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Graphical Enumeration of the Coefficients of the Secular Polynomials of the Hückel Molecular Orbitals

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A general and simple method for graphical enumeration of the coefficients of the secular polynomials of the Hückel molecular orbitals is presented with examples. The essential procedure is to count for the graph and its subgraphs the non-adjacent numbers, $p(\boldsymbol{G}, k)$'s, which appear as the coefficients of the Z-counting polynomial $Q(Y)$. Two composition principles are proposed and shown to simplify these procedures to a great extent. Application to biphenylene shows the superiority of this method to others, *e.g.*, the method of polygons.

Eine einfache und allgemeine Methode zur graphischen Bestimmung der Koeffizienten des Säkularpolynoms bei Hückelproblemen wird angegeben. Das Wesentliche für den Graphen und seine Untergraphen ist es, die Nichtnachbar-Zahlen abzuzählen. Letztere erscheinen im Z-zählenden Polynom. Zwei einfache Aufbau-Schemata werden vorgeschlagen. Am Beispiel von Biphenylen werden die Vorzüge diesen Verfahrens demonstriert.

Introduction

Since the secular determinant of the Hückel molecular orbitals for unsaturated hydrocarbons reflects only the neighbourship of the carbon atoms in molecules, it is closely related to what is called in the graph theory [1] an adjacency matrix but was named by Ham [2] a topological matrix [3, 4]. In this topological sense distinction between saturation and unsaturation in the C–C bonds is meaningless. There often arises a need for expanding the secular determinant into a polynomial $P(X)$, which is called a characteristic or secular polynomial. The method for deriving $P(X)$ from those of component subgraphs has been established [5, 6].

On the other hand "the method of polygons" has been proposed to count the coefficients in $P(X)$ graphically but with no generalised algorithm [7–10]. Very recently, however, it was shown that $P(X)$ for a tree graph, or a chain hydrocarbon, can be simply expressed by using the $p(\boldsymbol{G}, k)$ numbers as,

$$P_{\boldsymbol{G}}(X) = \sum_{k=0}^{m} (-1)^k \, p(\boldsymbol{G}, k) \, X^{N-2k}, \tag{1}$$

where $p(\boldsymbol{G}, k)$ is the number of ways in which disjoint k bonds are chosen from graph $\boldsymbol{G}$. This paper gives a generalised method for graphical enumeration of $P(X)$ of a given graph with or without rings.

Definitions

The followings are the necessary definitions for describing the enumeration method.

1) A graph $\boldsymbol{G}$ consists of points (vertices or atoms) and lines (edges or bonds) [1]. We are concerned with such connected non-directed graphs that have no loop (a line joining a point to itself) and no multiple lines (double or triple bonds).

2) An adjacency matrix $\boldsymbol{A}$ for graph $\boldsymbol{G}$ with N points is a square matrix of the order N with elements,

$$a_{ij} = \begin{cases} 1 & \text{if the points } i \text{ and } j \text{ are neighbours,} \\ 0 & \text{otherwise.} \end{cases} \tag{2}$$

The matrix character is independent of the way of numbering the points.

3) A characteristic polynomial or a secular polynomial $P(X)$ is defined as

$$P(X) = \det|X\boldsymbol{E} + \boldsymbol{A}| = \sum_{i=0}^{N} C_i X^{N-i} \tag{3}$$

where $\boldsymbol{E}$ is a unit matrix of the same oder N as that of $\boldsymbol{A}$, X is a scalar variable and C_i is the coefficient which we are going to obtain.

4) A non-adjacent number $p(\boldsymbol{G}, k)$ is the number of ways in which disjoint k bonds are chosen from $\boldsymbol{G}$; $p(\boldsymbol{G}, 0)$ being unity and $p(\boldsymbol{G}, 1)$ the number of lines.

5) A Z-counting polynomial $Q(Y)$ for $\boldsymbol{G}$ is defined as

$$Q_{\boldsymbol{G}}(Y) = \sum_{k=0}^{m} p(\boldsymbol{G}, k)\, Y^k \tag{4}$$

where m is the maximum number of k for $\boldsymbol{G}$. Both for a single point and a vacant graph let us define $Q(Y) = 1$. The integer $p(\boldsymbol{G}, m)$ is the number of the Kekulé structures for an unsaturated hydrocarbon with the carbon skeleton $\boldsymbol{G}$ [11].

6. A topological index Z for $\boldsymbol{G}$ is defined as

$$Z_{\boldsymbol{G}} = \sum_{k=0}^{m} p(\boldsymbol{G}, k) = Q_{\boldsymbol{G}}(1)\,. \tag{5}$$

Interesting properties of the quantities, $p(\boldsymbol{G}, k)$, $Q(Y)$ and Z are discussed elsewhere [4].

Theorems

Fundamental Equation

The fundamental equation for the graphical enumeration of $P(X)$ from $\boldsymbol{G}$ is as follows:

$$\begin{aligned} P_{\boldsymbol{G}}(X) = & \sum_{k=0}^{m} (-1)^k\, p(\boldsymbol{G}, k)\, X^{N-2k} \\ & - 2 \sum_{i}^{\boldsymbol{G}} \sum_{k=0}^{m_i} (-1)^{k+n_i}\, p(\boldsymbol{G} - \boldsymbol{R}_i, k)\, X^{N-n_i-2k} \\ & + 2^2 \sum_{i>j}^{\boldsymbol{G}} \sum_{k=0}^{m_{ij}} (-1)^{k+n_i+n_j}\, p(\boldsymbol{G} - \boldsymbol{R}_i - \boldsymbol{R}_j, k)\, X^{N-n_i-n_j-2k} \\ & - \cdots . \end{aligned} \tag{6}$$

$\boldsymbol{G}-\boldsymbol{R}_i$: A subgraph of $\boldsymbol{G}$ derived by deleting a ring $\boldsymbol{R}_i$ and all the lines incident to $\boldsymbol{R}_i$. It may or may not be a disjoint graph.

$\boldsymbol{G}-\boldsymbol{R}_i-\boldsymbol{R}_j$: A subgraph of $\boldsymbol{G}$ derived by deleting a pair of disjoint rings $\boldsymbol{R}_i$ and $\boldsymbol{R}_j$ and all the lines incident to $\boldsymbol{R}_i$ and/or $\boldsymbol{R}_j$.

n_i: The number of points in $\boldsymbol{R}_i$.

m_i: The maximum number of k for $\boldsymbol{G}-\boldsymbol{R}_i$.

m_{ij}: The maximum number of k for $\boldsymbol{G}-\boldsymbol{R}_i-\boldsymbol{R}_j$.

$\sum_i^{\boldsymbol{G}}$: Summation over all the possible rings in $\boldsymbol{G}$.

$\sum_{i>j}^{\boldsymbol{G}}$: Summation over all the possible pairs of two disjoint rings in $\boldsymbol{G}$.

If necessary, one can continue to write the right-hand side of Eq. (6) as far as he wishes. Note that the second term can be expressed as

$$-2\sum_i^{\boldsymbol{G}}(-1)^{n_i}\left\{\sum_{k=0}^{m_i}(-1)^k\, p(\boldsymbol{G}_i,k)\, X^{N_i-2k}\right\}$$

with $\boldsymbol{G}_i=\boldsymbol{G}-\boldsymbol{R}_i$ and $N_i=N-n_i$ and that the term in the brackets has quite the same form as the first term of Eq. (6). This is also the case for the remaining terms.

Now the problem is reduced to obtaining the $p(\boldsymbol{G},k)$ numbers for a given graph. It is easy to count the $p(\boldsymbol{G},k)$ numbers and therefore to write out $P(X)$ for graphs with smaller N or those of special classes as will be shown later. On the other hand, for most larger graphs the procedure for counting the $p(\boldsymbol{G},k)$ numbers is as formidable as that for expanding the determinant by minors.

By the aid of the Z-counting polynomial $Q(Y)$, the $p(\boldsymbol{G},k)$ numbers can be obtained rather mechanically. The following two Composition Principles are useful for this purpose.

Composition Principle I

Consider a graph $\boldsymbol{G}$ and choose from it a line l as exemplified in Fig. 1. 1) Delete line l and we get subgraphs $\boldsymbol{L}$ and $\boldsymbol{M}$. 2) Delete all the lines in $\boldsymbol{L}$ and $\boldsymbol{M}$ that were incident to l and we get subgraphs $\boldsymbol{A}, \boldsymbol{B}, \ldots \boldsymbol{F}$. The Z-counting polynomial $Q_{\boldsymbol{G}}$

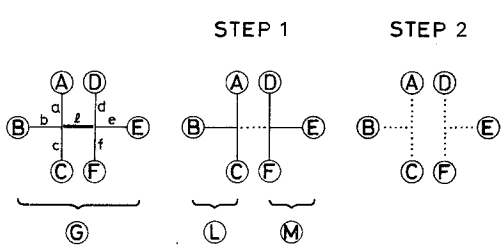

Fig. 1. Illustration for Composition Principle I. In this example no such lines are deleted that are constituents of a ring. See also Fig. 5 for the case where rings are opened by deletion of a line or a group of lines

for G can be expressed as

$$Q_G = Q_L Q_M + Y \cdot Q_A Q_B Q_C Q_D Q_E Q_F , \tag{7}$$

or more generally as

$$Q_G = \prod^{l} Q_L + Y \cdot \prod^{l+\{a\}} Q_A . \tag{8}$$

Multiplication l runs over all the subgraphs $L's$ obtained by deleting bond l, while $l+\{a\}$ means deletion of l and all the bonds $a's$ incident to l. The $p(G, k)$ numbers appear as the coefficients of the term Y^k in $Q_G(Y)$. If one deletes a line which is a constituent of a ring, a single subgraph L, instead of L and M, is obtained in step 1). In this case the first term of Eq. (8) is no longer a product but a single polynomial Q_L. This principle also applies to step 2) and Composition Principle II. Thus all the polynomials Q's following a product sign should be mutually disjoint.

By putting $Y = 1$ into Eqs. (7) and (8) we get the expressions for the topological index Z.

$$Z_G = Z_L Z_M + Z_A Z_B Z_C Z_D Z_E Z_F \tag{9}$$

and

$$Z_G = \prod^{l} Z_L + \prod^{l+\{a\}} Z_A . \tag{10}$$

The proof is given in Appendix of Ref. [4].

Composition Principle II

Consider a graph G and choose from it a point p as exemplified in Fig. 2. The number of the lines incident to point p should be at least two, e.g., six as in this example. 1) Divide them into two groups. 2) Delete a group of lines a, b and c in G, and we get subgraphs A, B, C and M. 2) Delete another group of lines d, e and f in G, and we get subgraphs D, E, F and L. 4) Delete both the groups of lines $a, b, \ldots f$ in G, and we get subgraphs A, B, ... F. With these subgraphs we have

$$Q_G = Q_A Q_B Q_C Q_M + Q_D Q_E Q_F Q_L - Q_A Q_B Q_C Q_D Q_E Q_F \,^{1} \tag{11}$$

or more generally

$$Q_G = \prod^{\{p\}} Q_L + \prod^{\{\bar{p}\}} Q_{\bar{L}} - \prod^{\{p+\bar{p}\}} Q_A . \tag{12}$$

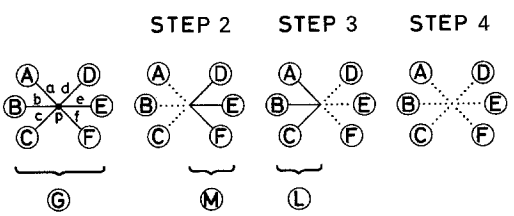

Fig. 2. Illustration for Composition Principle II. See also Fig. 3

[1] Eq. (11) may be expressed as

$$Q_G = Q_L Q_M - (Q_A Q_B Q_C - Q_L)(Q_D Q_E Q_F - Q_M) \tag{11'}$$

Multiplication $\{p\}$ runs over all the subgraphs L's obtained by deleting a group of lines incident to point p. The symbol $\{\bar{p}\}$ means deletion of the coset of $\{p\}$. The corresponding expressions for the topological index are

$$Z_G = Z_A Z_B Z_C Z_M + Z_D Z_E Z_F Z_L - Z_A Z_B Z_C Z_D Z_E Z_F \quad (13)$$

$$Z_G = \prod^{\{p\}} Z_L + \prod^{\{\bar{p}\}} Z_{\bar{L}} - \prod^{\{p+\bar{p}\}} Z_A . \quad (14)$$

Examples

Tree Graphs

For tree graphs Eq. (6) turns out to be Eq. (1) since a tree has no ring.

1) *Linear Graphs (normal paraffins).* The carbon atom skeletons of n-paraffins form the most simplest series of graphs. If a linear graph with N points is denoted as $\bar{N}$, the $p(G, k)$ numbers for $\bar{N}$ are given by

$$p(\bar{N}, k) = {}_{N-k}C_k = (N-k)(N-k-1)\ldots(N-2k+1)/k! \quad (15)$$

and we have

$$Q_{\bar{N}}(Y) = \sum_{k=0}^{[\frac{N}{2}]} {}_{N-k}C_k \, Y^k \quad (16)$$

and

$$P_{\bar{N}}(X) = \sum_{k=0}^{[\frac{N}{2}]} (-1)^k \, {}_{N-k}C_k X^{N-2k} . \quad (17)$$

2) *Trees (branched paraffins).* Many examples for the application of Composition Principle I to tree graphs are given elsewhere [4, 12]. Therefore let us apply Compositon Principle II to a multi-branched tree graph, or 3,3-diethylpentane, in Fig. 3. By noticing the central point one can obtain the Z-counting polynomial Q as

$$\begin{aligned} Q(Y) &= 2(1+4Y+3Y^2)(1+Y)^2 - (1+Y)^4 \\ &= 1+8Y+18Y^2+16Y^3+5Y^4 \end{aligned}$$

by decomposing the graph G into subgraphs as shown in Fig. 3 and by using Eq. (6). The $p(G, k)$ numbers appear as the coefficients of $Q(Y)$ and we get

$$P(X) = X^9 - 8X^7 + 18X^5 - 16X^3 + 5X$$

and $Z = 48$. The topological index Z is useful for checking the calculation of the polynomials Q and P.

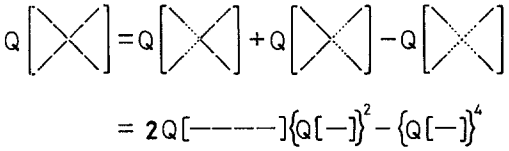

Fig. 3. Example of the application of Composition Principle II

[2] Eq. (13) may be expressed as

$$Z_G = Z_L Z_M - (Z_A Z_B Z_C - Z_L)(Z_D Z_E Z_F - Z_M) \quad (13')$$

Non-Tree Graphs

1) *Ring Graphs (cyclo-paraffins).* The $p(\boldsymbol{G}, k)$ numbers for an N-membered ring (denoted as N^0) are given by

$$p(N^0, k) = {}_{N-k}C_k N/(N-k)$$
$$= \begin{cases} 1 & k=0 \\ N & k=1 \\ N(N-k-1)(N-k-2)\ldots(N-2k+1)/k! & k>1 \end{cases} \quad (18)$$

and we have

$$Q_{N^0}(Y) = \sum_{k=0}^{[\frac{N}{2}]} \{{}_{N-k}C_k N/(N-k)\}\, Y^k . \quad (19)$$

Since in this case the ring $\boldsymbol{R}_1$ is identical to $\boldsymbol{G}$ (namely $n_1 = N$), the second term of Eq. (6) becomes $-2(-1)^N$. Thus we have

$$P_{N^0}(X) = \sum_{k=0}^{[\frac{N}{2}]} (-1)^k\, p(N^0, k)\, X^{N-2k} - 2(-1)^N . \quad (20)$$

The resultant polynomials for smaller rings are well known and not shown here [4–6, 13].

2) *Multi-Ring Graphs.* Consider a graph $\boldsymbol{G}$ in Fig. 4, or the carbon atom skeleton of biphenylene. See also Table 1 for explanation. The first step is to set up all the possible subgraphs $\boldsymbol{G}_i$'s ($i = 1-6$ in this example and marked with heavy lines, $\boldsymbol{G}_6$ being a vacant graph) with N_i points by deleting from $\boldsymbol{G}$ a ring $\boldsymbol{R}_i$ (framed) and the lines (crossed) incident to it. Next try to find out the possibility if a pair of disjoint rings can be chosen from $\boldsymbol{G}$. In this example we get a vacant graph $\boldsymbol{G}_7$ by deleting two disjoint hexagons and two lines joining them. Continue this process until as many disjoint rings are chosen from $\boldsymbol{G}$ as possible. Write out the set of the polynomials $Q_{\boldsymbol{G}_i}(Y)$'s together with that of the original graph

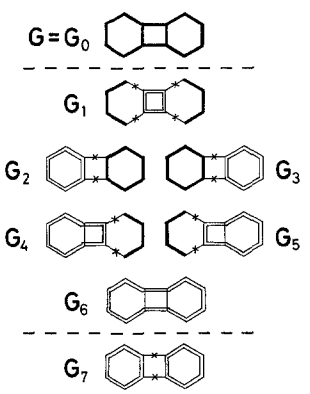

Fig. 4. Subgraphs for enumerating the characteristic polynomial of biphenylene. See also Table 1 for explanation

Table 1. Components of the characteristic polynomial $P_G(X)$ of biphenylene[a]

i[b]	l_i[c]	N_i[d]	Y-Expression, $Q_{G_i}(Y)$	Ref.	X-Expression[e]	Weight[f]
0	0	12	$1+14Y+71Y^2+162Y^3$ $+164Y^4+60Y^5+5Y^6$	Fig. 5 / Eqs. (16) (19)	$X^{12}-14X^{10}+71X^8-162X^6$ $+164X^4-60X^2+5$	1
1	1	8	$(1+3Y+Y^2)^2$ $=1+6Y+11Y^2+6Y^3+Y^4$	Eq. (16)	$X^8-6X^6+11X^4-6X^2+1$	−2
2,3	1	6	$2(1+6Y+9Y^2+2Y^3)$	Eq. (19)	$2(X^6-6X^4+9X^2-2)$	−2
4, 5	1	4	$2(1+3Y+Y^2)$	Eq. (16)	$2(X^4-3X^2+1)$	−2
6	1	0	1	Def. 5)	1	−2
7	2	0	1	Def. 5)	1	4

[a] The characteristic polynomial $P_G(X)$ for biphenylene is obtained by adding the X-expressions with weights given in the last column.
[b] The suffix referring to the subgraph given in Fig. 4.
[c] The number of disjoint rings deleted from G to give G_i.
[d] The number of points in G_i.
[e] The polynomial begins with $(-1)^N(-X)^{N_i}$.
[f] $(-2)^{l_i}$.

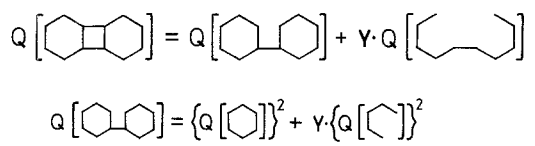

Fig. 5. Illustration for obtaining $Q_G(Y)$ of the carbon atom skeleton of biphenylene. By the use of Eqs. (16) and (19) the polynomial $Q_G(Y)$ is obtained as in Table 1

$G(\equiv_0)$ as in Table 1. The method for obtaining $Q_G(Y)$ is illustrated in Fig. 5. Now transfer each Y-expression into such an X-expression that begins with the term $(-1)^N(-X)^{N_i}$, descends in its power by two, alternates in the sign and has the same set of the coefficients $p(G, k)$'s. Finally add up all the X-expressions with weights $(-2)^{l_i}$ to get $P_G(X)$, where l_i is the number of the disjoint rings deleted from G to give G_i. In this example we get

$$\begin{aligned} P(X) &= X^{12}-14X^{10}+71X^8-162X^6+164X^4-60X^2+5 \\ &\quad -2(X^8-4X^6+X^4+6X^2)+4 \\ &= X^{12}-14X^{10}+69X^8-154X^6+162X^4-72X^2+9\,. \end{aligned}$$

Compare the present method with the "method of polygons" for the same example [8, 9] and find out the simplicity and generality of the former.

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