International Journal of Pure and Applied Mathematics
Volume 12 No. 1 2004, 33-46

ON CHARACTERISTIC POLYNOMIALS OF WEIGHTED MOLECULAR GRAPHS

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Abstract: We present explicit formulas and recursive procedures to determine the characteristic polynomials of molecular graphs whose vertices and edges are arbitrarily weighted. Starting from a set of paths and cycles we construct new graphs by joining connected components and adding or inserting edges in a certain way such that the characteristic polynomials of the arising graphs can be recursively obtained. A full description of the class of molecular graphs arising this way is given.

AMS Subject Classification: 92E10, 05C50
Key Words: molecular graph, weighted graph, characteristic polynomial, LCAO method

1. Introduction

A weighted molecular graph is a finite simple undirected graph whose vertices and edges are weighted by real numbers. In chemistry the knowledge of the characteristic polynomials of weighted molecular graphs is of importance in order to determine molecular orbitals and their energy values by means of the LCAO method (linear combination of atomic orbitals) (cf. Bonchev et al [1], Goodrich [4], Gutmann et al [5], Heilbronner et al [6]). The vertices of the molecular graph then correspond to the atoms of the molecule and the edges

Received: December 20, 2003
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represent bonds or overlapping forces between atoms. As for the weights, the (negative) weights of the vertices are values of Coulomb integrals and the (negative) weights of the edges values of resonance and overlap integrals. The energy values and orbitals are the roots and eigenvectors of the characteristic polynomial of the molecular graph. Hence it is of interest to know this polynomial.

Our goal is to provide procedures to find the characteristic polynomials of arbitrarily weighted molecular graphs that can be constituted by adding edges to trees and cycles and joining connected components by edges. These procedures give rise to explicit and recursive formulas for various classes of graphs that are of interest in chemistry, like the class of all acyclic compounds or derivatives of cyclic compounds.

Our paper can be viewed as a continuation of the paper by Dorninger at al [2] in which only individual atoms and their bonds were allowed to carry weights different from all the other weights which were assumed to be the same for the atoms and also the same for all bonds, respectively.

2. Paths and Cycles

We start with two technical lemmata we later need for calculating the characteristic polynomials of arbitrarily weighted paths and cycles.

For the rest of the paper let m, n denote fixed positive integers with $m \leq n$ and let a_{st} be a real number for all positive integers s, t. Further we define

$$A_{mn} := \begin{vmatrix} a_{mm} & a_{m,m+1} & 0 & \dots & 0 \\ a_{m+1,m} & a_{m+1,m+1} & a_{m+1,m+2} & \ddots & \vdots \\ 0 & a_{m+2,m+1} & a_{m+2,m+2} & \ddots & 0 \\ \vdots & \ddots & \ddots & \ddots & a_{n-1,n} \\ 0 & \dots & 0 & a_{n,n-1} & a_{nn} \end{vmatrix}.$$

Lemma 2.1.

$$A_{mn} = \sum_{\substack{I \subseteq \{m,\dots,n-1\} \\ i-j \neq \pm 1 \text{ for all } i,j \in I}} (-1)^{|I|} \Big(\prod_{k \in I} a_{k,k+1} a_{k+1,k}\Big) \times \Big(\prod_{s \in \{m,\dots,n\} \setminus \bigcup_{t \in I} \{t,t+1\}} a_{ss}\Big).$$

(as usual, the empty product is interpreted as 1).

Proof. We use induction on n. For $n \in \{m, m+1, m+2\}$ the assertion is obviously true. Now assume $n \geq m+2$ and that the lemma holds for n. Expanding $A_{m,n+1}$ along its last row and expanding the first of the determinants arising this way along the last column yields

$$\begin{aligned}
A_{m,n+1} &= -a_{n+1,n}a_{n,n+1}A_{m,n-1} + a_{n+1,n+1}A_{mn} \\
&= -a_{n,n+1}a_{n+1,n} \sum_{\substack{I\subseteq\{m,\dots,n-2\} \\ i-j\neq\pm1 \text{ for all } i,j\in I}} (-1)^{|I|} \\
&\quad \times \Big(\prod_{k\in I} a_{k,k+1}a_{k+1,k}\Big)\Big(\prod_{s\in\{m,\dots,n-1\}\setminus\bigcup_{t\in I}\{t,t+1\}} a_{ss}\Big) \\
&\quad + a_{n+1,n+1} \sum_{\substack{I\subseteq\{m,\dots,n-1\} \\ i-j\neq\pm1 \text{ for all } i,j\in I}} (-1)^{|I|} \\
&\quad \times \Big(\prod_{k\in I} a_{k,k+1}a_{k+1,k}\Big)\Big(\prod_{s\in\{m,\dots,n\}\setminus\bigcup_{t\in I}\{t,t+1\}} a_{ss}\Big) \\
&= \sum_{\substack{I\subseteq\{m,\dots,n\} \\ i-j\neq\pm1 \text{ for all } i,j\in I}} (-1)^{|I|}\Big(\prod_{k\in I} a_{k,k+1}a_{k+1,k}\Big) \\
&\qquad \times \Big(\prod_{s\in\{m,\dots,n+1\}\setminus\bigcup_{t\in I}\{t,t+1\}} a_{ss}\Big). \quad \square
\end{aligned}$$

For $n \geq 3$ we set

$$A_n := \begin{vmatrix}
a_{11} & a_{12} & 0 & \dots & 0 & a_{1n} \\
a_{21} & a_{22} & a_{23} & 0 & & 0 \\
0 & a_{32} & a_{33} & a_{34} & \ddots & \vdots \\
\vdots & 0 & a_{43} & a_{44} & \ddots & 0 \\
0 & & \ddots & \ddots & \ddots & a_{n-1,n} \\
a_{n1} & 0 & \dots & 0 & a_{n,n-1} & a_{nn}
\end{vmatrix}.$$

Lemma 2.2. *For $n \geq 3$,*

$$A_n = \sum_{\substack{I\subseteq\{1,\ldots,n\} \\ i-j\not\equiv\pm 1 \bmod n \text{ for all } i,j\in I}} (-1)^{|I|}\Big(\prod_{k\in I} a_{k,k+1}a_{k+1,k}\Big) \times \Big(\prod_{s\in\{1,\ldots,n\}\setminus\bigcup_{t\in I}\{t,t+1\}} a_{ss}\Big) + (-1)^{n+1}\Big(\prod_{k=1}^{n} a_{k,k+1} + \prod_{k=1}^{n} a_{k+1,k}\Big),$$

where $n+1$ is to be interpreted as 1.

Proof. Expanding A_n along its last row and expanding the first and the second of the determinants arising this way along their last columns yields

$$\begin{aligned}
A_n &= (-1)^{n+1}a_{n1}(-1)^n a_{1n}A_{2,n-1} + (-1)^{n+1}a_{n1}a_{n-1,n}\prod_{k=1}^{n-2} a_{k,k+1} \\
&\quad - a_{n,n-1}(-1)^n a_{1n}\prod_{k=1}^{n-2} a_{k+1,k} - a_{n,n-1}a_{n-1,n}A_{1,n-2} \\
&= -a_{1n}a_{n1}A_{2,n-1} - a_{n-1,n}a_{n,n-1}A_{1,n-2} + (-1)^{n+1}\Big(\prod_{k=1}^{n} a_{k,k+1} + \prod_{k=1}^{n} a_{k+1,k}\Big) \\
&= -a_{1n}a_{n1}\sum_{\substack{I\subseteq\{2,\ldots,n-2\} \\ i-j\neq\pm 1 \text{ for all } i,j\in I}} (-1)^{|I|}\Big(\prod_{k\in I} a_{k,k+1}a_{k+1,k}\Big) \\
&\quad \times \Big(\prod_{s\in\{2,\ldots,n-1\}\setminus\bigcup_{t\in I}\{t,t+1\}} a_{ss}\Big) - a_{n-1,n}a_{n,n-1}\sum_{\substack{I\subseteq\{1,\ldots,n-3\} \\ i-j\neq\pm 1 \text{ for all } i,j\in I}} (-1)^{|I|} \\
&\quad \times \Big(\prod_{k\in I} a_{k,k+1}a_{k+1,k}\Big)\Big(\prod_{s\in\{1,\ldots,n-2\}\setminus\bigcup_{t\in I}\{t,t+1\}} a_{ss}\Big) \\
&\quad + (-1)^{n+1}\Big(\prod_{k=1}^{n} a_{k,k+1} + \prod_{k=1}^{n} a_{k+1,k}\Big) \\
&= \sum_{\substack{I\subseteq\{1,\ldots,n\} \\ i-j\not\equiv\pm 1 \bmod n \text{ for all } i,j\in I}} (-1)^{|I|}\Big(\prod_{k\in I} a_{k,k+1}a_{k+1,k}\Big) \\
&\quad \times \Big(\prod_{s\in\{1,\ldots,n\}\setminus\bigcup_{t\in I}\{t,t+1\}} a_{ss}\Big) + (-1)^{n+1}\Big(\prod_{k=1}^{n} a_{k,k+1} + \prod_{k=1}^{n} a_{k+1,k}\Big),
\end{aligned}$$

where $n+1$ is interpreted as 1. □

Now we turn to molecular graphs. For a molecular graph G we will always assume that $V=\{1,\dots,n\}$ is its vertex-set and $b_{ii}\neq 0$ (for which we will also write a_i) is the weight of vertex i, $i=1,\dots,n$. Moreover, if there is an edge $[i,j]$ in G then we will denote its weight by $b_{ij}=b_{ji}\neq 0$, otherwise we assume $b_{ij}=0$.

Let $B=(b_{ij})$ be the matrix obtained this way, I the $n\times n$-unit matrix and let x a variable. Then $\varphi(G)=|xI-B|$ is the characteristic polynomial of G in the variable x (which is invariant to the choice of assigning the numbers $1,\dots,n$ to the vertices of G).

We further agree that:

P_n should denote a path with n vertices in which the vertices occur in natural order.

C_n should denote a cycle with $n\geq 3$ vertices in which the vertices occur in natural order.

If $a_i=a$ for $i=1,\dots,n$ and all $b_{ij}\neq 0$ are equal to the same b, we will write $P_n(a,b)$ and $C_n(a,b)$ for P_n and C_n, respectively. □

Lemma 2.1 immediately yields.

Theorem 2.1.

$$\varphi(P_n)=\sum_{\substack{I\subseteq\{1,\dots,n-1\}\\ i-j\neq\pm 1 \text{ for all } i,j\in I}}(-1)^{|I|}\Big(\prod_{k\in I}b^2_{k,k+1}\Big)\times\Big(\prod_{s\in\{1,\dots,n\}\setminus\bigcup_{t\in I}\{t,t+1\}}(x-a_s)\Big)\,.$$

Corollary 2.1.

$$\varphi(P_n(a,b))=\sum_{\substack{I\subseteq\{1,\dots,n-1\}\\ i-j\neq\pm 1 \text{ for all } i,j\in I}}(-1)^{|I|}b^{2|I|}(x-a)^{n-2|I|}=b^nU_n\Big(\frac{x-a}{2b}\Big)\,.$$

Proof. That $\varphi(P_n(a,b))=b^nU_n((x-a)/(2b))$ is a known result (cf. Dorninger at al [2] and Gutmann et al [5]). To see how this result follows from Theorem 2.1

observe that

$$\varphi(P_n(a,b)) = b^n \sum_{k=0}^{[n/2]} \sum_{\substack{I\subseteq\{1,\ldots,n-1\} \\ i-j\neq\pm 1 \text{ for all } i,j\in I \\ |I|=k}} (-1)^{|I|}\left(\frac{x-a}{b}\right)^{n-2|I|}$$

$$= b^n \sum_{k=0}^{[n/2]} (-1)^k \binom{n-k}{k}\left(\frac{x-a}{b}\right)^{n-2k} = b^n U_n\left(\frac{x-a}{2b}\right).$$

To verify the last but one identity we define

$$c_{nk} := |\{I \subseteq \{1,\ldots,n-1\} \mid i-j\neq\pm 1 \text{ for all } i,j\in I, |I|=k\}$$

for $k = 0,\ldots,[n/2]$. Then using induction on n and exploiting combinatorial identities one can see that $c_{nk} = \binom{n-k}{k}$ for $k = 0,\ldots,$ $[n/2]$. □

By means of Lemma 2.2 we obtain the following theorem.

Theorem 2.2. *For* $n \geq 3$,

$$\varphi(C_n) = \sum_{\substack{I\subseteq\{1,\ldots,n\} \\ i-j\not\equiv\pm 1 \bmod n \text{ for all } i,j\in I}} (-1)^{|I|}\left(\prod_{k\in I} b_{k,k+1}^2\right) \times \left(\prod_{s\in\{1,\ldots,n\}\setminus\bigcup_{t\in I}\{t,t+1\}} (x-a_s)\right) - 2\prod_{k=1}^{n} b_{k,k+1}\,,$$

where $n+1$ *should be interpreted as* 1.

Corollary 2.2. *For* $n \geq 3$,

$$\varphi(C_n(a,b)) = \sum_{\substack{I\subseteq\{1,\ldots,n\} \\ i-j\not\equiv\pm 1 \bmod n \text{ for all } i,j\in I}} (-b^2)^{|I|}(x-a)^{n-2|I|} - 2b^n.$$

According to Theorem 3.3 there is a close connection between (arbitrarily weighted) paths and cycles from which one can immediately obtain a formula for $\varphi(C_n(a,b))$ depending on Chebyshev polynomials similar to the formula for $P_n(a,b)$ given in Corollary 2.1 (see Remark 3.1).

3. Recursive Procedures

If we add an edge $[i, n+1]$ of weight $b_{i,n+1}$ to a given graph G by connecting a new vertex $n+1$ of weight a_{n+1} to the vertex i of G, the graph arising this way will be denoted by $G + [i, n+1]$.

If we add two edges $[i, n+1]$ and $[n+1, j]$ of weight $b_{i,n+1} \neq 0$ and $b_{j,n+1} \neq 0$ to G by connecting a new vertex $n+1$ of weight a_{n+1} to the vertices i and j of G with $i \neq j$ then the obtained graph will be denoted by $G + [i, n+1, j]$.

If we add an edge $[i, j]$ to a given graph G (which does not have an edge between i and j) then the arising graph will be denoted by $G[i, j]$.

Moreover, we assume that $G - i_1 - \ldots - i_k$ is the graph we obtain by deleting the (pairwise different) vertices $i_1, \ldots, i_k$ $(k \geq 1)$ of G and all edges of G from G incident to $i_1, \ldots, i_k$.

For $i, j \in \{1, \ldots, n\}$, $D_{ij}(G)$ shall always denote the algebraic complement of the element in the i-th row and j-th column of the $n \times n$-matrix $xI - B$.

In order to indicate the dependence of a set or a matrix on G we will add G in brackets, e.g. $V(G)$, $B(G)$, etc. To emphasize that a vertex, edge, etc. belongs to a graph G we will use G as a subscript.

Lemma 3.3. (cf. Dorninger et al [3]) *For* $1 \leq i \leq n$,

$$\varphi(G + [i, n+1]) = (x - a_{n+1})\varphi(G) - b_{i,n+1}^2 \varphi(G - i).$$

Lemma 3.4. *For* $1 \leq i < j \leq n$,

$$\varphi(G + [i, n+1, j]) = (x - a_{n+1})\varphi(G) - b_{i,n+1}^2 \varphi(G - i) - b_{j,n+1}^2 \varphi(G - j) - 2 b_{i,n+1} b_{j,n+1} D_{ij}(G).$$

Proof. Expanding $\varphi(G + [i, n+1, j])$ along its last row and expanding the first and second of the determinants arising this way along their last columns yields

$$\begin{aligned}
\varphi(G + [i, n+1, j]) &= (-1)^{n+i+1}(-b_{n+1,i})(-1)^{n+i}(-b_{i,n+1})\varphi(G - i) \\
&\quad + (-1)^{n+i+1}(-b_{n+1,i})(-1)^{n+j}(-b_{j,n+1})(-1)^{i+j} D_{ij}(G) \\
&\quad + (-1)^{n+j+1}(-b_{n+1,j})(-1)^{n+i}(-b_{i,n+1})(-1)^{j+i} D_{ji}(G) \\
&\quad + (-1)^{n+j+1}(-b_{n+1,j})(-1)^{n+j}(-b_{j,n+1})\varphi(G - j) + (x - a_{n+1})\varphi(G) \\
&= (x - a_{n+1})\varphi(G) - b_{i,n+1}^2 \varphi(G - i) - b_{j,n+1}^2 \varphi(G - j) \\
&\quad - 2 b_{i,n+1} b_{j,n+1} D_{ij}(G). \quad \square
\end{aligned}$$

Lemma 3.5. *For $1 \leq i < j \leq n$,*

$$\varphi(G[i,j]) = \varphi(G) - 2b_{ij}D_{ij}(G) - b_{ij}^2\varphi(G-i-j).$$

Proof. Let $|(h_{st})|$ be the determinant $\varphi(G[i,j])$ and conceive of the i-th and j-th row of (h_{st}) as the sums of two vectors, namely

$$(h_{i1}, \ldots, h_{i,j-1}, 0, h_{i,j+1}, \ldots, h_{in}) + (0, \ldots, 0, h_{ij}, 0, \ldots, 0) \text{ and}$$
$$(h_{j1}, \ldots, h_{j,i-1}, 0, h_{j,i+1}, \ldots, h_{jn}) + (0, \ldots, 0, h_{ji}, 0, \ldots, 0).$$

Because of the multilinearity of the determinant function we can then split $|(h_{st})|$ into the sum of four determinants which are equal to

$$\varphi(G), h_{ji}D_{ji}(G), h_{ij}D_{ij}(G) \text{ and } (-1)^{i+1}h_{ij}((-1)^{j-1+i}h_{ij}\varphi(G-i-j)),$$

respectively. Taking into account that $h_{ji} = h_{ij} = -b_{ij}$ and summing up we obtain the assertion of the lemma. □

Because of the occurrence of $D_{ij}(G)$ in Lemma 3.4 and Lemma 3.5 we will study $D_{ij}(G)$ more closely for some classes of graphs G.

Lemma 3.6. *If $i \in V(G_1)$, $j \in V(G_2)$ and $G_1 \cap G_2 = \emptyset$ then $D_{ij}(G_1 \cup G_2) = 0$.*

Proof. W. l. o. g. we assume $V(G_1) = \{1, \ldots, m\}$, $V(G_2) = \{m+1, \ldots, n\}$ and $m < n$. Then the matrix M one obtains from $xI - B$ by deleting its i-th row and j-th column is of the form $\begin{pmatrix} M_1 & O \\ O & M_2 \end{pmatrix}$, where M_1 is an $(m-1) \times m$-matrix. From this we infer that the columns of M_1 are linearly dependent and therefore the same is true for the first m columns of M. □

Lemma 3.7. *Let G' be an arbitrary molecular graph with vertex-set $\{m, \ldots, \ldots, n\}$. Then*

$$D_{1m}(P_m \cup G') = (\prod_{k=1}^{m-1} b_{k,k+1})\varphi(G'-m).$$

Proof. Studying the determinant $\varphi(P_m \cup G')$ one immediately obtains

$$D_{1m}(P_m \cup G') = (-1)^{1+m}(\prod_{k=1}^{m-1}(-b_{k,k+1}))\varphi(G'-m)$$
$$= (\prod_{k=1}^{m-1} b_{k,k+1})\varphi(G'-m). \quad \square$$

Theorem 3.3. *For $n \geq 3$,*

$$\varphi(C_n) = \varphi(P_n) - b_{1n}^2 \varphi(P_{n-1} - 1) - 2b_{1n} \prod_{k=1}^{n-1} b_{k,k+1}.$$

Proof. According to Lemma 3.4, Lemma 3.3 and Lemma 3.7

$$\begin{aligned}\varphi(C_n) = \varphi(P_{n-1} + [1, n, n-1]) &= (x - a_n)\varphi(P_{n-1}) - b_{1n}^2 \varphi(P_{n-1} - 1) \\ &- b_{n-1,n}^2 \varphi(P_{n-1} - (n-1)) - 2b_{1n} b_{n-1,n} D_{1,n-1}(P_{n-1}) \\ &= \varphi(P_n) - b_{1n}^2 \varphi(P_{n-1} - 1) - 2b_{1n} \prod_{k=1}^{n-1} b_{k,k+1}. \quad \square\end{aligned}$$

As a consequence of Theorem 3.3 and Corollary 2.1 we can now state

Remark 3.1. (cf. Dorninger et al [2])

$$\varphi(C_n(a,b)) = b^n \left(\frac{x-a}{b} U_{n-1}\left(\frac{x-a}{2b}\right) - 2\left(U_{n-2}\left(\frac{x-a}{2b}\right) + 1\right)\right).$$

Lemma 3.8. *For $m \geq 2$ and $n \geq 3$,*

$$\begin{aligned}D_{1m}(C_n) &= \left(\prod_{k=1}^{m-1} b_{k,k+1}\right)\varphi(P_n - 1 - \ldots - m) \\ &+ b_{1n}\left(\prod_{k=m}^{n-1} b_{k,k+1}\right)\varphi(P_n - 1 - m - (m+1) - \ldots - n).\end{aligned}$$

Proof. As the determinant $\varphi(C_n)$ shows,

$$\begin{aligned}D_{1m}(C_n) = (-1)^{1+m} &\left(\prod_{k=1}^{m-1} (-b_{k,k+1})\right)\varphi(P_n - 1 - \ldots - m) \\ &+ (-1)^{1+m}(-1)^{n-1+1}(-b_{1n})\left(\prod_{k=m}^{n-1} (-b_{k,k+1})\right) \\ &\times \varphi(P_n - 1 - m - (m+1) - \ldots - n) \\ &= \left(\prod_{k=1}^{m-1} b_{k,k+1}\right)\varphi(P_n - 1 - \ldots - m) \\ &+ b_{1n}\left(\prod_{k=m}^{n-1} b_{k,k+1}\right)\varphi(P_n - 1 - m - (m+1) - \ldots - n). \quad \square\end{aligned}$$

Proposition 3.1. *If $m \geq 2$, $n \geq 3$ and $[1,m]$ has weight b then*

$$\varphi(C_n(a,b)[1,m]) = b^n(\frac{x-a}{b}U_{n-1} - 2(U_{n-2}+1) \\ - 2U_{m-2} - 2U_{n-m} - U_{m-2}U_{n-m}),$$

where the Chebyshev polynomials U_k are to be evaluated at $(x-a)/(2b)$.

Proof. From Lemma 3.5, Remark 3.1, Lemma 3.8 and Corollary 2.1 we infer

$$\begin{aligned}\varphi(C_n(a,b)[1,m]) &= b^n(\frac{x-a}{b}U_{n-1} - 2(U_{n-2}+1)) \\ &- 2b(b^{m-1}b^{n-m}U_{n-m} + bb^{n-m}b^{m-2}U_{m-2}) - b^2b^{m-2}U_{m-2}b^{n-m}U_{n-m} \\ &= b^n(\frac{x-a}{b}U_{n-1} - 2(U_{n-2}+1)2U_{m-2} - 2U_{n-m} - 2U_{m-2} + U_{m-2}U_{n-m}),\end{aligned}$$

where the Chebyshev polynomials U_k are evaluated at $(x-a)/(2b)$. □

Example 3.1. If for a graph $C_n(a,b)[1,m]$ with $n \geq 4$ the number n is even and $m = n/2+1$, which e.g. is the case for Naphtalene ($n = 10$, $m = 6$), then

$$\varphi(C_n(a,b)[1,\frac{n}{2}+1]) = b^nU_{n/2-1}(2T_{n/2+1} - 2T_{n/2-1} - U_{n/2-1} - 4),$$

where the Chebyshev polynomials T_k, U_k are to be evaluated at $(x-a)/(2b)$.

This can be seen as follows: Using Proposition 3.1 and Lemma 3.5 of Dorninger et al [3] we obtain

$$\begin{aligned}&\varphi(C_n(a,b)[1,\frac{n}{2}+1]) \\ &= b^n(2\frac{x-a}{b}T_{n/2}U_{n/2-1} - 4T_{n/2-1}U_{n/2-1} - 4U_{n/2-1} - U^2_{n/2-1}) \\ &= b^nU_{n/2-1}(2(\frac{x-a}{b}T_{n/2} - T_{n/2-1} - T_{n/2-1}) - 4 - U_{n/2-1}) \\ &= b^nU_{n/2-1}(2T_{n/2+1} - 2T_{n/2-1} - U_{n/2-1} - 4),\end{aligned}$$

where the Chebyshev polynomials T_k, U_k are evaluated at $(x-a)/(2b)$.

Now we generalize Proposition 3.1.

Theorem 3.4. *For $n \geq 3$,*

$$\begin{aligned}\varphi(C_n[1,m]) = \varphi(P_n) - b_{1n}^2\varphi(P_{n-1} - 1) - 2b_{1n}\prod_{k=1}^{n-1} b_{k,k+1} \\ - 2b_{1m}(\prod_{k=1}^{m-1} b_{k,k+1})\varphi(P_n - 1 - \ldots - m) \\ - 2b_{1m}b_{1n}(\prod_{k=m}^{n-1} b_{k,k+1})\varphi(P_n - 1 - m - (m+1) - \ldots - n) \\ - b_{1m}^2\varphi(P_n - 1 - \ldots - m)\varphi(P_n - 1 - m - (m+1) - \ldots - n).\end{aligned}$$

Proof. From Lemma 3.5, Theorem 3.3 and Lemma 3.8 we deduce that for $n \geq 3$

$$\begin{aligned}\varphi(C_n[1,m]) &= \varphi(C_n) - 2b_{1m}D_{1m}(C_n) - b_{1m}^2\varphi(C_n - 1 - m) \\ &= \varphi(P_n) - b_{1n}^2\varphi(P_{n-1} - 1) - 2b_{1n}\prod_{k=1}^{n-1} b_{k,k+1} \\ &\quad - 2b_{1m}(\prod_{k=1}^{m-1} b_{k,k+1})\varphi(P_n - 1 - \ldots - m) \\ &\quad - 2b_{1m}b_{1n}(\prod_{k=m}^{n-1} b_{k,k+1})\varphi(P_n - 1 - m - (m+1) - \ldots - n) \\ &\quad - b_{1m}^2\varphi(P_n - 1 - \ldots - m)\varphi(P_n - 1 - m - (m+1) - \ldots - n). \quad \square\end{aligned}$$

Putting together Lemma 3.4, Theorem 3.3 and Lemma 3.8 we obtain the following result.

Theorem 3.5. *For $m \geq 2$ and $n \geq 3$,*

$$\begin{aligned}\varphi(C_n + [1, n+1, m]) = (x - a_{n+1})(\varphi(P_n) - b_{1n}^2\varphi(P_{n-1} - 1) - 2\prod_{k=1}^{n-1} b_{k,k+1}) \\ - b_{1,n+1}^2\varphi(C_n - 1) - b_{m,n+1}^2\varphi(C_n - m) \\ - 2b_{1,n+1}b_{m,n+1}((\prod_{k=1}^{m-1} b_{k,k+1})\varphi(P_n - 1 - \ldots - m) \\ + b_{1n}(\prod_{k=1}^{m} b_{k,k+1})\varphi(P_n - 1 - m - \ldots - n)).\end{aligned}$$

Lemma 3.9. *If $n \geq 3$, $b_{1i} = b_{i,n-1} = b_{in}$ for $i = 2, \ldots n-2$ and $b_{1n} = b_{n-1,n}$ then*

$$D_{1n}(G) = -(x - a_{n-1} + b_{1,n-1})(\varphi(G - 1 - n) - (x - a_{n-1} + b_{1n})\varphi(G - 1 - (n-1) - n)).$$

Proof. Due to the special choice of the entries b_{ij} the determinant $D_{1n}(G)$ can be evaluated in the following way: We start by subtracting the last column of $D_{1n}(G)$ from its first column, which leaves $-b_{1n} - (x - a_{n-1})$ as the only non-vanishing element in this column. Then we expand the determinant along this column and represent the last row of the determinant that arises, i.e. $(-b_{12}, -b_{13}, \ldots, -b_{1,n-2}, -b_{1n})$, as the sum of two vectors, namely

$$(-b_{12}, -b_{13}, \ldots, -b_{1,n-2}, x - a_{n-1}) + (0, 0, \ldots, 0, -(x - a_{n-1} + b_{1n})),$$

which immediately yields the assertion of the lemma if we take into account the multilinearity of the determinant function. □

The assumption of Lemma 3.9 is e.g. satisfied if G is a graph with vertices $1, \ldots, 4$ of weight $a_1, \ldots, a_4$ and edges $[1,2], [2,3], [2,4]$ of weight b. Then $D_{14}(G) = -(x - a_3)((x - a_2)(x - a_3) - b^2 + (x - a_3)(x - a_2)) = b^2(x - a_3)$.

Another example would be a graph G with vertices $1, \ldots, 6$ of weight $a_1, \ldots, a_6$ and edges $[1,2], [2,5], [2,6]$ of weight b_1, $[1,3], [3,5], [3,6]$ of weight b_2 and $[1,4], [4,5], [4,6]$ of weight b_3. Such a graph may occur if a molecule has the form of a pyramid with apex b, base $1, 2, 5, 4$ and 3 as the center of its base, or we can think of a circular compound $1, 2, 6, 4, 5, 3, 1$ with three cords. In both cases Lemma 3.9 yields $D_{16}(G) = (x - a_5)(b_1^2(x - a_3)(x - a_4) + b_2^2(x - a_2)(x - a_4) + b_3^2(x - a_2)(x - a_3))$.

4. Classes of Graphs Covered by the Recursive Procedures of Section 3

Our goal is to determine the class of graphs for which one can recursively obtain their characteristic polynomials by means of the procedures we have described in the last section.

Let us call graphs of the form $C_n[i,j]$ and $C_n + [i, n+1, j]$ double cycles. Moreover, let TC denote the class of graphs (with arbitrary weights) which can be obtained in the following way:

Given an arbitrary edge-weighted tree T substitute some of its vertices i (at random) by a cycle or double cycle $C(i)$ such that any neighbour of i in T that is not substituted by a cycle or double cycle will be connected to an arbitrary vertex of $C(i)$. If a neighbour j of a substituted vertex i is also substituted by a cycle or double cycle either omit the edge $[i,j]$ and assume that $C(i)$ and $C(j)$ share exactly one vertex or consider i and j as vertices of $C(i)$ and $C(j)$, respectively, which are then connected by the edge $[i,j]$. However, if two neighbouring vertices of T are both substituted by double cycles $C(i)$ and $C(j)$ the subgraph $C(i) \cup C(j)$ of the resulting graph should be separable by a bridge connecting $C(i)$ and $C(j)$ (as we will explain later this restriction can be discarded for certain double cycles).

We will refer to TC as a class of treelike graphs.

Next we agree to say that we "add a hair" to G if we construct the graph $G+[i,n+1]$. Moreover, we will say that we "add a new cycle" to G if we proceed as follows: Starting with a vertex i_G of G we successively add hairs to the graph that arises such that we obtain a graph $H = G \cup P_m$ with $G \cap P_m = \{i_G\}$. Then we close the path P_m which we assume to have the last vertex i_H to a cycle by forming $H + [i_H, (n+1)_H, i_G]$.

Next we explain what "connecting disjoint components by paths" should mean. We consider a graph G that consists of two disjoint components $G_1 \cup P_{m_1}$ and $G_2 \cup P_{m_2}$ (as defined above). If $i_{G_1} = i_1, \ldots, i_r =: i$ and $j_{G_2} = j_1, \ldots, j_s =: j$ are the vertices of P_{m_1} and P_{m_2}, respectively, we connect $G_1 \cup P_{m_1}$ and $G_2 \cup P_{m_2}$ by inserting an edge $[i,j]$ into G.

We observe that the characteristic polynomial of a graph $G+[i,n+1]$ that is obtained by adding a hair to G can be determined by means of $\varphi(G)$ and $\varphi(G-i)$ as explained by Lemma 3.3. Morerover, referring to G, H, i_G and i_H as defined above we see that Lemma 3.4 and Lemma3.7 allow to reduce the calculation of the characteristic polynomial of a graph that arises by adding a new cycle to determining $\varphi(H)$, $\varphi(H - i_H)$, $\varphi(H - i_G)$ and $\varphi(G - i_G)$. Finally, according to Lemma 3.5 and Lemma 3.6, the calculation of the characteristic polynomial of a graph obtained by connecting disjoint components by paths can be reduced to computing $\varphi(G)$ and $\varphi(G - i - j)$, where $G = (G_1 \cup P_{m_1}) \cup (G_2 \cup P_{m_2})$ with $(G_1 \cup P_{m_1}) \cap (G_2 \cup P_{m_2}) = \emptyset$, from which we infer that $\varphi(G) = \varphi(G_1 \cup P_{m_1})\varphi(G_2 \cup P_{m_2})$.

As we have shown before the characteristic polynomials of paths (Theorem 2.1), cycles (Theorem 2.2) and double cycles (Theorem 3.4 and Theorem 3.5) can be explicitly calculated. Taking it all around we therefore obtain the following proposition.

Proposition 4.1. *The characteristic polynomials of molecular graphs of the class TC of treelike graphs can be recursively obtained from the above formulas for the characteristic polynomials of paths, cycles and double cycles by adding hairs, adding new cycles and connecting disjoint components* *by paths.*

The class TC can be further enlarged by inserting into trees also double cycles with four or five vertices (satisfying a weak restriction about their weights) for which the assumption to be separable by bridges can be omitted. This can be seen as follows:

Adding three new edges $[i_G, j]$, $[i_G, k]$ and $[i_G, l]$ of the same weight to a graph G (with j, k, l not in G) the graph G' that arises fulfills the assumptions of Lemma 3.9 (where one conceives of $n-2$ as i_G, n as l, $n-1$ as k and 1 as j). Moreover, also $G'[j,l]$ fulfills the assumptions of Lemma 3.9 (with reversed roles of k and l) so that we can recursively calculate $\varphi((G'[j,l])[j,k])$ and $\varphi(G'[j,l]+[j,n+1,k])$ with $n+1$ as newly added vertex to $G'[j,l]$. This way the double cycles i_G, k, j, l, i_G and $i_G, k, n+1, j, l, i_G$, both with chord $[i_G, j]$, can be added to G.

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