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COUNTING POLYNOMIALS (COUNT-POLY)

Lorentz JÄNTSCHI[1], Sorana D. BOLBOACĂ[2]

[1] Technical University of Cluj-Napoca
[2] Iuliu Haţieganu University of Medicine and Pharmacy Cluj-Napoca

DEFINITION

Topological description of a molecule requires storing the adjacencies (the bonds) between the atoms as well as the identities (the atoms). If this problem is simplified at maximum, by disregarding the bond and atom types then adjacencies are simply stored with 0 and 1 in the vertex adjacency matrix ([Ad]) and the identities are stored with 0 and 1 into the identity matrix ([Id]). Even more, any square matrix derived from adjacencies by keeping its symmetry (relative to the main diagonal, $Ad_{i,j}=Ad_{j,i}$) or not carries a series of structural features of the originating molecule. The counting polynomial (CoP) is a construction of a polynomial in which the values in the originating matrix (let's label this matrix [Tm]) are expressed in a polynomial function in which the coefficient of each monomial count the occurrences of the value used to express the degree of the monomial (for instance $7x^8$ for [Tm] express that are exactly 7 occurrences of the value of 8 in [Tm]):

$$\mathrm{CoP} \overset{\mathrm{def}}{=} \sum_{k\geq 0} \mathrm{Count}(\mathrm{Tm}_{i,j} = k) \cdot x^k \text{ , where [Tm] is any topological matrix}$$

It is a convenience that the counting polynomial to be constructed for matrices containing integer (or natural) numbers.

KEYWORDS:

Topological theory of aromaticity; Structure-resonance theory; Quantum chemistry; Counts of random walks; Eigenvectors; Eigenvalues

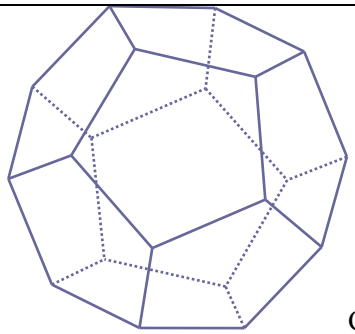
HISTORICAL ORIGIN(S)

The concept of a counting polynomial was first introduced in chemistry by Polya in 1936 (Polya 1936[1]). Its use appeared later (Hosoya et al. 1973[2]). Although the counting polynomials has no direct chemical interpretation, one might be able to use it as a device for coding, sorting, or classifying graphs - adapted from (Hosoya 1988[3]) where it is actually discussing about distance counting polynomials, but works for all others as well). A particular case of Count-poly is Hosoya polynomial, when is calculated on the distance matrix (Gutman et al. 2001[4]).

An generalized definition of the counting polynomials is given by Diudea and its co-authors as (Diudea et al., 2007[5]): A counting polynomial P(G,x) is a description of a graph property P(G) in terms of a sequence of numbers so that the exponents express the extent of its partitions while the coefficients are related to the frequency of the occurrence of partitions.

NANO-SCIENTIFIC DEVELOPMENT(S)

It is much easier to compute a counting polynomial than a characteristic one since it is calculated directly on the matrix with which is feed. For exemplification of the calculation, let's take (see Figure 1) a molecular graph (C_{20}) and calculate some typical matrices on (Adjacency, Distance and unsymmetrical Szeged). Please note that the numbering is not relevant to the formula of the counting polynomial; in other words, it is an invariant relative to the numbering of the atoms. Even further, the adjacency matrix is actually contained in the distance matrix - adjacency matrix contains all zeros and ones from distance, everything else is zero too.



C_{20}

Distance matrix (Di)	Unsymmetrical Szeged matrix (USzp)
0 1 1 2 2 2 3 3 2 3 4 1 2 3 2 3 4 5 4 3	0 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 10 8 8
1 0 2 2 1 3 4 3 3 4 5 2 2 3 1 2 3 4 3 2	8 0 8 8 8 8 8 8 8 8 10 8 8 8 8 8 8 8 8 8
1 2 0 1 2 1 2 2 2 3 3 2 3 4 3 4 5 4 3 3	8 8 0 8 8 8 8 8 8 8 8 8 8 8 8 8 10 8 8 8
2 2 1 0 1 2 2 1 3 4 3 3 4 5 3 3 4 3 2 2	8 8 8 0 8 8 8 8 8 8 8 8 8 10 8 8 8 8 8 8
2 1 2 1 0 3 3 2 4 5 4 3 3 4 2 2 3 3 2 1	8 8 8 8 0 8 8 8 8 10 8 8 8 8 8 8 8 8 8 8
2 3 1 2 3 0 1 2 1 2 2 2 3 3 4 5 4 3 3 4	8 8 8 8 8 0 8 8 8 8 8 8 8 8 10 8 8 8 8 8
3 4 2 2 3 1 0 1 2 2 1 3 4 3 5 4 3 2 2 3	8 8 8 8 8 8 0 8 8 8 8 8 8 8 8 10 8 8 8 8
3 3 2 1 2 2 1 0 3 3 2 4 5 4 4 3 3 2 1 2	8 8 8 8 8 8 8 0 8 8 8 8 10 8 8 8 8 8 8 8
2 3 2 3 4 1 2 3 0 1 2 1 2 2 3 4 3 3 4 5	8 8 8 8 8 8 8 8 0 8 8 8 8 8 8 8 8 8 8 10
3 4 3 4 5 2 2 3 1 0 1 2 2 1 3 3 2 2 3 4	8 8 8 8 10 8 8 8 8 0 8 8 8 8 8 8 8 8 8 8
4 5 3 3 4 2 1 2 2 1 0 3 3 2 4 3 2 1 2 3	8 10 8 8 8 8 8 8 8 8 0 8 8 8 8 8 8 8 8 8
1 2 2 3 3 2 3 4 1 2 3 0 1 2 2 3 3 4 5 4	8 8 8 8 8 8 8 8 8 8 8 0 8 8 8 8 8 8 10 8
2 2 3 4 3 3 4 5 2 2 3 1 0 1 1 2 2 3 4 3	8 8 8 8 8 8 8 10 8 8 8 8 0 8 8 8 8 8 8 8
3 3 4 5 4 3 3 4 2 1 2 2 1 0 2 2 1 2 3 3	8 8 8 10 8 8 8 8 8 8 8 8 8 0 8 8 8 8 8 8
2 1 3 3 2 4 5 4 3 3 4 2 1 2 0 1 2 3 3 2	8 8 8 8 8 8 10 8 8 8 8 8 8 8 0 8 8 8 8 8
3 2 4 3 2 5 4 3 4 3 3 3 2 2 1 0 1 2 2 1	8 8 8 8 8 10 8 8 8 8 8 8 8 8 8 0 8 8 8 8
4 3 5 4 3 4 3 3 3 2 2 3 2 1 2 1 0 1 2 2	8 8 10 8 8 8 8 8 8 8 8 8 8 8 8 8 0 8 8 8
5 4 4 3 3 3 2 2 3 2 1 4 3 2 3 2 1 0 1 2	10 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 0 8 8
4 3 3 2 2 3 2 1 4 3 2 5 4 3 3 2 2 1 0 1	8 8 8 8 8 8 8 8 8 8 8 10 8 8 8 8 8 8 0 8
3 2 3 2 1 4 3 2 5 4 3 4 3 3 2 1 2 2 1 0	8 8 8 8 8 8 8 8 10 8 8 8 8 8 8 8 8 8 8 0

Counting polynomials	
CoP([Ad],C_{20}) =	$60x^1 + 20x^0$
CoP([Di],C_{20}) =	$20x^5 + 60x^4 + 120x^3 + 120x^2 + 60x^1 + 20x^0$
CoP([USzP],C_{20}) =	$20x^{10} + 360x^8 + 20x^0$

Figure 1. Some counting polynomials for C_{20}

As can be seen in figure 1, always the counting polynomial on distances contains separable the polynomial on adjacencies (as the monomials of zero and one degree). Also the monomial of degree one is double of the number of bonds (actually the number of bonds counted from both directions of the ending atoms) and the free term is always the number of the atoms.

Always the complexity of the calculation for a counting polynomial is of $O(n^2)$. If the matrix is symmetrical, is required to count the frequencies for n(n-1)/2 atom pairs (upper part relative to the main diagonal for instance), to twice the obtained numbers (lower part relative to the main diagonal contains exactly the same numbers), and to add the free term which is always n (multiplied with x^0 to formally describe the number of the atoms). If the matrix is

unsymmetrical, then is required count the frequencies for n(n-1) atom pairs (excepting the zero's from the main diagonal).

The complexity of the calculation for the Count-poly comes actually from the complexity of the calculation of the matrices. Here helpful are following algorithms, calculating the distance and unsymmetrical Szeged matrix from adjacency matrix (see Figure 2).

Input data: ÷ adjacency matrix ([Ad]) ÷ number of atoms (n) ÷ number of bonds (m)	Input data: ÷ distance matrix ([Di]) ÷ number of atoms (n)

For each i from 1 to n do
$Di_{i,i} \leftarrow 0$
For each j from 1 to i-1 do
If $Ad_{i,j} = 0$ then
$Di_{i,j} \leftarrow m + 1$
$Di_{i,i} \leftarrow m + 1$
else
$Di_{i,j} \leftarrow 1$
$Di_{i,i} \leftarrow 1$
End if
End for
End for
For each k from 1 to n do
For each i from 1 to n do
For each j from 1 to n do
If $Di_{i,k} + Di_{k,j} < Di_{i,j}$ then
$Di_{i,j} \leftarrow Di_{i,k} + Di_{k,j}$
$Di_{j,i} \leftarrow Di_{i,j}$
End if
End for
End for
End for
	For each i from 1 to n do
	For each j from 1 to n do
	$USzp_{i,j} \leftarrow 0$
	End for
	End for
	For each i from 1 to n do
	For each j from 1 to n do
	If i = j then
	Continue
	End if
	For each k from 1 to n do
	If $Di_{i,k} < Di_{i,k}$ then
	$USzp_{i,j} \leftarrow USzp_{i,j} + 1$
	End if
	End for
	End for
	End for

Output data: distance matrix ([Di])	Output data: unsymmetrical Szeged matrix ([USzp])

Figure 2. Szeged unsymmetrical from distances which from adjacencies

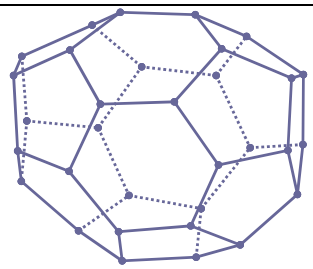
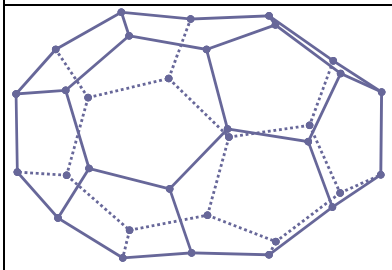
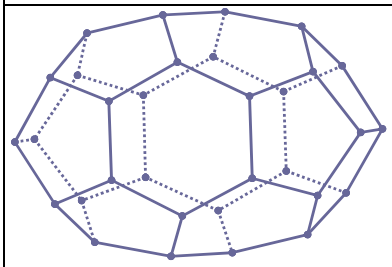
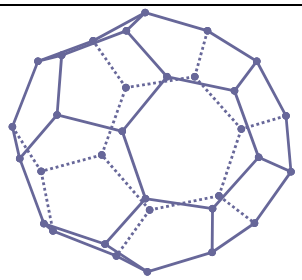
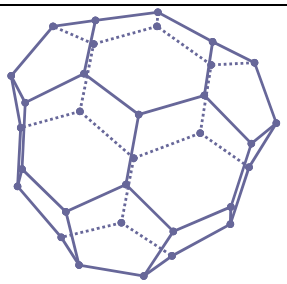
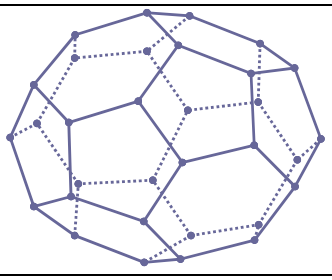
As can be seen, the previous given algorithms have a complexity of $O(n^3)$ for both calculating the distance matrix and the unsymmetrical Szeged matrix. The algorithm for the distance matrix derived from (Floyd 1962[6]).

NANO-CHEMICAL APPLICATION(S)

Count-poly is very useful in discriminating among similar structures. To exemplify, let's take the isomers of C_{32} fullerene. There are exactly six isomers (see Goedgebeur 2012[7]). In the following table (see Table 1) are given the six isomers of the C_{32} fullerene along with their InChi strings as well as the calculated Count-poly's.

As can be seen in Table 1, actually are no identical formulas for any different C_{32} isomers for any of the Count-poly given (on Distance and on unsymmetrical Szeged matrices). Thus, the discriminating power of a Count-poly formula is high.

Table 1. Counting polynomials for C_{32} fullerene isomers

Structure	InChi strings & Polynomials (on [Di] & [USzp])
	1S/C32/c1-3-9-13-5(1)17-19-7(1)15-11(3)23-20-8 -2-4-10-14-6(2)18(20)28-29(21(9)23)25(13)31-27 (17)30(26(14)32(28)31)22(10)24(19)12(4)16(8)15 CoP([Di]) = $2x^7 + 64x^6 + 180x^5 + 230x^4 + 228x^3 + 192x^2 + 96x^1 + 32x^0$ CoP([USzp]) = $6x^{17} + 54x^{16} + 160x^{15} + 330x^{14} + 224x^{13} + 148x^{12} + 40x^{11} + 24x^{10} + 6x^9 + 32x^0$
	1S/C32/c1-5-6-2-10-17(5)21-13(1)29-23-15-4-7-8 -3-11(19(7)23)26-25(29)9(1)18(6)22-14(2)32-24 (16(3)31(22)26)20(8)12(4)28(27(10)32)30(15)21 CoP([Di]) = $4x^7 + 64x^6 + 180x^5 + 228x^4 + 228x^3 + 192x^2 + 96x^1 + 32x^0$ CoP([USzp]) = $4x^{17} + 88x^{16} + 144x^{15} + 336x^{14} + 176x^{13} + 164x^{12} + 40x^{11} + 24x^{10} + 12x^9 + 4x^8 + 32x^0$
	1S/C32/c1-2-14-5-7-15-4-3(13(1)31(14)15)21-19 (1)22-6-8-17-11-12-18-10-9(16(6)32(17)18)23(22) 20(2)24(5)27(10)30(12)29(7)26(4)28(11)25(8)21 CoP([Di]) = $8x^7 + 60x^6 + 180x^5 + 228x^4 + 228x^3 + 192x^2 + 96x^1 + 32x^0$ CoP([USzp]) = $80x^{16} + 168x^{15} + 336x^{14} + 168x^{13} + 168x^{12} + 36x^{11} + 12x^{10} + 12x^9 + 12x^8 + 32x^0$
	1S/C32/c1-2-4-8-5(1)11-9-3(1)7-6(2)12-10(4)14-20 -16(12)24-17(7)21-13(9)19-15(11)23-18(8)22(14)26 -28(20)32-30(24)25(21)27(19)31(32)29(23)26 CoP([Di]) = $64x^6 + 180x^5 + 232x^4 + 228x^3 + 192x^2 + 96x^1 + 32x^0$ CoP([USzp]) = $6x^{17} + 14x^{16} + 172x^{15} + 346x^{14} + 266x^{13} + 138x^{12} + 38x^{11} + 6x^{10} + 6x^9 + 32x^0$
	1S/C32/c1-13-2-20-6-15-3(19(1)20)27-8-16(15)10 -24-12-18-9(23(8)24)28-7-17(18)11-22-5(26(2)32 (29(6)10)30(11)12)14(13)4(21(7)22)25(1)31(27)28 CoP([Di]) = $68x^6 + 180x^5 + 228x^4 + 228x^3 + 192x^2 + 96x^1 + 32x^0$ CoP([USzp]) = $72x^{16} + 246x^{15} + 162x^{14} + 278x^{13} + 126x^{12} + 78x^{11} + 24x^{10} + 6x^9 + 32x^0$
	1S/C32/c1-7-2-10-15(1)27-24-13-5-8-4-12-18(5)29 (27)21-9(1)16-3(7)11-17(2)30-26-14(6(8)19(13)31 (30)22(10)24)20(4)32(25(11)26)28(16)23(12)21 CoP([Di]) = $2x^7 + 60x^6 + 180x^5 + 234x^4 + 228x^3 + 192x^2 + 96x^1 + 32x^0$ CoP([USzp]) = $32x^{16} + 174x^{15} + 318x^{14} + 270x^{13} + 144x^{12} + 48x^{11} + 6x^9 + 32x^0$

MULTI-/TRANS- DISCIPLINARY CONNECTION(S)

Other one connected polynomial with the Count-poly is the chromatic polynomial (Birkhoff 1912[8]) generalized later in the Tutte polynomial (Tutte 1954[9]; Crapo 1969[10]).

Also Hosoya introduced Z-counting polynomial (Hosoya 1971[11]), which is related by its name to the Count-poly, but by its definition to the Charact-poly.

Sextet polynomial (Ohkami et al. 1981[12]) and the Omega polynomial (Diudea 2006[13]) are also different sorts of counting polynomials.

The independence polynomial (Gutman & Hosoya 1990[14]) counts the selections of k-independent vertices of G. Other related graph polynomials are the king, domino and star polynomials (Motoyama & Hosoya 1977[15]; Farrell & De Matas 1988[16]).

If one counts sets of mutually adjacent vertices instead of the sets of independent vertices, one obtains the clique polynomial (Hoede & Li 1994[17]).

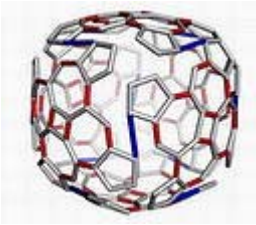
OPEN ISSUES

It is a convenience that the counting polynomial to be constructed for matrices containing integer (or natural) numbers.

RELATED LIST OF ABBREVIATIONS

The term secular function has been used for what is now called characteristic polynomial (in some literature the term secular function is still used). The term comes from the fact that the characteristic polynomial was used to calculate secular perturbations (on a time scale of a century, i.e. slow compared to annual motion) of planetary orbits, according to Lagrange's theory of oscillations.

RELATED BIOGRAPHICAL NOTE



Mircea Vasile Diudea (born: November 11, 1950; died: June 25, 2019) received his B.Sc. and M.Sc. in Chemistry from the Faculty of Chemistry, Babeş-Bolyai University of Cluj-Napoca (1974), and Ph.D. in Chemistry (1977) from the Institute of Chemistry Cluj-Napoca. He started to work as chemist at 'Terapia' drug factory (in 1974), then as researcher at Chemical-Pharmaceutical Institute of Cluj-Napoca (in 1980), and finally taking a position at Department of Chemistry from Babeş-Bolyai University (in 1987). He was the founder (in 2009) and the president of the European Society of Mathematical Chemistry (logo in the left) and for a short period of time (in 2017) the president of the International Academy of Mathematical Chemistry. He wrote over 200 papers (most of them on molecular topology) and several books, including (Diudea et al. 2001[18]), (Diudea 2006[19]) and (Diudea 2010[20]) being rated as the first scientist from Cluj-Napoca in 2019 by the number of citations (Google Scholar). He is the pioneer of using the counting polynomials in chemistry and the inventor of Cluj and Omega polynomials. Partly adapted from http://chem.ubbcluj.ro/~diudea/.

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