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ON CHARACTERISTIC POLYNOMIALS OF MOLECULAR GRAPHS WITH HETEROATOMS

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Abstract: We consider molecular graphs whose vertices and edges are both weighted by real numbers corresponding to Coulomb and resonance integrals of the underlying chemical compounds. Given a molecular graph G we derive recursive procedures to find the characteristic polynomials of graphs that are obtained when new vertices and edges carrying new weights are added to G or vertices and edges of G are substituted. Exploiting these recursions, if G is a cycle or path, we obtain explicit formulas for the characteristic polynomials of the compounds that arise. Since the zeros of the characteristic polynomials approximately correspond to the energy values of electrons it is of interest to know about the influence of heteroatoms when added to a given compound or when atoms of a compound are substituted. For this end we determine factors of the characteristic polynomials that do not depend on the weights of the newly introduced atoms and their bonds which leads to the investigation of common divisors of Chebyshev polynomials of the first and second kind.

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1. Introduction

In chemistry the knowledge of characteristic polynomials of molecular graphs is of importance in order to determine molecular orbitals and their energy levels by means of the LCAO-method (linear combination of atomic orbitals) (cf. Bonchev et al [1], Dorninger et al [2], Goodrich [4], Gutmann et al [5] and Heilbronner et al [6]). A molecular graph is a finite simple undirected graph, whose vertices and edges are weighted by real numbers, that correspond to the values of Coulomb and resonance integrals, respectively. In case that the weights of all vertices are equal and also the weights of all edges are the same, which means that the underlying structure consists of only one type of atoms, usually C-atoms, the problem of finding the characteristic polynomial can be easily reduced to finding the characteristic polynomial of a graph with adjacency matrix containing only elements 0 and 1, a problem, which has often been considered in the literature (cf. e. g. Godsil et al [3]). On the other hand, if heteroatoms are involved, i. e. atoms of different kinds occur in a chemical compound which gives rise to more than two kinds of weights, graph-theoretical procedures to determine the characteristic polynomials are comparatively rare.

In the following paper we will provide some recursive formulas to find the characteristic polynomial of a molecular graph by adding new atoms to a given compound or substituting an atom by another one. These formulas will allow to explicitely determine the characteristic polynomials of compounds that are built up of cycles and paths. Moreover, we will describe factors of the characteristic polynomials that show that a certain number of energy levels will not be (very much) influenced if heteroatoms are added or substituted in cyclic compounds.

2. Graph-Theoretic Procedures

We will denote a molecular graph by G_B, where $B = (b_{ij})$, $i, j = 1, \dots, n$ is a matrix of non-positive real values (we assume energy values to be negative) defined in the following way: Let $V(G_B) = \{1, \dots, n\}$ be the vertex set of G_B. Then $b_{ii} \neq 0$ will denote the weight of vertex $i, i = 1, \dots, n$, and if there exists an undirected edge between i and j, which we will denote by $[i, j]$, then $b_{ij} \neq 0$ is assumed to be the weight of this edge otherwise we put $b_{ij} = 0$.

Writing I for the $n \times n$-unit-matrix, the *characteristic polynomial* of G_B in the variable x is then given by

$$\varphi(G_B, x) := |xI - B| \,,$$

for which we will write $\varphi(G_B)$ if there is no doubt about the indeterminant. $\varphi(G_B)$ is an invariant in respect to assigning the numbers $1,\dots,n$ to the vertices of G_B.

If we add an edge $[u,w]$ of weight d to a given graph G_B by connecting a new vertex w of weight c to $u \in V(G_B)$, the graph arising this way will be denoted by $G_B + [u, w(c)](d)$.

If we add two edges $[u,w]$ and $[w,v]$ of weight d with $u, v \in V(G_B)$ to G_B such that the vertex $w \notin V(G_B)$ has weight c, then the obtained graph will be denoted by $G_B + [u, w(c), v](d)$.

Moreover, we assume that $G_B - u$ is the graph we obtain by deleting the vertex $u \in V(G_B)$ and all edges of G_B incident to u from G_B.

Finally, we will agree on the following notations for determinants of quadratic matrices related to the determinant $D := |xI - B|$ and an arbitrary row vector $\mathbf{d} \in \mathbb{R}^n$:

$|\underline{D}$:= determinant of $xI - B$ without its last row and first column,

$\overline{D}|$:= determinant of $xI - B$ without its first row and last column,

$\overline{D}_{\mathbf{d}}$:= determinant of $xI - B$ with its first row deleted and $\mathbf{d}$ added as last row and

$\underline{D}_{\mathbf{d}}$:= determinant of $xI - B$ with its last row substituted by $\mathbf{d}$.

Lemma 2.1. $\varphi(G_B + [u, w(c)](d)) = (x - c)\varphi(G_B) - d^2\varphi(G_B - u)$.

Proof. Let u be the vertex 1 of G_B and assume w to be $n+1$ and put $\mathbf{d} := (-d, 0, \dots, 0)$. Then

$$\begin{aligned}\varphi(G_B + [u, w(c)](d)) &= \begin{vmatrix} & & & & -d \\ & & & & 0 \\ & & xI - B & & \vdots \\ & & & & 0 \\ -d & 0 & \cdots & 0 & x - c \end{vmatrix} \\ &= -d(-1)^n \overline{D}_{\mathbf{d}} + (x - c)\varphi(G_B) \\ &= (-1)^n(-1)^{n+1} d^2 \varphi(G_B - u) + (x - c)\varphi(G_B) \\ &= -d^2\varphi(G_B - u) + (x - c)\varphi(G_B). \qquad \square\end{aligned}$$

Corollary 2.1. *Let $P_n(a, b)$ be a path with n vertices, which are all equally weighted by a and with b being the weight of all its edges. Then $\varphi(P_n(a, b), x) = b^n U_n((x - a)/(2b))$, where $U_n(x)$ is the Chebyshev polynomial of the second kind of degree n.*

Proof. Taking into account that $U_1(x) = 2x$, $U_2(x) = 4x^2 - 1$ and $U_n(x) = 2xU_{n-1}(x) - U_{n-2}(x)$ for $n > 2$ as well as $\varphi(P_1(a,b)) = x - a$, $\varphi(P_2(a,b)) = (x-a)^2 - b^2$ and $\varphi(P_n(a,b)) = (x-a)\varphi(P_{n-1}(a,b)) - b^2\varphi(P_{n-2}(a,b))$ for $n > 2$ (according to Lemma 2.1) the assertion follows immediately by induction on n. □

Remark 2.1. Corollary 2.1 also follows from the well-known fact that for paths P_n without weights, i. e. $P_n(0,1), \varphi(P_n) = U_n(x/2)$ (cf. e. g. Gutmann et al [5]).

Next we agree on the meaning of the following notations: For pairwise different $u_1, \ldots, u_m \in V(G_B)$ and pairwise different $w_1, \ldots, w_m \notin V(G_B)$

$$\begin{aligned}
&G_B + \sum_{i=1}^{m} [u_i, w_i(c_i)](d_i) \\
&:= (\ldots((G_B + [u_1, w_1(c_1)](d_1)) + [u_2, w_2(c_2)](d_2)) + \ldots) \\
&+[u_m, w_m(c_m)](d_m), \\
&G_B - \sum_{i=1}^{m} u_i := (\ldots((G_B - u_1) - u_2) - \ldots) - u_m \,,
\end{aligned}$$

and further $G_B - \sum\limits_{i\in\emptyset} u_i := G_B$ and $\prod\limits_{k\in\emptyset} p_k(x) = 1$ for arbitrary polynomials $p_k(x)$ in x.

Theorem 2.1. *For pairwise different vertices $u_i \in V(G_B)$ and pairwise different vertices $w_i \notin V(G_B)$, $i = 1, \ldots, m$*

$$\begin{aligned}
&\varphi(G_B + \sum_{i=1}^{m} [u_i, w_i(c_i)](d_i)) \\
&= \sum_{I \subseteq \{1,\ldots,m\}} (-1)^{|I|} \prod_{k\in I'} (x - c_k)(\prod_{j\in I} d_j^2)\varphi(G_B - \sum_{j\in I} u_j)\,,
\end{aligned}$$

where $I' := \{1, \ldots, m\} \setminus I$ and $|I|$ is the cardinality of I.

Proof. By induction on m: The case $m = 1$ follows directly from Lemma 2.1. Now let $m > 1$ and assume the theorem to hold for less than m vertices added to G_B. Writing $G_B(k)$ for $G_B + \sum\limits_{i=1}^{k} [u_i, w_i(c_i)](d_i)$ and I^* for $\{1, \ldots, m-1\} \setminus I$

if $I \subseteq \{1,\dots,m-1\}$ we obtain by means of Lemma 2.1

$$\begin{aligned}
&\varphi(G_B(m)) = \varphi(G_B(m-1) + [u_m, w_m(c_m)](d_m)) \\
&\quad = (x - c_m)\Big(\sum_{I\subseteq\{1,\dots,m-1\}} (-1)^{|I|} \prod_{k\in I^*}(x-c_k)\Big(\prod_{j\in I} d_j^2\Big)\varphi\Big(G_B - \sum_{j\in I} u_j\Big)\Big) \\
&\qquad - d_m^2 \varphi\Big((G_B - u_m) + \sum_{i=1}^{m-1}[u_i, w_i(c_i)](d_i)\Big) \\
&\quad = \sum_{I\subseteq\{1,\dots,m-1\}} (-1)^{|I|}(x-c_m) \prod_{k\in I^*}(x-c_k)\Big(\prod_{j\in I} d_j^2\Big)\varphi\Big(G_B - \sum_{j\in I} u_j\Big) \\
&\quad - \sum_{I\subseteq\{1,\dots,m-1\}} (-1)^{|I|} \prod_{k\in I^*}(x-c_k) d_m^2\Big(\prod_{j\in I} d_j^2\Big)\varphi\Big((G_B - u_m) - \sum_{j\in I} u_j\Big) \\
&\quad = \sum_{I\subseteq\{1,\dots,m\}} (-1)^{|I|} \prod_{k\in I'}(x-c_k)\Big(\prod_{j\in I} d_j^2\Big)\varphi\Big(G_B - \sum_{j\in I} u_j\Big). \quad \Box
\end{aligned}$$

Corollary 2.2. *For pairwise different $u_i \in V(G_B)$, pairwise different vertices $w_i \notin V(G_B)$ of the same weight c, and d assumed to be the weight of all the edges $[u_i, w_i]$, $i = 1,\dots,m$,*

$$\varphi\Big(G_B + \sum_{i=1}^{m}[u_i, w_i(c)](d)\Big) = \sum_{I\subseteq\{1,\dots,m\}} (-1)^{|I|}(x-c)^{m-|I|} d^{2|I|}\varphi\Big(G_B - \sum_{j\in I} u_j\Big).$$

Lemma 2.2.

$$\varphi(G_B + [u, w(c), v](d)) = d^2\Big[\frac{x-c}{d^2}\varphi(G_B) - \varphi(G_B - u) - \varphi(G_B - v) + 2(-1)^n |\underline{D}\Big].$$

If G_B is a path, whose edges are weighted by b, then $|\underline{D} = (-b)^{n-1}$. If u and v denote the vertices 1 and n of G_B, respectively, and G_B has the property $b_{12} = \cdots = b_{1,n-1} = 0$ then $|\underline{D} = (-1)^{n+1} b_{1n}\varphi(G_B - u - v)$.

Proof. Let u, v be the vertices 1 and n, respectively, and put $w := n+1$.

Further, put $\mathbf{d} := (-d, 0, \ldots, 0, -d)$. Then

$$\varphi(G_B + [u, w(c), v](d)) = \begin{vmatrix} & & & & & -d \\ & & & & & 0 \\ & & xI - B & & & \vdots \\ & & & & & 0 \\ & & & & & -d \\ -d & 0 & \cdots & 0 & -d & x - c \end{vmatrix}$$

$$= (-1)^n(-d)\overline{D}_{\mathbf{d}} + d\underline{D}_{\mathbf{d}} + (x - c)\varphi(G_B),$$

$$\overline{D}_{\mathbf{d}} = (-1)^{n+1}(-d)\varphi(G_B - u) + (-d)\overline{D}| = (-1)^n d\varphi(G_B - u) - d\overline{D}$$

and

$$\underline{D}_{\mathbf{d}} = (-1)^{n+1}(-d)|\underline{D} + (-d)\varphi(G_B - v) = (-1)^n d|\underline{D} - d\varphi(G_B - v).$$

Therefore,

$$\begin{aligned} &\varphi(G_B + [u, w(c), v](d)) \\ &= -d^2\varphi(G_B - u) + (-1)^n d^2\overline{D}| + (-1)^n d^2|\underline{D} - d^2\varphi(G_B - v) \\ &+ (x - c)\varphi(G_B) \\ &= d^2[\frac{x - c}{d^2}\varphi(G_B) - \varphi(G_B - u) - \varphi(G_B - v) + 2(-1)^n|\underline{D}] \end{aligned}$$

because $|\underline{D} = \overline{D}|$.

The assertions about $|\underline{D}$ for the two special cases follow immediately from the form of the matrix $xI - B$ for those graphs. □

Corollary 2.3. *Let $C_n(a, b)$ (with $n \geq 3$) denote a cycle with n vertices which are all equally weighted by a and with b being the weight of all the cycle's edges, then*

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

Proof. We apply Lemma 2.2 to the path $P_{n-1}(a, b)$ with $c = a$ and $d = b$ and make use of the formula given in Corollary 2.1:

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

Remark 2.2. Corollary 2.3 also follows from the well-known fact that for cycles C_n without weights, i. e. $C_n(0,1)$, $\varphi(C_n) = U_n(x/2) - U_{n-2}(x/2) - 2$, which equals $xU_{n-1}(x/2) - 2U_{n-2}(x/2) - 2$ because $U_n(x) = 2xU_{n-1}(x) - U_{n-2}(x)$ for $n > 1$ (cf. e. g. Gutmann et al [5]).

In the following theorem we deal with the typical situation known from organic chemistry, where a new atom or group is added to a cycle that takes part in a π-bonding, e.g. when substituting an H-atom in benzene by an NH_2-group.

Theorem 2.2.

$$\varphi(C_n(a,b) + [u, w(c)](d)) = (x-c)b^n[\frac{x-a}{b}U_{n-1}(\frac{x-a}{2b}) \\ - 2U_{n-2}(\frac{x-a}{2b}) - 2] - d^2 b^{n-1} U_{n-1}(\frac{x-a}{2b})\,.$$

Proof. Combine the results of Corollary 2.3 and Corollary 2.1 by means of Lemma 2.1. □

Next, we describe the situation that a heteroatom occurs within a cycle like in pyroll or in pyridine.

Theorem 2.3. *Let $C_n^*(a,b,c,d)$ be a cycle of $n \geq 3$ vertices with one vertex n of weight c adjacent to the vertices 1 and $n-1$ such that the edges $[1,n]$ and $[n-1,n]$ have weight d; all the other vertices should carry weight a and the weight of the remaining edges should be b. Then*

$$\varphi(C_n^*(a,b,c,d)) = b^{n-2}d^2[\frac{b(x-c)}{d^2}U_{n-1}(\frac{x-a}{2b}) - 2U_{n-2}(\frac{x-a}{2b}) - 2].$$

Proof. Use Lemma 2.2 with $P_{n-1}(a,b)$ for G_B and take into account the formula given in Corollary 2.1. □

For the special case $n = m$ in Corollary 2.2 we can give an explicit formula for the sum that occurs there:

Lemma 2.3. *For pairwise different $u_i \in V(G_B)$ and pairwise different $w_i \notin V(G_B)$ of weight c such that the weight of all edges $[u_i, w_i]$ is d for $i = 1, \ldots, n$ ($n =$number of vertices of G_B)*

$$\varphi(G_B + \sum_{i=1}^{n}[u_i, w_i(c)](d), x) = (x-c)^n \varphi(G_B, x - \frac{d^2}{x-c}).$$

Proof. Consider the determinant of order $2n$

$$\left|\begin{array}{cccc|cccc} & & & & -d & 0 & \cdots & 0 \\ & & & & 0 & -d & \cdots & 0 \\ & xI-B & & & \vdots & & & \\ & & & & 0 & 0 & \cdots & -d \\ \hline -d & 0 & \cdots & 0 & x-c & 0 & \cdots & 0 \\ 0 & -d & \cdots & 0 & 0 & x-c & & 0 \\ \vdots & & & & \vdots & & & \\ 0 & 0 & \cdots & -d & 0 & 0 & \cdots & x-c \end{array}\right|.$$

Factoring out $x-c$ of each of the last n columns, multiplying the columns obtained this way by d and then adding the $(n+j)$-th column to the j-th column for $j=1,\ldots,n$ will produce the desired result. □

The next theorem could be of interest for calculating the so-called HOMO-LUMO difference (energy of the highest occupied molecular orbital – energy of the lowest unoccupied molecular orbital, cf. Bonchev et al [1]). The HOMO-LUMO difference is a measure for the reactivity of the molecule for which to determine one has to know the total order of the energy levels, i. e. the characteristic roots:

Theorem 2.4. *$\varphi(C_n(a,b)+\sum_{i=1}^{n}[u_i,w_i(c)](d))=\prod_{i=1}^{2n}(x-x_i)$ with $x_1\leq\cdots\leq x_{2n}$ and*

$$x_i=\frac{1}{2}(a+c+2b\cos\frac{2[i/2]\pi}{n}-\sqrt{(a-c+2b\cos\frac{2[i/2]\pi}{n})^2+4d^2})$$

if $1\leq i\leq n$ and

$$x_i=\frac{1}{2}(a+c+2b\cos\frac{2[(i-n)/2]\pi}{n}+\sqrt{(a-c+2b\cos\frac{2[(i-n)/2]\pi}{n})^2+4d^2})$$

if $n<i\leq 2n$.

Proof. Since for the determinants of circulant matrices it holds

$$\begin{vmatrix} a_0 & a_1 & \cdots & a_{n-1} \\ a_{n-1} & a_0 & \cdots & a_{n-2} \\ \vdots & \vdots & \ddots & \vdots \\ a_1 & a_2 & \cdots & a_0 \end{vmatrix}=\prod_{j=1}^{n}(\sum_{k=0}^{n-1}a_k e^{2ijk\pi/n})$$

(cf. e. g. Hofbauer et al [7]), we obtain

$$\varphi(G_B, x) = \prod_{j=1}^{n}(x - a - 2b\cos\frac{2j\pi}{n}) = \prod_{j=1}^{n}(x - a - 2b\cos\frac{2[j/2]\pi}{n}).$$

Substituting x by $x - d^2/(x-c)$ according to Lemma 2.3 yields pairs of roots given by

$$\begin{aligned} x - \frac{d^2}{x-c} - a - 2b\cos\frac{2[j/2]\pi}{n} \\ = \frac{1}{x-c}(x^2 - (a + c + 2b\cos\frac{2[j/2]\pi}{n})x - (d^2 - ac - 2bc\cos\frac{2[j/2]\pi}{n})). \end{aligned}$$

Solving the quadratic equation corresponding to the above polynomial in x and ordering the roots obtained this way yields the assertion of the theorem (observe that the function $x + \sqrt{x^2 + 4d^2}$ is increasing). □

3. Factors of the Characteristic Polynomial

In this section we will focus on molecular graphs depending on a four-parametric manifold of weights that arise when in a molecule that consists of one kind of atoms one atom is substituted by a heteroatom or when a heteroatom or a new atomic group is added to such a compound. Though we will formulate theorems for the case that the original compound is cyclic our methods can also be applied to non-cyclic compounds and to compounds that depend on a larger variety of heteroatoms.

Our goal is to find out how many energy levels, i. e. roots of the characteristic polynomial are not influenced by the process of substituting an atom or adding new atoms and atomic groups, respectively. For this end we will study some properties of Chebyshev polynomials of the first and second kind in the first place.

Recall the definitions and defining recursions of Chebyshev polynomials $T_n(x)$ and $U_n(x)$ of the first and second kind, respectively:

$$\begin{aligned} T_n(\cos y) &:= \cos(ny) \quad \text{and} \\ U_n(\cos y) &:= \frac{\sin((n+1)y)}{\sin y}\,, \end{aligned}$$

for $n \geq 0$. Moreover,

$$
\begin{aligned}
T_0(x) &= 1,\\
T_1(x) &= x,\\
T_n(x) &= 2xT_{n-1}(x) - T_{n-2}(x) \text{ for } n \geq 2,\\
U_0(x) &= 1,\\
U_1(x) &= 2x,\\
U_n(x) &= 2xU_{n-1}(x) - U_{n-2}(x) \text{ for } n \geq 2.
\end{aligned}
$$

Both, $T_n(x)$ and $U_n(x)$ are polynomials of degree n of the form

$$
\begin{aligned}
&a_n x^n + a_{n-2}x^{n-2} + \cdots + a_0 \text{ if } n \text{ is even, and}\\
&a_n x^n + a_{n-2}x^{n-2} + \cdots + a_1 x \text{ if } n \text{ is odd.}
\end{aligned}
$$

Next, we introduce two kinds of new polynomials related to Chebyshev polynomials by defining at first

$$
\begin{aligned}
t_k(x) &:= \frac{T_{2k+1}(\sqrt{(x+1)/2})}{\sqrt{(x+1)/2}} \quad \text{and}\\
u_k(x) &:= U_{2k}(\sqrt{\frac{1}{2}(x+1)}),
\end{aligned}
$$

for $k \geq 0$.

Lemma 3.4. *$t_k(x)$ and $u_k(x)$ are both polynomials of degree k over $\mathbb{R}$.*

Proof. If $n = 2k+1$, then x is a divisor of $T_n(x)$ and $T_n(x)/x$ is a polynomial in which all powers of x are even, which shows that $t_k(x)$ is a polynomial of degree k. On the other hand, starting with $n = 2k$, this argument shows that $u_k(x)$ is also a polynomial of degree k. □

Lemma 3.5.

$$
\begin{aligned}
U_{2k+1}(x) &= 2T_{k+1}(x)U_k(x),\\
U_{2k}(x) &= t_k(x)u_k(x),\\
U_{2k+1}(x) + 1 &= t_k(x)u_{k+1}(x),\\
U_{2k}(x) + 1 &= 2T_k(x)U_k(x),
\end{aligned}
$$

for $k \geq 0$.

Proof.

$$U_{2k+1}(\cos y) = \frac{\sin((2k+2)y)}{\sin y} = \frac{2\sin((k+1)y)\cos((k+1)y)}{\sin y}$$
$$= 2T_{k+1}(\cos y)U_k(\cos y)\,,$$

and

$$U_{2k}(\cos y) = \frac{\sin((2k+1)y)}{\sin y}$$
$$= \frac{2\sin((2k+1)(y/2))\cos((2k+1)(y/2))}{2\sin(y/2)\cos(y/2)}$$
$$= \frac{T_{2k+1}(\cos(y/2))}{\cos(y/2)}U_{2k}(\cos(y/2)) = t_k(\cos y)u_k(\cos y).$$

If we take into account that $\cos y = 2\cos^2(y/2) - 1$ we have $\cos(y/2) = \pm\sqrt{(\cos y+1)/2}$. Using the trigonometric formula $\sin\alpha + \sin\beta = 2\sin((\alpha+\beta)/2)\cos((\alpha-\beta)/2)$ we obtain

$$U_{2k+1}(\cos y) + 1 = \frac{\sin((2k+2)y) + \sin y}{\sin y}$$
$$= \frac{2\sin((2k+3)(y/2))\cos(2k+1)(y/2))}{2\sin(y/2)\cos(y/2)}$$
$$= \frac{T_{2k+1}(\cos(y/2))}{\cos(y/2)}U_{2k+2}(\cos\frac{y}{2}) = t_k(\cos y)u_{k+1}(\cos y)\,,$$

and

$$U_{2k}(\cos y) + 1 = \frac{\sin((2k+1)y) + \sin y}{\sin y} = \frac{2\sin((2k+1)y)\cos(ky)}{\sin y}$$
$$= 2T_k(\cos y)U_k(\cos y).\quad \square$$

Lemma 3.6. *For $n \geq 1$, $U_{n-1}(x)$ and $U_n(x)+1$ have a common polynomial divisor of degree $[n/2]$, namely $T_{n/2}(x)$ if n is even and $t_{(n-1)/2}(x)$ if n is odd.*

Proof. If $n = 2k$, then according to Lemma 3.5 $U_{n-1}(x) = U_{2k-1}(x) = 2T_k(x)U_{k-1}(x)$ and $U_n(x) + 1 = U_{2k}(x) + 1 = 2T_k(x)U_k(x)$, and if $n = 2k+1$, then again by Lemma 3.5 we obtain $U_{n-1}(x) = U_{2k}(x) = t_k(x)u_k(x)$ and $U_n(x) + 1 = U_{2k+1}(x) + 1 = t_k(x)u_{k+1}(x)$. $\square$

Lemma 3.7. *For $n \geq 1$, $U_n(x)$ and $U_{n-1}(x)+1$ have a common polynomial divisor of degree $[n/2]$, namely $u_{n/2}(x)$ if n is even and $U_{(n-1)/2}(x)$ if n is odd.*

Proof. If $n = 2k+2$ then $U_n(x) = t_{k+1}(x)u_{k+1}(x)$ and $U_{n-1}(x)+1 = t_k(x)u_{k+1}(x)$ by Lemma 3.5, and again by Lemma 3.5 if $n = 2k+1$ then $U_n(x) = 2T_{k+1}(x)U_k(x)$ and $U_{n-1}(x)+1 = 2T_k(x)U_k(x)$. □

According to Theorem 2.4 all energy levels of a molecule, whose graph is of the form $C_n(a,b) + \sum_{i=1}^{n}[u_i, w_i(c)](d)$ depend on all four parameters a, b, c, d. However, if we consider the molecular graph $C_n(a,b) + [u, w(c)](d)$, i. e. if we add only one heteroatom to a given cyclic compound, which consists of one kind of atoms, the situation is different.

Theorem 3.5. *For any molecular graph $C_n(a,b) + [u, w(c)](d)$ there are at least$[(n-1)/2]$ roots of its characteristic polynomial that only depend on the weights a and b, namely the zeros of $U_{n/2-1}((x-a)(2b))$ if n is even and the zeros of $u_{(n-1)/2}((x-a)/(2b))$ is n is odd.*

Proof. As shown in Theorem 2.2

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

and according to Lemma 3.7 there exist the common polynomial factors of $U_{n-1}((x-a)(2b))$ and $U_{n-2}((x-a)(2b))+1$, we have claimed to exist in the theorem. □

According to Theorem 2.1 for $u_1 \neq u_2, u_1, u_2 \in V(C_n(a,b))$ and $w_1 \neq w_2, w_1, w_2$
$\notin V(C_n(a,b))$, we obtain

$$\begin{aligned}&\varphi(C_n(a,b) + [u_1, w_1(c_1)](d_1) + [u_2, w_2(c_2)](d_2))\\ &= (x-c_1)(x-c_2)\varphi(C_n(a,b)) - (x-c_1)d_2^2\varphi(C_n(a,b) - u_2)\\ &- (x-c_2)d_1^2\varphi(C_n(a,b) - u_1) + d_1^2d_2^2\varphi(C_n(a,b) - u_1 - u_2).\end{aligned}$$

This shows that though $\varphi(C_n(a,b))$, $\varphi(C_n(a,b) - u_2) = \varphi(P_{n-1}(a,b))$ and $\varphi(C_n(a,b) - u_1) = \varphi(P_{n-1}(a,b))$ will always have a common polynomial divisor of degree $[(n-1)/2]$ (cf. Corollary 2.1 and Corollary 2.3 and Lemma 3.7), a common polynomial divisor the roots of which are only functions of a and b will entirely depend on the geometry of the compound because the characteristic polynomial $\varphi(C_n(a,b) - u_1 - u_2)$ will be entirely dependent on the places where u_1 and u_2 sit within $C_n(a,b)$.

Finally we consider the situation that an atom of a chemical compound of the form $C_n(a,b)$ is substituted by a heteroatom.

Theorem 3.6. *For the molecular graph $C_n^*(a,b,c,d)$ (cf. Theorem 2.3) at least $[(n-1)/2]$ roots of its characteristic polynomial only depend on the weights a and b, namely the zeros of $U_{n/2-1}((x-a)(2b))$ if n is even and the zeros of $u_{(n-1)/2}((x-a)(2b))$ if n is odd.*

Proof.

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

by Theorem 2.3 and because of Lemma 3.7 we obtain that for even n, $U_{n-1}(x)$ and $U_{n-2}(x)+1$ have the common divisor $U_{n/2-1}(x)$, and if n is odd there is the common divisor $u_{(n-1)/2}(x)$. □

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