

On Graph Theoretical Polynomials of Annulenes and Radialenes

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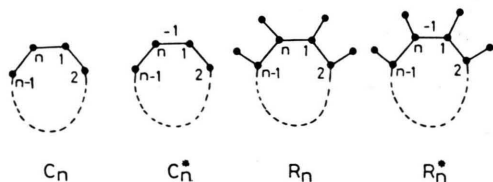
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Three graphic polynomials of annulenes and radialenes are examined, namely the matching polynomial, the characteristic polynomial of the Hückel graph and the characteristic polynomial of the Möbius graph. Several relations between them are obtained. These six polynomials and their zeros are mutually closely related.

Introduction

In theoretical chemistry three polynomials have been associated with a molecular graph and extensively used in various applications. These are $\varphi(G) = \varphi(G, x)$, the characteristic polynomial of the Hückel graph G , $\varphi(G^*) = \varphi(G^*, x)$, the characteristic polynomial of the Möbius graph G^* and $\alpha(G) = \alpha(G, x)$, the matching polynomial of either G or G^* .

In our terminology the Hückel graph G is the molecular graph whose all edges have the weight $+1$. The Möbius graph G^* coincides with G except that one of its edges (which belongs to a cycle) is weighted by -1 . In the present paper we shall consider the molecular graph C_n of $[n]$ -annulene and R_n of $[n]$ -radialene. Because of their symmetry, the position of the edge with negative



weight in C_n^* and R_n^* is immaterial. Note that C_n and C_n^* have n vertices, while R_n and R_n^* have $2n$ vertices.

Two further graphs which will be used in the following discussion are P_n , the path with n vertices and Q_n , the comb with $2n$ vertices.



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$\varphi(G)$ is the secular polynomial of a conjugated π -electron system as calculated within the framework of the Hückel molecular orbital (HMO) model [1]. The zeros of $\varphi(G)$ coincide with the HMO energy levels (in β units). Analytical formulas for $\varphi(C_n)$ and its zeros have been obtained by Hückel [2] in the early days of molecular orbital theory and have been thereafter thoroughly examined [3]. Analytical formulas for $\varphi(R_n)$ and its zeros are also known [4].

In the recent years the Möbius strip concept was developed for describing certain photochemical phenomena and chemical reactions [5]. The zero of $\varphi(G^*)$ correspond to the orbital energy levels of a π -electron system in a twisted „Möbius strip” conformation [6]. The zeros of $\varphi(C_n^*)$ have been calculated [7].

The matching polynomial was introduced within a novel theory of aromaticity [8]. It also plays an important role in statistical physics [9]. The zeros of $\alpha(C_n)$ were first determined by Heilmann and Lieb [9] and also later by others [10]. The matching polynomial of a graph G with n vertices is defined as [8]

$$\alpha(G) = \alpha(G, x) = \sum_k (-1)^k p(G, k) x^{n-2k}, \quad (1)$$

where $p(G, k)$ is the number of ways in which one can select k independent edges in G . According to this definition, $\alpha(G) = \alpha(G^*)$ for all graphs G . In addition, if G is an acyclic graph, then $\alpha(G) = \varphi(G) = \varphi(G^*)$.

Although the polynomials $\varphi(C_n)$, $\varphi(C_n^*)$ and $\alpha(C_n)$ have been investigated several times [2, 3, 7, 9, 10], the intimate relationship between them seems not to be recognized formerly. Some identities between the graphic polynomials of C_n and R_n were also not yet reported. In the present paper we deduce various relations between the poly-

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nomials $\varphi(C_n)$, $\varphi(C_n^*)$, $\alpha(C_n)$, $\varphi(R_n)$, $\varphi(R_n^*)$ and $\alpha(R_n)$, and their zeros.

The Graphic Polynomials of Annulenes

The graphs C_n and C_n^* contain just a single cycle (of the size n). Then an elementary application of the Sachs theorem [1, 11] yields

$$\varphi(C_n) = \alpha(C_n) - 2, \quad (2)$$

$$\varphi(C_n^*) = \alpha(C_n) + 2. \quad (3)$$

The recurrence relation (4) was deduced elsewhere [12].

$$\alpha(C_n) = x \alpha(C_{n-1}) - \alpha(C_{n-2}). \quad (4)$$

Combination of (4) with (2) and (3) results in recurrence relations for $\varphi(C_n)$ and $\varphi(C_n^*)$, viz.

$$\varphi(C_n) = x \varphi(C_{n-1}) - \varphi(C_{n-2}) + 2x - 4,$$

$$\varphi(C_n^*) = x \varphi(C_{n-1}^*) - \varphi(C_{n-2}^*) - 2x + 4.$$

Knowing that $\alpha(C_3) = x^3 - 3x$ and $\alpha(C_4) = x^4 - 4x^2 + 2$, one can calculate

$$\begin{aligned} \alpha(C_n) = & [(x + \sqrt{x^2 - 4})/2]^n \\ & + [(x - \sqrt{x^2 - 4})/2]^n. \end{aligned} \quad (5)$$

Substitution of $x = 2 \cos t$ in (5) gives a considerable simplification, namely

$$\alpha(C_n) = 2 \cos n t. \quad (6)$$

Hence

$$\varphi(C_n) = 2 \cos n t - 2;$$

$$\varphi(C_n^*) = 2 \cos n t + 2. \quad (7)$$

The Chebyshev functions of the first kind are defined via $T_n(x) = \cos(n \arccos x)$ [13] and therefore Eq. (6) can be rewritten as

$$\alpha(C_n) = 2 T_n(x/2). \quad (8)$$

Relation (8) is interesting since it enables the use of the results known for Chebyshev polynomials [13] in the theoretical chemistry of annulenes. For example, the coefficients $p(C_n, k)$ in Eq. (1) are found to be equal to

$$n(n-k-1)!/k!(n-2k)!.$$

As another application we can transform the identity $T_n(T_m) = T_{nm}$ into

$$\alpha(C_n, \alpha(C_m, x)) = \alpha(C_{nm}, x). \quad (9)$$

Using the elementary trigonometric identity: $2 \cos 2nt = (2 \cos nt)^2 - 2$, we deduce from (6) and (7)

$$\alpha(C_{2n}) = (\alpha(C_n))^2 - 2.$$

Therefore,

$$\begin{aligned} \varphi(C_{2n}) &= (\alpha(C_n))^2 - 4 \\ &= (\alpha(C_n) - 2)(\alpha(C_n) + 2) \\ &= \varphi(C_n) \varphi(C_n^*) \end{aligned} \quad (10)$$

and

$$\varphi(C_{2n}^*) = (\alpha(C_n))^2. \quad (11)$$

Another identity of this kind,

$$\alpha(C_{2n}) = \alpha(C_n, x^2 - 2) \quad (12)$$

is a special case of Equation (9).

The zeros of $\alpha(C_n)$, $\varphi(C_n)$ and $\varphi(C_n^*)$ will be denoted by $X(n, k)$, $Y(n, k)$ and $Z(n, k)$, respectively $k=1, 2, \dots, n$. They are easily obtained from Eqs. (6) and (7), viz.

$$X(n, k) = 2 \cos(2k+1)\pi/2n,$$

$$Y(n, k) = 2 \cos 2k\pi/n,$$

$$Z(n, k) = 2 \cos(2k+1)\pi/n.$$

These expressions are, of course, well known [2, 7, 9]. From the above formulas it is evident that

$$Y(n, k) = Y(mn, m k) \quad \text{for } m = 2, 3, \dots, \quad (13)$$

$$Z(2n, k) = X(n, k). \quad (14)$$

By elementary trigonometric transformations one can verify also

$$X(n, k)^2 - 2 = Z(n, k); \quad (15a)$$

$$X(2n, k)^2 - 2 = X(n, k), \quad (15b)$$

$$Y(n, k)^2 - 2 = Y(n, 2k); \quad (16a)$$

$$Y(2n, k)^2 - 2 = Y(n, k), \quad (16b)$$

$$Z(n, k)^2 - 2 = Y(n, 2k+1); \quad (17a)$$

$$Z(2n, k)^2 - 2 = Z(n, k). \quad (17b)$$

Further, if n is odd and $2j = n - 2k - 1$, then

$$Z(n, k) = -Y(n, j). \quad (18)$$

The identity (12) yields the previously given relation (15b). Similarly, from other special cases of Eq. (9) we obtain additional identities for the zeros of $\alpha(C_n)$. For instance, from

$$\alpha(C_{3n}, x) = \alpha(C_n, x^3 - 3x)$$

it follows

$$X(3n, k)^3 - 3X(3n, k) = X(n, k).$$

The above results can be summarized in the following rules.

1) One can calculate the zeros of $\varphi(C_n^*)$ from the zeros of $\alpha(C_n)$ and vice versa (Equation (15a)).

2) The zeros of $\alpha(C_{2n})$ can be calculated from the zeros of $\alpha(C_n)$ (Eqs. (12) and (15b)); the zeros of $\varphi(C_{2n})$ can be calculated from the zeros of $\varphi(C_n)$ (Eq. (16b)); the zeros of $\varphi(C_{2n}^*)$ can be calculated from the zeros of $\varphi(C_n^*)$ (Equation (17b)).

3) If n is odd, then the zeros of $\alpha(C_n)$ are equal to the zeros of $\varphi(C_n)$ with opposite sign (Equation (18)).

4) The zeros of $\varphi(C_{2n})$ are composed of the zeros of $\varphi(C_n)$ and $\varphi(C_n^*)$ (Eqs. (10) and (13)).

5) The zeros of $\varphi(C_{2n}^*)$ are composed of two collections of the zeros of $\alpha(C_n)$ (Eqs. (11) and (14)).

In addition, we mention the relations

$$\alpha(C_n) \varphi(P_{n-1}) = \varphi(P_{2n-1}) \quad (19)$$

and

$$\varphi(C_{2n}) = (x^2 - 4) \varphi(P_{n-1})^2, \quad (20)$$

which result in the following rules.

6) The zeros of $\alpha(C_n)$ are composed of those zeros of $\varphi(P_{2n-1})$ which are not the zeros of $\varphi(P_{n-1})$.

7) The zeros of $\varphi(C_{2n})$ are composed of the numbers $+2, -2$ and two collections of the zeros of $\varphi(P_{n-1})$.

In order to prove Eq. (19) note that [11]

$$\varphi(P_{2n-1}) = \varphi(P_n) \varphi(P_{n-1}) - \varphi(P_{n-1}) \varphi(P_{n-2}).$$

Formula (19) follows then from [12]

$$\begin{aligned} \alpha(C_n) &= \alpha(P_n) - \alpha(P_{n-2}) \\ &= \varphi(P_n) - \varphi(P_{n-2}). \end{aligned} \quad (21)$$

Equation (20) can be deduced from

$$\begin{aligned} \varphi(C_{2n}) &= 2 \cos 2nt - 2 \\ &= (4 \cos^2 t - 4) (\sin nt / \sin t)^2 \end{aligned}$$

and the fact that $\varphi(P_{n-1}) = \sin nt / \sin t$ and $x = 2 \cos t$.

The Graphic Polynomials of Radialenes

It is long known [4] that the characteristic polynomial of C_n and R_n are related as

$$\varphi(R_n, x) = x^n \varphi(C_n, x - 1/x). \quad (22)$$

We show now that two analogous identities are also valid, namely

$$\varphi(R_n^*, x) = x^n \varphi(C_n^*, x - 1/x) \quad (23)$$

and

$$\alpha(R_n, x) = x^n \alpha(C_n, x - 1/x). \quad (24)$$

Let O_k denote the graph with k vertices and without edges. Then $\varphi(O_k) = \alpha(O_k) = x^k$. The matching polynomial of R_n conforms to the recursion formula [8, 12]

$$\begin{aligned} \alpha(R_n) &= \alpha(Q_n) - \alpha(O_2) \alpha(Q_{n-2}) \\ &= \varphi(Q_n) - x^2 \varphi(Q_{n-2}). \end{aligned}$$

It was proved elsewhere that [14]

$$\varphi(Q_n, x) = x^n \varphi(P_n, x - 1/n). \quad (25)$$

Therefrom

$$\begin{aligned} \alpha(R_n, x) &= x^n [\varphi(P_n, x - 1/x) - \varphi(P_{n-2}, x - 1/x)] \\ &= x^n \alpha(C_n, x - 1/x) \end{aligned}$$

which proves Equation (24). In order to deduce Eq. (23), note that the application of the Sachs theorem gives [6, 11]

$$\begin{aligned} \varphi(R_n^*) &= \varphi(Q_n) - \varphi(O_2) \varphi(Q_{n-2}) + 2\varphi(O_n) \\ &= \varphi(Q_n) - x^2 \varphi(Q_{n-2}) + 2x^n. \end{aligned}$$

Further,

$$\begin{aligned} \varphi(R_n^*) &= x^n [\varphi(P_n, x - 1/x) \\ &\quad - \varphi(P_{n-2}, x - 1/x) + 2] \end{aligned}$$

because of (25). Combination of this expression with Eqs. (3) and (21) yields finally the formula (23).

Three additional results which now immediately follow from Eqs. (2)–(4) are

$$\varphi(R_n) = \alpha(R_n) - 2x^n; \quad (26a)$$

$$\varphi(R_n^*) = \alpha(R_n) + 2x^n \quad (26b)$$

and

$$\alpha(R_n) = (x^2 - 1) \alpha(R_{n-1}) - x^2 \alpha(R_{n-2}). \quad (26c)$$

Let $x(n, k)$, $y(n, k)$ and $z(n, k)$ be the zeros of $\alpha(R_n)$, $\varphi(R_n)$ and $\varphi(R_n^*)$, respectively ($k =$

1, 2, ..., 2n). Then from Eqs. (22)–(24) one deduces

$$x(n, k)^2 - x(n, k) X(n, k) = 1,$$

$$y(n, k)^2 - y(n, k) Y(n, k) = 1,$$

$$z(n, k)^2 - z(n, k) Z(n, k) = 1.$$

Thus the zeros of $\alpha(R_n)$ are given by

$$x(n, k) = [X(n, k) + \sqrt{X(n, k)^2 + 4}]/2,$$

$$x(n, n+k) = [X(n, k) - \sqrt{X(n, k)^2 + 4}]/2$$

for $k=1, 2, \dots, n$. Expressions for the zeros of $\varphi(R_n)$ and $\varphi(R_n^*)$ are analogous.

We finally offer some more identities for the graphic polynomials of radialenes.

$$\varphi(R_{2n}) = \varphi(R_n) \varphi(R_n^*); \quad (27a)$$

$$\varphi(R_{2n}^*) = \alpha(R_n)^2, \quad (27b)$$

$$\alpha(R_n) \varphi(Q_{n-1}) = \varphi(Q_{2n-1}), \quad (28a)$$

and

$$\varphi(R_{2n}) = (x^4 - 6x^2 + 1) \varphi(Q_{n-1})^2. \quad (28b)$$

These are obtained from the previous results (10), (11), (19) and (20) by taking into account the Equations (22)–(25).

In concluding the present paper we would like to emphasize that although the graphic polynomials of annulenes and radialenes were extensively studied in the past [2–4, 7, 9, 10], we were able to offer some new results. As to the author's knowledge, the relations (9)–(20), (23) and (26)–(28) are reported here for the first time.

Appendix 1

Let G be a graph with n vertices. Let the graph G^+ be obtained by joining a new vertex to each vertex of G . Hence G^+ possesses $2n$ vertices. It is known [11] that for an arbitrary graph G ,

$$\varphi(G^+, x) = x^n \varphi(G, x - 1/x). \quad (29)$$

Equation (22) is a special case of the above identity.

We now prove a generalization of Eq. (24), namely

$$\alpha(G^+, x) = x^n \alpha(G, x - 1/x). \quad (30)$$

The proof will be performed by induction on the number r of cycles in G . Since for acyclic graphs the matching and the characteristic polynomials coincide, Eq. (30) is true because of Equation (29).

Suppose now that Eq. (30) holds for all graphs with less than r cycles. We show that Eq. (30) is then true also for graphs with r cycles.

Let G be a graph with r cycles and let e_{vw} be an edge joining the vertices v and w . Let e_{vw} belong to at least one cycle of G . Then the graphs $G - e_{vw}$, $G - v - w$, $G^+ - e_{vw} = (G - e_{vw})^+$, $G^+ - v - w$ and $(G - v - w)^+$ possess less than r cycles. Further [12]

$$\alpha(G) = \alpha(G - e_{vw}) - \alpha(G - v - w)$$

and

$$\begin{aligned} \alpha(G^+) &= \alpha(G^+ - e_{vw}) - \alpha(G^+ - v - w) \\ &= \alpha((G - e_{vw})^+) - \alpha(O_2) \alpha((G - v - w)^+). \end{aligned}$$

By the induction hypothesis, Eq. (30) is valid for the graphs $(G - e_{vw})^+$ and $(G - v - w)^+$. Therefore,

$$\begin{aligned} \alpha(G^+, x) &= \alpha((G - e_{vw})^+, x) - x^2 \alpha((G - v - w)^+, x) \\ &= x^n \alpha(G - e_{vw}, x - 1/x) \\ &\quad - x^2 x^{n-2} \alpha(G - v - w, x - 1/x) \\ &= x^n [\alpha(G - e_{vw}, x - 1/x) \\ &\quad - \alpha(G - v - w, x - 1/x)] \\ &= x^n \alpha(G, x - 1/x), \quad \text{q.e.d.} \end{aligned}$$

Appendix 2

Let $h(G)$, $h^0(G)$ and $h(G^*)$ be the smallest non-negative zero of $\varphi(G)$, $\alpha(G)$ and $\varphi(G^*)$, respectively. If n is even, then $h(C_n) - h^0(C_n)$ can be interpreted as the effect of the n -membered cycle on the energy of the highest occupied molecular orbital (HOMO) of $[n]$ -annulene [15]. Similarly,

$$h(C_n^*) - h^0(C_n)$$

is the effect of the n -membered cycle on the HOMO energy of the Möbius annulene. Direct calculation yields

$$\begin{aligned} h(C_n) - h^0(C_n) &= \begin{cases} 2 \left(\sin \frac{\pi}{n} - \sin \frac{\pi}{2n} \right) & \text{if } n \equiv 2 \pmod{4}, \\ -2 \sin \frac{\pi}{2n} & \text{if } n \equiv 0 \pmod{4}; \end{cases} \end{aligned}$$

$$\begin{aligned} h(C_n^*) - h^0(C_n) &= \begin{cases} -2 \sin \frac{\pi}{2n} & \text{if } n \equiv 2 \pmod{4}, \\ 2 \left(\sin \frac{\pi}{n} - \sin \frac{\pi}{2n} \right) & \text{if } n \equiv 0 \pmod{4}. \end{cases} \end{aligned}$$

Hence, the $(4m+2)$ -membered cycles stabilize the HOMO level of Hückel annulenes, but destabilize it in the case of Möbius annulenes. Reversely, $(4m)$ -membered cycles destabilize the HOMO level of Hückel annulenes, but stabilize it in the case of Möbius annulenes. One should note that for large n ,

$$2(\sin(\pi/n) - \sin(\pi/2n)) \sim 2\sin(\pi/2n) \sim (\pi/n).$$

It is demonstrated separately [15] that a similar topological effect occurs in all polycyclic alternant conjugated Hückel and Möbius systems.

The n -membered cycle in R_n is not a conjugated circuit [15] and there is no essential difference in the behaviour of $[4m+2]$ - and $[4m]$ -radialenes. For all even values of n ,

$$\begin{aligned} h(R_n) - h^0(R_n) &= \sqrt{2} - 1 - \sqrt{\cos^2 \frac{\pi}{2n} + 1 - \cos \frac{\pi}{2n}} \\ &\sim -(2 - \sqrt{2})(\pi/4n)^2; \end{aligned}$$

$$\begin{aligned} h(R_n^*) - h^0(R_n) &= \left(\sqrt{\cos^2 \frac{\pi}{n} + 1 - \cos \frac{\pi}{n}} \right) \\ &\quad - \left(\sqrt{\cos^2 \frac{\pi}{2n} + 1 - \cos \frac{\pi}{2n}} \right) \\ &\sim 3(2 - \sqrt{2})(\pi/4n)^2. \end{aligned}$$

Hence $h(R_n) - h^0(R_n)$ and $h(R_n^*) - h^0(R_n)$ have opposite sign and are much smaller than the corresponding values for annulenes.

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