds of submatrices of the type $A(i_1, \ldots, i_{N-3} \mid i_1, \ldots, i_{N-3})$. Characteristic representatives of these submatrices are the following,

$$\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad \begin{bmatrix} 0 & 1 & 1 \\ 1 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix} \quad \begin{bmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{bmatrix} \tag{23}$$

However, only the last one has a permanent different from zero. This submatrix corresponds to the adjacency matrix of the C_3 ring. Therefore, the number of these matrices will give the number of C_3 rings in G. Factor 2 appears because for each C_3 ring the permanent of the corresponding adjacency matrix is equal to 2.

(*iv*) The result (20d) follows directly from the well-known result for bipartite graphs,[2,17]

$$\text{per } A = K^2 \tag{24}$$

and the relation

$$c_N = (-1)^N \text{ per } A \tag{25}$$

Note that if N is odd, then necessarily per $A = K = 0$.

Let the characteristic polynomial of the graph G be defined as,[17,19]

$$\det |xI - A| = \sum_{k=0}^{N} a_k x^{N-k} \tag{26}$$

and, in particular,

$$a_N = (-1)^N \det A \tag{27}$$

Then by the Sachs theorem,[14,17,19]

$$a_0 = 1 \tag{28}$$

and

$$a_k = \Sigma (-1)^{e(G')} 2^{c(G')} \tag{29}$$

where e is the total number of Sachs graphs in G'.

The summation in (29) is over all Sachs graphs G' with k vertices.

1.8 *Proposition*

If G is a bipartite graph which does not contain (4m)-membered cycles, then for $k = 0, 1, 2, \ldots$,

$$a_{2k} = (-1)^k c_{2k} \tag{30}$$

and, of course,

$$a_{2k+1} = c_{2k+1} = 0 \tag{31}$$

The proposition applies to chains (linear alkanes), cycles (annulenes) and cata--fused benzenoids.

As a consequence of relation (30), the recurrence formulae for permanental polynomials of *chains* (representing [N]-polyenes) and cycles (representing [N]-annulenes) may easily be produced from the knowledge of the corresponding characteristic polynomials. The characteristic polynomials of chains and cycles are symbolized, for brevity, by L_N and C_N. The corresponding permanental polynomials are denoted by $P(L_N)$ and $P(C_N)$, respectively.

(a) Chains

The recurrence relation which enables the calculation of the characteristic polynomials of linear polyenes is given by,[20]

$$L_N = xL_{N-1} - L_{N-2} \tag{32}$$

The recurrence relation for the permanental polynomials of polyenes is simply,

$$P(L_N) = x\,P(L_{N-1}) + P(L_{N-2}) \tag{33}$$

starting with $P(L_0) = 1$ and $P(L_1) = x$. The analytical expression for zeros of the permanental polynomials of polyenes is given by,

$$x_k = 2i \cos \frac{k\pi}{N+1}\ ; \ k = 1,2,\ldots, N \qquad (34)$$

Eqs. (32) and (33) are related by,

$$L_N(x) = (-i)^N P(L_N, ix) \qquad (35)$$

Example

L_2 L_3 L_4 L_5 L_6

$$P(L_2) = x\,P(L_1) + P(L_0) = x^2 + 1$$
$$P(L_3) = x\,P(L_2) + P(L_1) = x^3 + 2x$$
$$P(L_4) = x\,P(L_3) + P(L_2) = x^4 + 3x^2 + 1$$
$$P(L_5) = x\,P(L_4) + P(L_3) = x^5 + 4x^3 + 3x$$
$$P(L_6) = x\,P(L_5) + P(L_4) = x^6 + 5x^4 + 6x^2 + 1$$

A general formula for the permanental polynomial of a linear polyene chain with N atoms is given by,

$$P(L_N) = x^N + \frac{(N-1)}{1!}x^{N-2} + \frac{(N-2)(N-3)}{2!}x^{N-4} + \frac{(N-3)(N-4)(N-5)}{3!}x^{N-6} +$$
$$+ \ldots + \frac{(N-k)(N-k-1)\ldots(N-2k+1)}{k!}x^{N-2k} + \ldots \qquad (36)$$

(b) Cycles

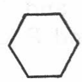
The recurrence relation for the characteristic polynomial of cycles is given by,[21]

$$C_N = L_N - L_{N-2} - 2 \qquad (37)$$

The recurrence formula for the corresponding permanental polynomial of cycles is simply,

$$P(C_N) = P(L_N) + P(L_{N-2}) + 2(-1)^N \qquad (38)$$

Example



C_6

$$P(C_6) = P(L_6) + P(L_4) + 2(-1)^6$$
$$= x^6 + 6x^4 + 9x^2 + 4;\ c_N = K^2 = 4 \Rightarrow K = 2$$

It can be shown that the zeros of $P(C_N)$ are given by,

$$x_k = 2i \cos \frac{(2x+1)\pi}{N} \quad \text{if} \quad N = 4m \qquad (39)$$

$$x_k = 2i \cos \frac{2k\pi}{N} \quad \text{if} \quad N = 4m + 2 \tag{40}$$

$$x_k = (-1)^k \left[\sqrt[N]{\sqrt{2}+1} - \sqrt[N]{\sqrt{2}-1} \right] \sin \frac{(2k+1)\pi}{2N}$$

$$+ i \left[\sqrt[N]{\sqrt{2}+1} + \sqrt[N]{\sqrt{2}-1} \right] \cos \frac{(2k+1)\pi}{2N}$$

if $N = 4m + 1$ (41)

$$x_k = (-1)^{k+1} \left[\sqrt[N]{\sqrt{2}+1} - \sqrt[N]{\sqrt{2}-1} \right] \sin \frac{(2k+1)\pi}{2N}$$

$$+ i \left[\sqrt[N]{\sqrt{2}+1} + \sqrt[N]{\sqrt{2}-1} \right] \cos \frac{(2k+1)\pi}{2N}$$

if $N = 4m + 3$ (42)

A generalized expression for the permanental polynomial of a N-cycle with the (4m + 2) number of atoms is given by,

$$P(C_N) = x^N + \frac{N}{1!} x^{N-2} + \frac{N(N-3)}{2!} x^{N-4} + \frac{N(N-4)(N-5)}{3!} x^{N-6} + \ldots$$

$$\ldots + \frac{N(N-k-1)(N-k-2)\ldots(N-2k+1)}{k!} x^{N-2k} + \ldots \tag{43}$$

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SAŽETAK

Kemijska teorija crteža. III. O permanentnom polinomu

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Opisan je permanentni polinom crteža (grafa). Pokazano je kako se može konstruirati pomoću Sachsove formule. Dane su rekurzivne relacije za računanje permanentnog polinoma lanaca (poliena) i prstenova (anulena). Diskutirana su svojstva koeficijenata permanentnog polinoma. Pokazana je veza između karakterističnog i permanentnog polinoma.

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