

ON SOME COUNTING POLYNOMIALS IN CHEMISTRY

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Various counting polynomials suggested by chemical and physical problems are discussed. Mathematical relations among them and physico-chemical interpretations are given.

1. Introduction

The concept of a counting polynomial was first introduced in chemistry by Pólya [55] in 1936. However, the subject received little attention from chemists for several decades even though the spectra of the characteristic polynomial of graphs were studied extensively by numerical means in order to obtain the molecular orbitals of unsaturated hydrocarbons [41]. Some researchers realized the importance of graph-theoretical concepts and techniques for solving this problem. The results of this paper arise from fifteen years of research by the present author and his colleagues into the applications of the counting polynomials to many different areas of chemistry and physics. Important contributions by other researchers in this area are described in [61]. Most of the graph-theoretical terminology appears in standard works on graph theory and combinatorial theory [7, 22, 45, 57].

2. Characteristic polynomials and the topological index

The *characteristic polynomial* $P_G(x)$ of a graph G was originally not defined as a counting polynomial but as the expansion of the determinant of $A - xE$, where A is the adjacency matrix of G and E the identity matrix:

$$P_G(X) = (-1)^N \det(A - xE) = \sum_{k=0}^N a_k x^{N-k}. \quad (1)$$

Sachs [11, 16, 58] and the present author [28, 31] independently found a combinatorial interpretation. Namely, the characteristic polynomial of a tree can be expressed in terms of the *non-adjacent numbers* $p(G, k)$, by

$$P_G(x) = \sum_{k=0}^{\lfloor N/2 \rfloor} (-1)^k p(G, k) x^{N-2k} \quad (G: \text{tree}). \quad (2)$$

Here, $p(G, k)$ is the number of ways of choosing k disjoint lines from G , and can

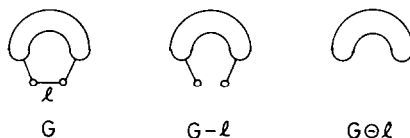


Fig. 1.

be obtained from the two subgraphs $G-l$ and $G \ominus l$ (for an arbitrarily chosen line l) using the recursion

$$p(G, k) = p(G-l, k) + p(G \ominus l, k-1). \quad (3)$$

The two subgraphs $G-l$ and $G \ominus l$ are illustrated in Fig. 1. The relation (3) is a natural consequence of the inclusion-exclusion principle [45, 57]: the first and second terms correspond, respectively, to the choices of lines from G by excluding and including l . In many of the counting polynomials introduced in this paper recurrence relations similar to (3) play an important role in dealing with large graphs [24, 31]. An operator technique is useful for obtaining the recurrence formulas of counting polynomials for periodic large graphs [36, 38].

For non-tree graphs we have to add some correction terms to (2) (see [29, 33]) as follows:

$$P_G(x) = \sum_{k=0}^{[N/2]} (-1)^k p(G, k) x^{N-2k} + \sum_i^{\text{cycles}} (-2)^{r_i} \sum_{k=0}^{[(N-n_i)/2]} p(G \ominus R_i, k) x^{N-n_i-2k}, \quad (4)$$

where the index i extends over every set, R_i , of line-disjoint r_i -cycles and where R_i has n_i points. As the number of cycles increases the correction terms become complicated. Nevertheless, it is always true that the characteristic polynomial can be constructed by counting the number of the sets of disjoint lines in a given graph.

The sum of the $p(G, k)$ numbers is defined as the *topological index* Z_G as follows [28, 31]:

$$Z_G = \sum_{k=0}^{[N/2]} p(G, k). \quad (5)$$

The Z_G numbers for a series of path graphs $\{S_n\}$ and cycle graphs $\{C_n\}$ are the Fibonacci and Lucas numbers, respectively.

In chemistry we often need to know the electronic structure of a molecule so as to interpret the ultraviolet and visible absorption spectra of the molecule, to understand the reactivity and various related problems, and so on. Among all the several million known chemical compounds, the great majority contain carbon atoms and are called organic compounds. The most fundamental of these are composed of only carbon and hydrogen atoms, and are called *hydrocarbons*, either *saturated* with hydrogen or *unsaturated*. The electronic structure of a typical unsaturated hydrocarbon, such as benzene C_6H_6 , can be explained by solving a *secular equation* of the following form [41, 53] (see Fig. 2):

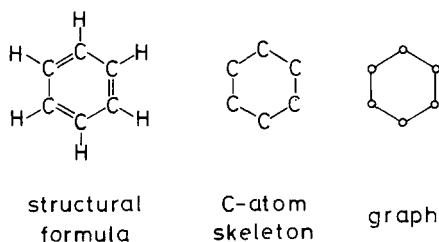


Fig. 2.

$$\begin{vmatrix} -x & 1 & 0 & 0 & 0 & 1 \\ 1 & -x & 1 & 0 & 0 & 0 \\ 0 & 1 & -x & 1 & 0 & 0 \\ 0 & 0 & 1 & -x & 1 & 0 \\ 0 & 0 & 0 & 1 & -x & 1 \\ 1 & 0 & 0 & 0 & 1 & -x \end{vmatrix} = 0,$$

This is simply the spectrum, or the set of zeros $\{x_n, n=1, 2, \dots, N \mid P_G(x)=0\}$ of the graph G corresponding to the carbon atom skeleton of the molecule. Usually the $\{x_n\}$ are listed in decreasing order. Several interesting properties of the molecule, such as the electronic energy, charge density, bond order, and so on, can be obtained as a functional of $P_G(x)$:

$$J(P) = \oint F\{P_G(z), P'_G(z), z\} dz \quad (6)$$

defined over a specified contour in the complex plane [10] – usually a semicircle of infinite radius: $+\infty i \rightarrow 0 \rightarrow -\infty i \rightarrow +\infty \rightarrow +\infty i$. For example, the *total π -electronic energy* E_π , defined by

$$E_\pi = 2 \sum_{n=1}^{[N/2]} x_n, \quad (7)$$

can be expressed as

$$E_\pi = \frac{1}{\pi i} \oint \left\{ \frac{z P'_G(z)}{P_G(z)} - N \right\} dz. \quad (8)$$

Thus analysis of the characteristic polynomial is important for understanding the global electronic structure of unsaturated hydrocarbon molecules [33, 34]. In particular the special stability of polycyclic aromatic hydrocarbons whose carbon skeletons form polyhex graphs, has offered a glamorous target for study by many theoretical chemists [61]. This stability, reflected in a large E_π value, is called *aromaticity*.

Based on extensive numerical analysis of (8), the modified topological index \tilde{Z}_G was proposed, and is defined in terms of the absolute magnitudes of the coefficients of the even terms of $P_G(x)$ for G :

$$\tilde{Z}_G = \sum_{k=0}^{\lfloor N/2 \rfloor} |a_{2k}|. \quad (9)$$

The total π -electronic energy E_π can then be estimated by

$$E_\pi \approx a \log \tilde{Z}_G + b. \quad (10)$$

For tree graphs \tilde{Z}_G is identical to Z_G while for non-tree graphs the following ΔZ_G -value,

$$\Delta Z_G = \tilde{Z}_G - Z_G, \quad (11)$$

gives additional stabilization energy for the molecule caused by the cycle closure. By extending this discussion we obtain the general (extended Hückel) rule for clarifying the stability ($4n+2$ -cycle) and instability ($4n$ -cycle) of polycyclic unsaturated hydrocarbon molecules.

Another line of approach was proposed by Randić [39,56]. The characteristic polynomial of a path graph S_n is

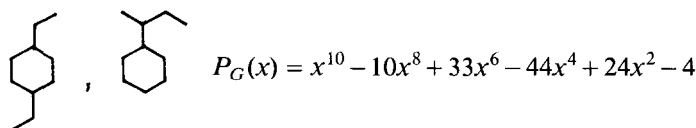
$$S_n(x) = \sum_{k=0}^{\lfloor n/2 \rfloor} (-1)^k \binom{n-k}{k} x^{n-2k}. \quad (12)$$

This yields:

$$x^n = \sum_{k=0}^{\lfloor n/2 \rfloor} B_{n,k} S_{n-2k}(x), \quad (13)$$

where the coefficients $\{B_{n,k}\}$ are related to the Catalan numbers. With this expression any characteristic polynomial can be expanded as a linear combination of $\{S_n(x)\}$ (called *Chebyshev expansion*), by which one can analyze the topological dependency of the characteristic polynomial.

Contrary to a conjecture that the characteristic polynomial can be used for graph discrimination, certain pairs of graphs, such as



have the same $P_G(x)$ and are called cospectral [23] or isospectral [27,61] graphs. While algorithms for finding isospectral graphs have been proposed, this problem is not of much interest to chemists. Many chemical problems depend heavily on the geometrical or metric factors rather than on the topological or non-metric factors.

3. Distance and Wiener polynomials

The *distance polynomial* $S_G(x)$ was independently defined by the present author [37] and Graham and Lovász [14,15] by

$$S_G(x) = (-1)^N \det(\mathbf{D} - x\mathbf{E}) = \sum_{k=0}^N b_k x^{N-k}, \quad (14)$$

where \mathbf{D} is the distance matrix. This is also not a counting polynomial. However, as we shall see the coefficients of the distance polynomial are related to certain counting problems through the Wiener polynomial defined below.

The element D_{ij} of the distance polynomial is the length of the shortest path connecting points i and j . Let $2d_k$ be the number of such elements of \mathbf{D} that are equal to k . Define the *Wiener polynomial* $H_G(x)$ of G as

$$H_G(x) = \sum_{k=1}^l d_k x^k, \quad (15)$$

where l is the largest element of \mathbf{D} , or the diameter of G . In 1947 (the year as Norbert Wiener presented his cybernetics) Harry Wiener proposed two structural parameters w and p which give good correlation with the thermodynamic properties of saturated hydrocarbon molecules [62]. Since then, a number of topological indices have been proposed and discussed in connection with various problems of chemistry, such as structure-activity correlation including carcinogenic compound search [42, 54], coding and classification of the chemical structures [3, 30], and information-theoretic analysis of various networks in chemistry [8].

The p and w indices are defined as d_3 and the half sum of the off-diagonal elements of \mathbf{D} , respectively. Using the following expressions for $H_G(x)$

$$H'_G(x) = \sum_{k=1}^l k d_k x^{k-1}, \quad (16)$$

$$H''_G(x) = \sum_{k=2}^l k(k-1) d_k x^{k-2}, \quad (17)$$

we can obtain the following relations:

$$w = \sum_{i < j} D_{ij} = \sum_{k=1}^l k d_k = H'_G(1) \quad (18)$$

$$p = d_3 = H''_G(0)/6, \quad (19)$$

or, generally,

$$d_k = H_G^{(k)}(0)/k!. \quad (20)$$

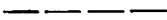


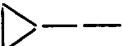





On the other hand, we can derive the following relations for the coefficients of $S_G(x)$ by expanding (14) as follows:

$$b_0 = 1, \quad b_1 = 0, \quad (21)$$

$$b_2 = -\sum_{i < j} D_{ij}^2 = \sum_{k=1}^l k^2 d_k = H'_G(1) + H''_G(1),$$

$$b_3 = -2 \sum_{i < j < k} D_{ij} D_{jk} D_{ki}.$$

Table 1. Examples of distance polynomial.

Graph	$S_G(x)$
	$x^5 - 50x^3 - 140x^2 - 120x - 32$
	$x^5 - 38x^3 - 116x^2 - 112x - 32$
	$x^5 - 28x^3 - 88x^2 - 96x - 32$
	$x^5 - 35x^3 - 88x^2 - 74x - 20$
	$x^5 - 30x^3 - 82x^2 - 72x - 20$
	$x^5 - 25x^3 - 70x^2 - 66x - 20$
	$x^6 - 44x^4 - 162x^3 - 201x^2 - 80x$
	$x^6 - 49x^4 - 176x^3 - 209x^2 - 80x$
	$x^6 - 49x^4 - 180x^3 - 220x^2 - 80x$

For higher b_k things get more involved and no neat expression can be expected. However, for a tree graph the last term of $S_G(x)$ can be shown to be

$$b_N = -2^{N-2}(N-1), \quad (22)$$

regardless of its branching mode as shown in Table 1 [15, 37].

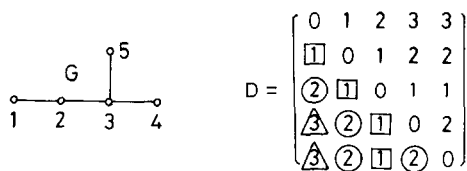
Further, the coefficient b_{N-1} for a tree graph can be expressed in terms of g_k , the number of points with degree k ,

$$b_{N-1} = -2^{N-3} \sum_{k=2}^l g_k(k-1)(2N-k+2). \quad (23)$$

These relations are illustrated in Fig. 3 with the second graph in Table 1 taken as an example.

More interestingly, the conjecture [37] that $b_N(G)$ of graph G is determined only by the number of points and the cycle skeleton was later proved to be true [14]. Thus, a good deal of information about the topological structure of a graph is contained in the distance polynomial. Namely, the term b_1 gives the number of lines of G , b_2 gives the 'roundness', b_{N-1} gives the 'branching', and b_N gives the cycle skeleton.

Although the distance polynomial has no direct chemical interpretation, one



$$-b_2 = 4 \times \underline{1}^2 + 4 \times \underline{2}^2 + 2 \times \underline{3}^2 = 38$$

$$-b_4 = 2^{5-3}(1 \times 1 \times 10 + 1 \times 2 \times 9) = 112$$

$$-b_5 = 2^{5-2}(5-1) = 32$$

$$S_G(x) = x^5 - 38x^3 - 116x^2 - 112x - 32$$

Fig. 3.

might be able to use it as a device for coding, sorting, or classifying graphs. Generating isospectral pairs is much slower when using the distance polynomial in comparison to using the characteristic polynomial.

4. Z-counting and matching polynomial

The topological index Z_G can also be defined as

$$Z_G = Q_G(1) \quad (24)$$

in terms of the *Z-counting polynomial* $Q_G(x)$ [28]:

$$Q_G(x) = \sum_{k=0}^{[N/2]} p(G, k) x^k \quad (25)$$

In statistical mechanics Heilman and Lieb [25, 26] and Kunz [44] proposed a similar polynomial. Aihara [1] also proposed the *reference polynomial*

$$\alpha_G(x) = \sum_{k=0}^{[N/2]} (-1)^k p(G, k) x^{N-2k} \quad (26)$$

to discuss the aromatic character of polycyclic hydrocarbons. Independently, Gutman et al. [21] proposed the same polynomial for the same purpose under the name of *acyclic polynomial*. Further, Farrell extended the idea of these polynomials and introduced the *matching polynomial* (26) [13]. The magnitudes of the difference between the E_π -values defined in (7) for the polynomials $P_G(x)$ and $\alpha_G(x)$ have been thoroughly discussed. However, the logical basis of these studies is simply the idea of our modified topological indices (see (11)). Great enrichment in the understanding of the aromaticity of polycyclic unsaturated hydrocarbons has been achieved by these researchers [61].

Aside from this problem these polynomials have important mathematical significance, as will be clear from the following discussion. The matching polynomials

Table 2. Correspondence between the orthogonal polynomials and the matching polynomials for certain series of graphs.

Orthogonal polynomial		Graph	
Chebyshev (1st kind)	T_n, C_n	Cycle graph	C_n
Chebyshev (2nd kind)	U_n, S_n	Path graph	P_n
Hermite	H_n, h_n	Complete graph	K_n
Laguerre	L_n	Complete bipartite graph	$K_{n,n}$
Associated Laguerre	L_m^{m-n}	Complete bipartite graph	$K_{m,n}$
Legendre	P_n	- - - -	

of several series of graphs are identical to typical orthogonal polynomials, such as Chebyshev, Hermite, and Laguerre polynomials, as summarized in Table 2 [18, 26, 32].

Because the Z -counting and matching polynomials are related,

$$\begin{aligned} \alpha_G(x) &= x^N Q_G(-1/x^2), \\ Q_G(x) &= (\sqrt{x/i})^N \alpha_G(i/\sqrt{x}), \end{aligned} \quad (27)$$

the relation between the Z -counting and orthogonal polynomials is straightforward (see [34]).

Let us turn to the adsorption of diatomic molecules, such as oxygen, onto the clean surface of a metal composed of a two-dimensional periodic lattice, such as the square or hexagonal lattice. The number of ways of placing k dimers in one layer on a given lattice G is exactly the number $p(G, k)$ defined already. If the energy needed for a dimer to be adsorbed onto two neighboring sites in the lattice is $\varepsilon > 0$ and the reaction is additive, the partition function is

$$\Omega = \sum_{k=0} p(G, k) \exp(-k\varepsilon/kT), \quad (28)$$

where k is the Boltzmann constant and T the temperature. By substituting $x = \exp(-\varepsilon/kT)$, (28) turns out to be (25).

Thus, the master equation of dimer statistics is equivalent to our Z -counting polynomial. To obtain the numbers $p(G, k)$ for larger graphs we need effective recursion formulas, an example of which is shown in Fig. 4. Together with the operator technique we can obtain the Z -counting polynomials for a variety of periodic rectangular and torus lattices [36]. Observing the distribution of $p(G, k)$ against k for large networks leads us to believe that it might approach that of the normal or Gaussian distribution, but this is not yet proved.

$$\begin{aligned}
 & \begin{array}{c} \square \\ \square \\ \square \end{array} = \begin{array}{c} \square \\ \diagup \diagdown \\ \square \end{array} + 4x \begin{array}{c} \square \\ \square \\ \square \end{array} - 2x^2 \begin{array}{c} \square \\ \square \end{array} \\
 & \qquad \qquad \qquad 1+8x+16x^2+8x^3+x^4 \quad 1+7x+11x^2+3x^3 \quad 1+4x+2x^2 \\
 \\
 & = \begin{array}{c} \square \\ \square \end{array} + 4x \begin{array}{c} \square \\ \square \\ \square \end{array} - 4x^2 \begin{array}{c} \square \\ \square \end{array} - 2x^2 \begin{array}{c} \diagup \diagdown \\ \square \end{array} + 4x^3 \begin{array}{c} \diagup \diagdown \\ \diagup \diagdown \end{array} - x^4 \phi \\
 & \qquad \qquad \qquad (1+4x+2x^2)^2 \quad 1+7x+11x^2+3x^3 \quad 1+4x+2x^2 \quad (1+x)^2 \quad 1+x \quad 1 \\
 \\
 & = 1+12x+42x^2+44x^3+9x^4
 \end{aligned}$$

Fig. 4.

5. Rotational polynomial [35]

Another connection between the counting polynomials and thermodynamic partition functions can be found in the analysis of the entropy of chain hydrocarbon molecules. All the carbon-carbon (C-C) single bonds in these molecules rotate rapidly with certain restricted conditions (potentials). Thus the thermodynamic properties, such as entropy and enthalpy, should be explained by averaging over numerous conformations.

The carbon atom chain of saturated hydrocarbons takes a restricted random walk along the diamond lattice, in which only four directions are allowed to each bond (Fig. 5). The directions of the terminal C-H bonds are also restricted in this way. Each pair of bonds at the opposite ends of a given C-C bond, or a pair of atoms X and Y whose distance D_{XY} is 3, takes either trans (T) or one of the two gauche (G, G') conformations (see Fig. 6) [46, 49, 59]. The conformations G and G' are mirror images of each other. Extra energy, $\Delta\varepsilon = \alpha > 0$, is needed for any four successive carbon atoms in the chains of saturated hydrocarbons to take a gauche form relative to the trans form.

According to Balaban [2] any conformation of a branchless saturated hydrocarbon $C_N H_{2N+2}$ ($N \geq 4$) with skeletal graph S_N can be expressed as a set of $N-1$ successive digits from 1 to 4 (4-digit code or 4-DC). Each of the 3^{N-3} conformations generated from S_N can be transformed into another TG -code which is a set of $N-3$ successive codes of T, G , and G' , as in Table 3 [46]. Thermodynamically equivalent conformations, such as TG and GT , are further regrouped as in the third

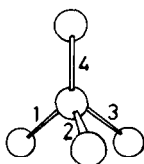


Fig. 5.

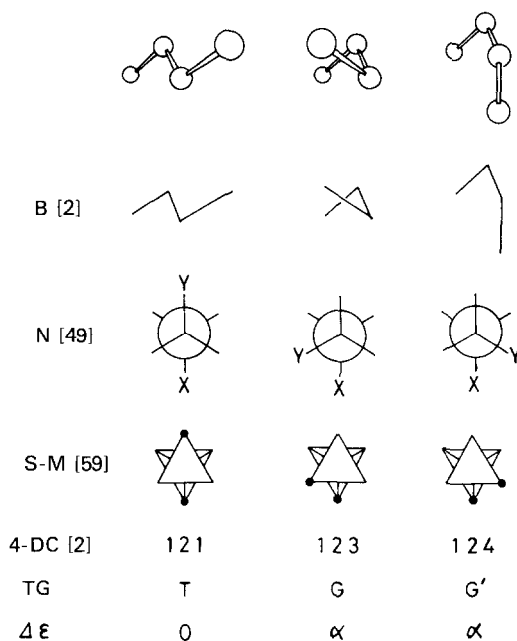


Fig. 6.

column in Table 3. Note that the GG' type conformation has an extra repulsion energy $\beta > 0$ between the pair of X and Y sites with $D_{XY} = 4$, relative to the GG type (see Fig. 7). Let us define the *rotational polynomial* $Q_G(X, Y)$ for hydrocarbon G by

$$Q_G(X, Y) = \sum_{m,n} (m, n) X^m Y^n, \quad (29)$$

where (m, n) is the number of conformations with m G -codes and n GG' -pair codes. The $Q_G(X, Y)$ for S_4 and S_5 graphs are,

$$1 + 2X \quad \text{and} \quad 1 + 4X + 2X^2 + 2X^2Y,$$

respectively. Further, if we delete all the conformations containing three successive $GG'G$ -codes from energy consideration, we immediately obtain

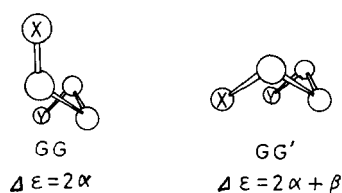


Fig. 7.

Table 3. Rotational polynomials of pentane graph (S_5).

4-DC	TG-code	Classification	Energy
1 2 1 2	T T	T T	0
1 2 1 3	T G		
1 2 1 4	T G'	T G	α
1 2 3 2	G T		
1 2 4 2	G'T		
1 2 3 4	G G	G G	2α
1 2 4 3	G'G'		
1 2 3 1	G G'	G G'	$2\alpha+\beta$
1 2 4 1	G'G		

$$Q_G(x, y) = 1 + 4x + 2x^2 + 2x^2y^2$$

$$Q_N(X, 0) = (X+1)Q_{N-1}(X, 0) + Q_{N-2}(X, 0), \quad (30)$$

$$(m, n)_N = \binom{m-n}{n} (m-n, n)_{N-n}, \quad (31)$$

and a few other recursion relations, where Q_N stands for the Q polynomial of S_N .

This rotational polynomial can be extended to branched hydrocarbons. Then by substituting

$$X = \exp(-\alpha/kT) \quad \text{and} \quad Y = \exp(-\beta/kT)$$

into (29) we get

$$Q_G = \sum_{m,n} (m, n) \exp\{-(m\alpha + n\beta)/kT\}, \quad (32)$$

which is the rotational part of the partition function of the saturated hydrocarbon chain, and is closely related to its entropy. Good correlation can be obtained between the experimentally observed entropies and the partition functions thus derived from the rotational polynomial.

6. King and domino polynomials [47, 48]

Although the rook polynomial has been known as an effective means for considering the enumeration problems of chess and Japanese shohgi games, it ap-

parently has not been used in the mathematics of the important models of physics and chemistry [45, 57].

We have proposed the *King polynomial* for enumerating the number of ways of putting non-taking kings on a given polyomino, square animal, or chessboard of an arbitrary size and shape [47, 48]. It turns out that the king polynomial is closely related to the perfect matching number problem already discussed in Section 4.

A king can take any of the eight neighboring cells, including the four point-contact ones. By drawing circles in a certain set of cells of a given polyomino graph G we get king patterns as in Fig. 8. If any pair of two cells occupied by the kings in a king pattern are not neighbors of each other, such a pattern is called a *non-taking king pattern*.

Define the *non-taking king number* $r(G, k)$ for a given polyomino graph G as the number of non-taking king patterns with k kings. In all cases, $r(G, 0)$ is defined to be unity. The king polynomial $K_G(x)$ for G is defined as

$$K_G(x) = \sum_{k=0} r(G, k) x^k. \tag{33}$$

For the polyomino given in Fig. 8 we get

$$K_G(x) = 1 + 6x + 4x^2.$$

It is interesting to note that the total number of non-taking king patterns for G , or $K_G(1)$ (=11 in this case), is equal to the number of perfect matchings, or the Kekulé number $K(G)$ of the rectangular lattice G . A perfect matching pattern is also

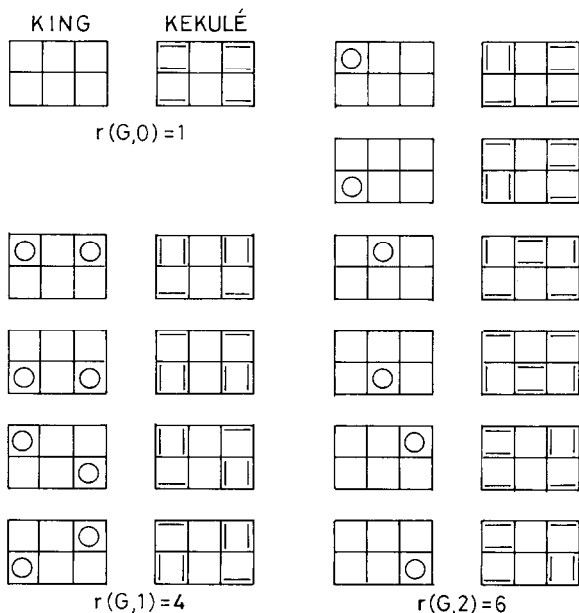


Fig. 8.

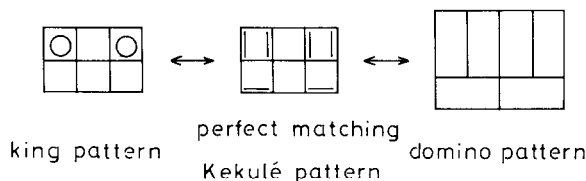


Fig. 9.

the pattern obtained by paving or tiling dominoes and is called the *domino pattern*. The relationship between these different patterns are illustrated in Fig. 9.

For ‘thin’ polyomino graphs there is a one-to-one correspondence between the king pattern and the Kekulé pattern as illustrated in Fig. 8:

$$K_G(1) = K(G). \quad (34)$$

However, for ‘fat’ polyominoes, provided certain correction terms are properly taken into account in constructing the domino polynomial $D_G(x)$, the relation

$$D_G(1) = K(G) \quad (35)$$

holds universally. More detailed discussion is given in [48].

The existence of this novel one-to-one correspondence between the two different graph-theoretical quantities reveals that the structural formula which has been drawn formally and used conventionally by chemists might have both a profound physical meaning and mathematically meaningful properties. This idea is more extensively analyzed in connection with the sextet polynomial.

7. The sextet polynomial [40, 52]

Consider a honeycomb or polyhex graph, composed of only hexagons, representing the carbon atom skeleton of polycyclic aromatic hydrocarbon molecules. If the number of carbon atoms (points) is even, most of those polyhexes have non-zero perfect matching or non-zero Kekulé patterns (see Fig. 10). If the set of three circularly arranged double bonds in the right hexagon of Fig. 10(a) are rotated by 60 degrees in either direction, we get another Kekulé pattern 10(b). In a chemical sense we interpret this as follows: the aromatic sextet, a union of six π -electrons, stabilizes the electronic structure in the benzene ring by the quantum-chemical resonance. So it is important to analyze what kinds of aromatic sextets can stabilize the whole molecule.

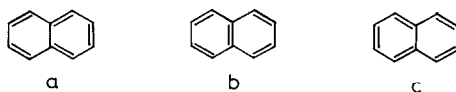


Fig. 10.

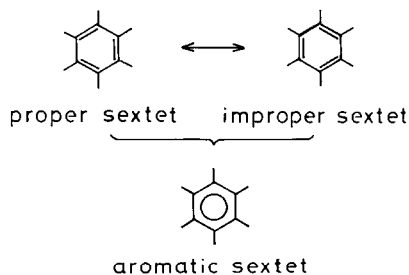


Fig. 11.

We call the sets of three double bonds as shown in Fig. 11 the *proper* and *improper sextets*, respectively. A pair of proper and improper sextets in a certain hexagon is called an *aromatic sextet* and is sometimes designated by a circle. No two sextets may share a bond. However, certain Kekulé patterns can have more than one sextet located on disjoint hexagons. Such disjoint sextets are said to be *resonant* with each other. Note that for certain kinds of Kekulé pattern there is no unique way of choosing a sextet or a set of resonant sextets (see Fig. 10(b)). According to Clar [9] we denote a sextet by a circle and suppress the remaining double bonds to give a *sextet pattern* s_i as shown in Fig. 12. Here the zero-sextet pattern is also defined to have no circle.

For a given polyhex graph G we define the *resonant sextet number* $r(G, k)$ to be the number of ways of choosing k disjoint resonant sextets from G . The *sextet polynomial* $B_G(x)$ is defined as

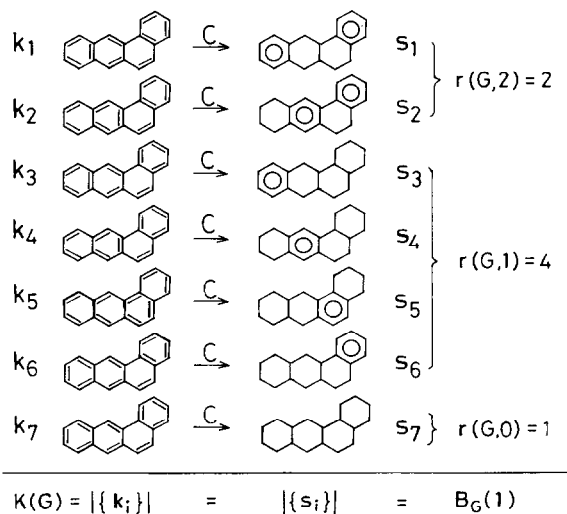


Fig. 12.

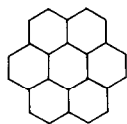


Fig. 13.

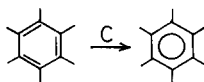


Fig. 14.

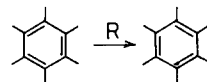


Fig. 15.

$$B_G(x) = \sum_{k=0}^m r(G, k) x^k. \quad (36)$$

For the graph in Fig. 12 we have

$$B_G(x) = 1 + 4x + 2x^2.$$

For 'thin' polyhex graphs that have no coronene skeleton (Fig. 13) the following relation holds,

$$B_G(1) = K(G), \quad (37)$$

we can extend the validity of the relation (37) to 'fat' polyhexes by defining the 'supersextet' [50, 52].

Since both sides of (37) are derived from quite different enumeration problems, this is a very important relation both in chemistry and graph theory. In order to analyze this problem we introduce the following two graphical operations.

Define the *Clar transformation* (C) as a simultaneous substitution of all the proper sextets by circles in a given Kekulé pattern k_i followed by the transformation of the remaining double bonds into single bonds (Fig. 14), as exemplified in Fig. 12. The Clar transformation can symbolically be expressed as

$$C(k_i) = s_i. \quad (38)$$

Define the *sextet rotation* (R) as a simultaneous rotation of all proper sextets in a given Kekulé pattern k_i into the improper sextets to give another Kekulé pattern k_j – or symbolically as

$$R(k_i) = k_j \quad (\text{see Fig. 15}). \quad (39)$$

For example, we get $R(k_1) = k_7$ for the graph in Fig. 12. Note that for such k_i with no proper sextet, such as k_7 in Fig. 12, we cannot operate the sextet rotation. In this case we put it down as

$$R(k_i) = \emptyset, \quad (40)$$

and call such k_i the root Kekulé pattern.

Now try to apply the sextet rotation to the set of the Kekulé patterns for the graph in Fig. 12. The resultant relationship among $\{k_i\}$ is a hierarchical structure and can be expressed by a directed rooted tree as shown in Fig. 16, where all entries in $\{k_i\}$ can find the corresponding points including the root. It has been shown that the proof of (37) and of the results in Figs 12 and 16 can be obtained straightforwardly from the following Lemma [50, 52]:

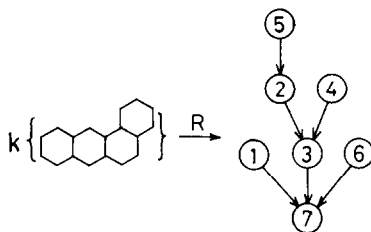


Fig. 16.

Lemma. For each polyhex graph, there exists exactly one root Kekulé pattern (a Kekulé pattern with no proper sextet).

Interesting mathematical properties of this challenging polynomial are being studied by several research groups [12, 20].

8. Concluding remarks

We have surveyed the counting polynomials proposed for analyzing problems arising from counting various elements in the structural formula. Their characteristic features and relations are summarized in Table 4. For other polynomials see [51, 61].

Within the last five years remarkable progress has been made in elucidating the

Table 4. Relation among various counting polynomials.

Polynomial	Definition	Characterization	Related problem	Relation
$P_G(x)$ characteristic	$\det(A - xE)$	all graphs	Hückel MO	
$Q_G(x)$ Z-counting	$p(G, k)$ non-adjacent king number	all graphs	Z_G topological index	
$\alpha_G(x)$ { matching acyclic reference }				
$S_G(x)$ distance	$\det(D - xE)$	all graphs	coding, ring analysis	
$H_G(x)$ Wiener	d_k in D			
$K_G(x)$ king	$r(G, k)$ non-taking king number	polyomino	partition function	
$D_G(x)$ domino				
$B_G(x)$ sextet	$r(G, k)$ resonant sextet number	polyhex, unsaturated	Kekulé structure	
$W_G(x)$ Wheland	matching patterns	all graphs, unsaturated	resonance structure	
$Q_G(x, y)$ rotational	gauche pairs, internal rotation	steric con- formation of tree	partition function, entropy	

mathematical structure of various counting polynomials and also in developing the algorithms for obtaining their coefficients and recursion relation [4, 5, 6, 19, 38, 39, 43, 56, 60]. By the use of these relations further progress is being expected in the analysis of the physico-chemical and mathematical features of molecules and crystals. However, there is still plenty of room for defining new counting polynomials for the various problems in this field.

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