A New Recursion Relation for the Characteristic Polynomial of a Molecular Graph

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Received September 8, 1995[⊗]

A recursion relation for the characteristic polynomial $\phi(G)$ of a molecular graph G is obtained, by means of which $\phi(G)$ is expressed as a linear combination of characteristic polynomials of certain edge- and vertex-deleted subgraphs of G. This result is a proper generalization of the long-known Heilbronner formula. The new recursion relation is extended to graphs with weighted edges and/or self-loops as well as to other polynomials of importance in chemical graph theory.

1. INTRODUCTION

Graph polynomials play an outstanding role in the chemical applications of graph theory.[1−5] Of all graph polynomials, the characteristic polynomial ϕ is best studied both in chemistry[1−6] and in mathematics.[7,8]

Let G be a molecular graph[1,2] possessing n vertices and m edges. Let $\mathbf{I}$ be the unit matrix of order n. If $\mathbf{A}$ is the adjacency matrix of the graph G, then the characteristic polynomial of this matrix, namely $\det(x\mathbf{I}-\mathbf{A})$ is called the characteristic polynomial of the graph G; we denote it by $\phi(G) = \phi(G,x)$. Recall that $\phi(G)$ is closely related to the secular equation of the tight-binding Hamiltonian, pertaining to a π-electron system whose topology is represented by the molecular graph G.[3,4,9]

A variety of approaches were put forward in the chemical literature, aimed at an easy calculation of the characteristic polynomial. (For more details see the books[1−5] in which additional references can be found.) Here we are concerned only with recursion relations for $\phi(G)$.

2. THE HEILBRONNER FORMULAS

The first recursion relations for $\phi(G)$ were put forward by Heilbronner.[10] In order to formulate them we have to define our notation.[1]

Let v be a vertex of G. Then $G-v$ is the subgraph obtained by deleting from G the vertex v and all incident edges. Let u and v be adjacent vertices in G. Then the edge connecting u and v will be denoted by uv and the subgraph obtained by deleting uv from G will be denoted G-uv. Further, G-u-v is the subgraph obtained by deleting from G both the vertices u and v. Observe that if G has n vertices, then G-uv, G-v, and G-u-v have n, $n-1$, and $n-2$ vertices, respectively.

The number $d(v)$ of first neighbors of the vertex v is called the degree (or valency) of this vertex. In what follows we often encounter summations over all first neighbors of v; a vertex that is first neighbor to v will be denoted by u and the respective summation indicated by $\sum_u$.

If Z is a circuit of the graph G, then $G-Z$ is the subgraph obtained by deleting from G all vertices of the circuit Z together will all incident edges. The sets of all circuits of G which contain the edge uv and the vertex v are denoted by $\mathbf{C}_{uv}$ and $\mathbf{C}_v$, respectively.

An edge uv is said to be a bridge if it does not belong to a circuit (or more formally: if $\mathbf{C}_{uv}$ is an empty set). Now, Heilbronner[10] proved the following

1. If uv is a bridge, then

$$\phi(G) = \phi(G\text{-}uv) - \phi(G\text{-}u\text{-}v) \tag{1}$$

2. If all the $d(v)$ edges ending at the vertex v are bridges, then

$$\phi(G) = x\,\phi(G\text{-}v) - \sum_u \phi(G\text{-}u\text{-}v) \tag{2}$$

A noteworthy special case of formula 2 is when $d(v) = 1$. Then the unique edge uv is necessarily a bridge and (2) reduces to

$$\phi(G) = x\,\phi(G\text{-}v) - \phi(G\text{-}u\text{-}v) \tag{3}$$

The recursion relations 1−3 are known under the name "Heilbronner formulas". As clearly seen, they express $\phi(G)$ in terms of the characteristic polynomials of the subgraphs G-v, G-uv, and/or G-u-v.

The Heilbronner formula (1) is applicable only if the edge uv does not belong to any circuit of G, namely if $\mathbf{C}_{uv} = \phi$. Similarly, formula 2 holds only if the vertex v does not belong to any circuit of G, or in other words if $\mathbf{C}_v = \phi$. If either $\mathbf{C}_{uv}$ or $\mathbf{C}_v$ is nonempty, then the recursion relations 1 and 2 have to be modified in the following manner

$$\phi(G) = \phi(G\text{-}uv) - \phi(G\text{-}u\text{-}v) - 2\sum_{Z\in\mathbf{C}_{uv}} \phi(G\text{-}Z) \tag{4}$$

$$\phi(G) = x\,\phi(G\text{-}v) - \sum_u \phi(G\text{-}u\text{-}v) - 2\sum_{Z\in\mathbf{C}_v} \phi(G\text{-}Z) \tag{5}$$

Here and later it is assumed that $\phi(G) \equiv 1$ whenever the cycle Z embraces all the vertices of G. It is not difficult to see that (5) is obtained by means of a repeated application of (4) to all edges ending at the vertex v. It seems to be overlooked by many that also formula (4) is mentioned in

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⊗ Abstract published in *Advance ACS Abstracts,* January 15, 1996.

0095-2338/96/1636-0527$12.00/0

Heilbronner's paper.[10] The expressions 4 and 5 were later rediscovered by Schwenk.[11]

3. BEYOND THE HEILBRONNER RECURSION RELATIONS

The problem with the eqs 4 and 5 lies in the fact that in the case of graphs representing polycyclic molecules, $\mathbf{C}_{uv}$ and $\mathbf{C}_v$ may contain scores of circuits, making the calculation of $\phi(G)$ very cumbersome and error prone. For instance, if uv is an edge lying on the perimeter of coronene (a heptacyclic, medium size, benzenoid molecule, see Figure 1), then $\mathbf{C}_{uv}$ consists of 47 circuits and thus the right-hand side of (4) contains 49 terms. The set $\mathbf{C}_v$ of coronene (see Figure 1) possesses 67 elements implying that on the right-hand side of (5) a total of 71 characteristic polynomials will appear. Detailed examples illustrating the application of eqs 4 and 5 were previously reported (see pp 37 and 133−176 in refs 1 and 2, respectively).

Recursion formulas aimed at overcoming this difficulty were proposed by one of the present authors[2,5,8,12] and, independently, by Kolmykov[5,13]

$$\phi(G) = \phi(G\text{-}uv) - \phi(G\text{-}u\text{-}v) - 2[\phi(G\text{-}u)\,\phi(G\text{-}v) - \phi(G\text{-}uv)\,\phi(G\text{-}u\text{-}v)]^{1/2} \quad (6)$$

Kolmykov[5,13] communicated also a related expression

$$\phi(G) = x\,\phi(G\text{-}v) - \sum_u \phi(G\text{-}u\text{-}v) - 2 \sum_{u' < u''} [\phi(G\text{-}u'\text{-}v)\,\phi(G\text{-}u''\text{-}v) - \phi(G\text{-}v)\,\phi(G\text{-}u'\text{-}u''\text{-}v)]^{1/2} \quad (7)$$

In eq 7 the last summation goes over all pairs of vertices u' and u'' which are adjacent to the vertex v. If no two such vertices exist, then the respective summation is zero and (7) reduces to (3).

In the recursion relations 6 and 7 essentially the same subgraphs occur as in the Heilbronner formulas 1 and 2, whereas subgraphs of the type $G\text{-}Z$ are avoided. This is an advantage of 6 and 7 over 4 and 5. The evident setback of 6 and 7 is their nonlinearity. We shall overcome this problem in the subsequent section.

At this point Rowlinson's[14] recursion formula should also be mentioned, namely

$$\phi(G) = \phi(G\text{-}uv) + \phi(G^*uv) + (x - 1)\,\phi(G\text{-}u\text{-}v) - \phi(G\text{-}u) - \phi(G\text{-}v)$$

where G^*uv is the graph obtained from $G\text{-}uv$ by identifying its vertices u and v, and keeping all the edges of $G\text{-}uv$.

4. THE NEW RECURSION RELATION

We first deduce an auxiliary combinatorial identity. Every cycle Z of G which contains the vertex v contains exactly two edges of G, incident to the vertex v. In other words, every element of $\mathbf{C}_v$ is contained in exactly two distinct sets $\mathbf{C}_{uv}$. This implies

$$\sum_u \sum_{Z \in \mathbf{C}_u} \equiv 2 \sum_{Z \in \mathbf{C}_v} \quad (8)$$

Now, we sum eq 4 over all vertices u which are adjacent to the vertex v, recalling that there are $\mathrm{d}(v)$ such vertices. From the sum thus obtained we subtract twice eq 5. This results in

$$[\mathrm{d}(v) - 2]\,\phi(G) = \Big[\sum_u \phi(G\text{-}uv) - \sum_u \phi(G\text{-}u\text{-}v) - 2 \sum_u \sum_{Z \in \mathbf{C}_{uv}} \phi(G\text{-}Z)\Big] - 2\Big[x\,\phi(G\text{-}v) - \sum_u \phi(G\text{-}u\text{-}v) - 2 \sum_{Z \in \mathbf{C}_v} \phi(G\text{-}Z)\Big]$$

which after simple rearrangements gives

$$[\mathrm{d}(v) - 2]\,\phi(G) = \Big[\sum_u \phi(G\text{-}uv) + \sum_u \phi(G\text{-}u\text{-}v) - 2\,x\,\phi(G\text{-}v)\Big] - 2\Big[\sum_u \sum_{Z \in \mathbf{C}_{uv}} \phi(G\text{-}Z) - 2 \sum_{Z \in \mathbf{C}_v} \phi(G\text{-}Z)\Big] \quad (9)$$

Because of (8) the last term on the right-hand side of (9) is zero, and we thus arrive at our main result[15]

$$[\mathrm{d}(v) - 2]\,\phi(G) = \sum_u \phi(G\text{-}uv) + \sum_u \phi(G\text{-}u\text{-}v) - 2x\,\phi(G\text{-}v) \quad (10)$$

i.e.

$$\phi(G) = \frac{1}{\mathrm{d}(v) - 2}\Big[\sum_u \phi(G\text{-}uv) + \sum_u \phi(G\text{-}u\text{-}v) - 2x\,\phi(G\text{-}v)\Big] \quad (11)$$

Formula 11 is a recursion relation for the characteristic polynomial of an arbitrary graph. To the author's best knowledge, it was communicated[15] the first time at a scientific conference in 1993 and has not been published so far. Formula 11 expresses $\phi(G)$ in terms of the characteristic polynomials of the subgraphs $G\text{-}uv$, $G\text{-}v$, and $G\text{-}u\text{-}v$, which are precisely those occurring in the Heilbronner relations 1−3. If the degree of the vertex v is $\mathrm{d}(v)$, then the number of terms occurring on the right-hand side of (11) is exactly $2\,\mathrm{d}(v) + 1$. All terms on the right-hand side of (11) are linear; hence (11) is a linear recurrence relation. For an example see Figure 1.

If $\mathrm{d}(v) = 1$, then formula 11 reduces to Heilbronner's relation 3. To see this, recall that in this case the vertex v has a single neighbor, denoted by u. Therefore $\sum_u \phi(G\text{-}uv)$ and $\sum_u \phi(G\text{-}u\text{-}v)$ become equal to $\phi(G\text{-}uv) \equiv x\,\phi(G\text{-}v)$ and $\phi(G\text{-}u\text{-}v)$, respectively.

Formula 11 is, clearly, not applicable to a vertex v whose degree is two. This, however, is no problem at all because all molecular graphs (with a single exception) possess vertices of degree different than two. The only molecular graph in which all vertices have degree two is the cycle C_n. General analytical expressions are known[1] for the characteristic polynomial and the eigenvalues of C_n. Consequently, the task to recursively evaluate $\phi(C_n)$ will hardly ever emerge in practical work. For all molecular graphs other than C_n, eq 11 is applicable.

Needless to say that if the graph contains bridges, then Heilbronner's formula 1, or its special cases 2 and 3, are

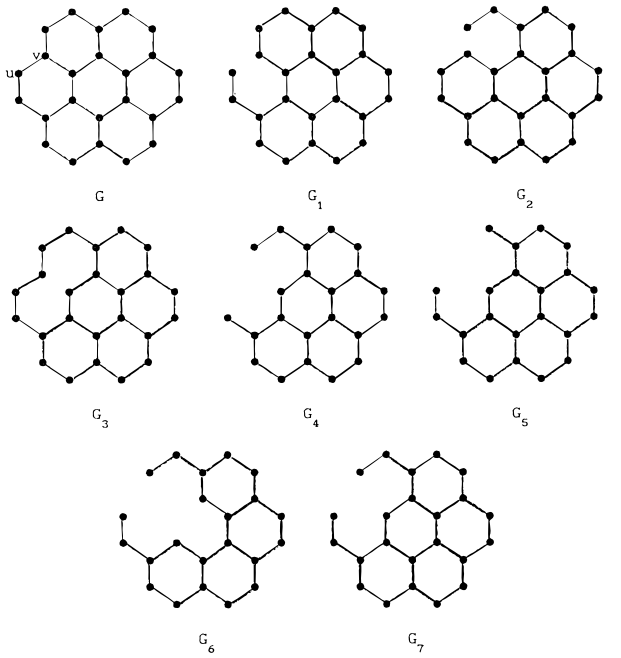

Figure 1. According to eqs 4 and 5 the characteristic polynomial of coronene (G) is expressed as a linear combination of characteristic polynomials of 49 and 71 subgraphs of G, respectively. In eq 11 only seven such subgraphs are involved: $G_1 - G_7$; because of symmetry, $\phi(G_1) = \phi(G_2)$ and $\phi(G_4) = \phi(G_5)$, which results in $\phi(G) = 2\,\phi(G_1) + \phi(G_3) + 2\,\phi(G_4) + \phi(G_6) - 2x\,\phi(G_7)$; observe that in this example $d(v) = 3$.

still the best means for recursive computation of the characteristic polynomial of a molecular graph. The new formula 11 is advantageous in the case of compact polycyclic graphs. For its applicability the molecule needs not possess any symmetry. If, nevertheless, the molecule possesses elements of symmetry, then the application of formula 11 is somewhat easier, as explained in the example given in Figure 1.

Recall that the graph G is assumed to possess n vertices and m edges. By summing eq 10 over all vertices of G and by taking into account the well-known identity[1,2]

$$\sum_{v=1}^{n} d(v) = 2m$$

we obtain

$$(m - n)\,\phi(G) = \sum_{uv} [\phi(G\text{-}uv) + \phi(G\text{-}u\text{-}v)] - 2x \sum_{v} \phi(G\text{-}v) \quad (12)$$

The first and second summations on the right-hand side of (12) go over all edges and over all vertices, respectively, of the graph G. Another way to write (12) is[7,8]

$$(m - n)\,\phi(G) = \sum_{uv} [\phi(G\text{-}uv) + \phi(G\text{-}u\text{-}v)] - 2x\,(d/dx)\phi(G) \quad (13)$$

Monocyclic graphs have an equal number of vertices and edges. For them the left-hand sides of (12) and (13) vanish. For monocyclic graphs we thus obtain the following noteworthy identity for the first derivative of the characteristic polynomial

$$(d/dx)\phi(G) = (2x)^{-1} \sum_{uv} [\phi(G\text{-}uv) + \phi(G\text{-}u\text{-}v)]$$

5. GENERALIZATIONS

Consider now the case when the graph G possesses directed and weighted edges as well as weighted self-loops.[1,3,16−20] (As well-known,[9,16,18] such weighted graphs are used in the theory of conjugated molecules containing heteroatoms.) Let w_{rs} be the weight of the directed edge starting from vertex r and ending at vertex s, $r \neq s$. Let w_{rr} be the weight of the self-loop on the vertex r. We set $w_{rs} = 0$ if there is no edge starting from vertex r and ending at vertex s. Further, we set $w_{rr} = 0$ if the vertex r possesses no self-loop. With these conventions the adjacency matrix of G is just $\mathbf{A} = ||w_{rs}||$.[20]

Then the following generalization of (11) holds

$$\phi(G) = \frac{1}{d(v) - 2}\Big[\sum_{u} \phi(G\text{-}uv) + w_{uv}w_{vu} \sum_{u} \phi(G\text{-}u\text{-}v) - 2(x - w_{vv})\,\phi(G\text{-}v)\Big] \quad (14)$$

For simple graphs formula 14 reduces to (11); to see this observe that for simple graphs $w_{uv} = w_{vu} = 1$ whenever the vertices u and v are adjacent and that $w_{vv} = 0$ for all vertices v.

The permanental polynomial of a graph G is defined as[8,21,22] $\phi^+(G) = \phi^+(G,x) = \mathrm{per}(x\,\mathbf{I} + \mathbf{A})$; recall that this polynomial has, so far, found no application in chemistry. Formulas 11 and 14 are straightforwardly modified so as to apply to the permanental polynomials

$$\phi^+(G) = \frac{1}{d(v) - 2}\Big[\sum_{u} \phi^+(G\text{-}uv) - \sum_{u} \phi^+(G\text{-}u\text{-}v) - 2x\,\phi^+(G\text{-}v)\Big]$$

$$\phi^+(G) = \frac{1}{d(v) - 2}\Big[\sum_{u} \phi^+(G\text{-}uv) - w_{uv}w_{vu} \sum_{u} \phi^+(G\text{-}u\text{-}v) - 2(x + w_{vv})\,\phi^+(G\text{-}v)\Big]$$

ACKNOWLEDGMENT

One author (I.G.) gratefully acknowledges the financial support by the Mathematical Institute, Belgrade (Grant No. 0401A) and by the Lady Davis Fellowship Trust, Jerusalem.

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CI9501148