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RELATIONS BETWEEN THE ROOTS OF THE ACYCLIC AND THE CHARACTERISTIC POLYNOMIALS OF HÜCKEL AND MÖBIUS CYCLES - EIGENVALUES OF CERTAIN HÜCKEL AND MÖBIUS FORMS OF POLYACENES

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Abstract

It is shown that the roots of the acyclic and the characteristic polynomials of homonuclear Hückel and Möbius cycles may be derived as intersections of certain straight lines and the function $Q_n(x)$ defined as

$$Q_n(x) \equiv P_n(x) - P_{n-2}(x),$$

where $P_n(x)$ and $P_{n-2}(x)$ are, respectively, the characteristic polynomials of path graphs consisting of n and $n-2$ centers, respectively. The analogous results for alternant heteronuclear Hückel and Möbius cycles are given. The eigenvalues for the cylindrical (Hückel) and the Möbius forms of polyacenes may be obtained by a similar procedure.

Further, a simple expression for the differential quotient $dP_n(x)/dx$ is derived and a generalized recurrence relation for the polynomials $P_n(x)$ is given.

1. Introduction

The HMO description of Hückel [1-3] and Möbius cycles [4-7] differ only in one respect: All the resonance integrals between pairs of consecutive centers equal β in the case of Hückel cycles, but in Möbius cycles for one such pair, say n and 1, the sign of the resonance integral is changed. Hence, the secular determinants of these two systems differ only in one off-diagonal element, namely $D_{1n} = D_{n1} = \rho$, $\rho \in \{+1,-1\}$, provided that both cycles consist of the same number of centers, n; since only under this condition does the comparison of the results obtained for the two type of cycles make sense it is assumed throughout the paper. For either value of ρ, the secular determinant of both systems defining the respective characteristic polynomials, $\chi_n(x,\rho)$, may be written as follows:

$$\det \underline{D}_n = \begin{vmatrix} x & 1 & 0 & \dots & 0 & \rho \\ 1 & x & 1 & \dots & 0 & 0 \\ 0 & 1 & x & \dots & 0 & 0 \\ \cdot & \cdot & \cdot & & \cdot & \cdot \\ \cdot & \cdot & \cdot & & \cdot & \cdot \\ \cdot & \cdot & \cdot & & \cdot & \cdot \\ 0 & 0 & 0 & \dots & x & 1 \\ \rho & 0 & 0 & \dots & 1 & x \end{vmatrix} = \chi_n(x,\rho) \qquad (1)$$

Partitioning first the last row and then the last column of the secular determinant into a sum of two rows and two columns, respectively, whereby the entries of the one row/column are ρ or zeros, one obtains the following expansion:

$$\chi_n(x,\rho) = \begin{vmatrix} x & 1 & 0 & \dots & 0 & 0 \\ 1 & x & 1 & \dots & 0 & 0 \\ 0 & 1 & x & \dots & 0 & 0 \\ \cdot & \cdot & \cdot & & \cdot & \cdot \\ \cdot & \cdot & \cdot & & \cdot & \cdot \\ \cdot & \cdot & \cdot & & \cdot & \cdot \\ 0 & 0 & 0 & \dots & x & 1 \\ 0 & 0 & 0 & \dots & 1 & x \end{vmatrix} + \begin{vmatrix} x & 1 & 0 & \dots & 0 & 0 \\ 1 & x & 1 & \dots & 0 & 0 \\ 0 & 1 & x & \dots & 0 & 0 \\ \cdot & \cdot & \cdot & & \cdot & \cdot \\ \cdot & \cdot & \cdot & & \cdot & \cdot \\ \cdot & \cdot & \cdot & & \cdot & \cdot \\ 0 & 0 & 0 & \dots & x & 1 \\ \rho & 0 & 0 & \dots & 0 & 0 \end{vmatrix} +$$

$$+ \begin{vmatrix} x & 1 & 0 & \dots & 0 & \rho \\ 1 & x & 1 & \dots & 0 & 0 \\ 0 & 1 & x & \dots & 0 & 0 \\ \cdot & \cdot & \cdot & & \cdot & \cdot \\ \cdot & \cdot & \cdot & & \cdot & \cdot \\ \cdot & \cdot & \cdot & & \cdot & \cdot \\ 0 & 0 & 0 & \dots & x & 0 \\ 0 & 0 & 0 & \dots & 1 & 0 \end{vmatrix} + \begin{vmatrix} x & 1 & 0 & \dots & 0 & \rho \\ 1 & x & 1 & \dots & 0 & 0 \\ 0 & 1 & x & \dots & 0 & 0 \\ \cdot & \cdot & \cdot & & \cdot & \cdot \\ \cdot & \cdot & \cdot & & \cdot & \cdot \\ \cdot & \cdot & \cdot & & \cdot & \cdot \\ 0 & 0 & 0 & \dots & x & 0 \\ \rho & 0 & 0 & \dots & 0 & 0 \end{vmatrix} ,$$

where $x = (\alpha-\varepsilon)/\beta$ and $\rho\varepsilon\{+1,-1\}$. Obviously, the first determinant equals $P_n(x)$, the last one $-\rho^2 P_{n-2}(x)$, where $P_n(x)$ denotes the characteristic polynomial of a path graph consisting of n centers; here, $P_n(x)$ is also identical to the acyclic polynomial [8-11] of this graph. The second as well as the third determinant equals $(-1)^{n-1}\rho$; they representing pure cyclic contributions.

It follows that eq. (1) takes the form:

$$\chi_n(x,\rho) = P_n(x) - P_{n-2}(x) - 2(-1)^n\rho. \qquad (2)$$

The last term of eq. (2) assumes the value of -2 in the case of even Hückel or odd Möbius cycles, and that of +2 in the case of odd Hückel or even Möbius cycles.

One should note that the acyclic polynomials of both the Hückel and the Möbius cycles are identically equal [12] and are given as follows:

$$A_n(x) = P_n(x) - P_{n-2}(x). \qquad (3)$$

The first term is produced by the matching of all the edges except the edge $\{n,1\}$, the second term by the matching of this edge with all the other ones; the difference in the sign of the two terms arises from the fact that the minimal cardinality of the sets of matching edges amounts to 0 for the first, but 1 for the second term.

2. Formulation of the problem treated here

The eigenvalues of the system considered can be obtained alternatively either by finding the roots of the characteristic polynomial, i.e.,

$$\chi_n(x,\rho) = 0,$$

or by searching for the intersections of the function $Q_n(x)$, defined by

$$Q_n(x) \equiv P_n(x) - P_{n-2}(x), \qquad (4)$$

with the straight line $g_n(x,\rho) = 2(-1)^n\rho$, i.e.,

$$Q_n(x) = 2(-1)^n\rho. \qquad (5)$$

According to eq. (3), the zeros of $Q_n(x)$ are identically the roots of the acyclic polynomial $A_n(x)$. Despite the apparent identity of the quantities defined in eqs. (3) and (4), different notations are used because $Q_n(x)$ denotes a quite general function (as is confirmed in Appendix B) which equals only accidentially the acyclic polynomial of the Hückel and the Möbius cycles.

The aim of this note is to relate the roots of the acyclic and characteristic polynomials of Hückel and Möbius cycles as is expressed by the following three equations:

(i) eigenvalues of Hückel cycles

$$Q_n(x) = 2.(-1)^n ; \qquad (6a)$$

(ii) eigenvalues of Möbius cycles

$$Q_n(x) = -2.(-1)^n ; \qquad (6b)$$

(iii) roots of the acyclic polynomial

$$Q_n(x) = 0 . \qquad (6c)$$

As is evident from these equations, the function $Q_n(x)$ plays a central role in this task: the roots of the three polynomials must be related to each other because they are derived from an unique function, namely $Q_n(x)$, in a rather transparent manner. For this reason, it seems to be worthwile to consider the function $Q_n(x)$ in some detail.

3. Some properties of $P_n(x)$

Due to the definition (4), the properties of $Q_n(x)$ depend on those of the functions $P_n(x)$ which, hence, should be reviewed here briefly:

(i) The function $P_n(x)$ may be expressed as follows:

$$P_n(x) = \sum_{\nu=0}^{n/2} (-1)^\nu \binom{n-\nu}{\nu} x^{n-2\nu} ; \qquad (7)$$

(ii) the roots of $P_n(x) = 0$ are given by

$$x_k = 2\cos k\pi/(n+1), \quad k = 1,2,\ldots,n , \qquad (8)$$

and belong to the open interval (-2,+2);

(iii) as proved in appendix A, the differential quotient

$dP_n(x)/dx$ is given by the following expression:

$$dP_n(x)/dx = \sum_{\kappa=0}^{n/2} (n-2\kappa)\cdot P_{n-1-2\kappa}(x) \quad ; \qquad (9)$$

(iv) in the interval [-2,+2], which also contains the roots of $P_n(x)$, the variable x may be expressed as $x = 2\cos\theta$, $0 \leq \theta \leq \pi$, and the function $P_n(x)$ may be transformed into a function $P_n(\theta)$ given by

$$P_n(\theta) = \sin(n+1)\theta/\sin\theta \ , \qquad (10)$$
$$x = 2\cos\theta, \quad 0 \leq \theta \leq \pi \quad .$$

4. Homonuclear Hückel and Möbius cycles and some properties of $Q_n(x)$

Since both Hückel and Möbius cycles are depicted by a regular graph of degree 2, all their eigenvalues [13] belong to the interval [-2,+2]. Hence, by the transformation of $Q_n(x)$ into $Q_n(\theta)$, no eigenvalues of both cycles are lost. From eqs. (4) and (10), one obtains straightforwardly:

$$Q_n(\theta) = 2.\cos n\theta. \qquad (11)$$

The following consequences of eq. (11) should be noted:

(i) in the interval of definition (11), i.e. $x \varepsilon [-2,+2]$, the values of the function $Q_n(x)$ lie in the interval [-2,+2], and they attain alternately one or the other boundary of the interval (n+1) times (see also Fig. 1):

$$x \ \varepsilon\ [-2,+2], \quad Q_n(x) \ \varepsilon\ [-2,+2] \ ; \qquad (12)$$

(ii) for $x = \pm 2$, corresponding with $\Theta = 0$ and $\Theta = \pi$, respectively, the function $Q_n(x)$ takes the following values:

$$Q_n(+2) = 2, \quad Q_n(-2) = 2.(-1)^n \; ; \tag{13}$$

in view of eq. (6), the first value corresponds to an eigenvalue of an even Hückel or an odd Möbius cycle whilst the second one always represents an eigenvalue of either an even or an odd Hückel cycle;

(iii) since the values given in eq. (13) coincide with the boundaries of the interval of $Q_n(x)$, it follows from (i) that in the open interval $(-2,+2)$ of the variable x, the function $Q_n(x)$ attains tangentially and alternately one or the other boundary of $[-2,+2]$, $(n-1)$ times;

(iv) the function $Q_n(x)$ has n zeros expressed by

$$x_j = 2.\cos(2j+1)\pi/2n \; , \quad j = 0,1,\ldots, n-1 \; ; \tag{14}$$

in view of eqs. (3) and (4), these are identically the roots of the acyclic polynomial $A_n(x)$.

Differentiating eq. (4) in respect to x and substituting eq. (9) into the primary result, one finally obtains the following expression:

$$dQ_n(x)/dx = n.P_{n-1}(x) \; . \tag{15}$$

Hence, the function $Q_n(x)$ has its extrema exactly at the zeros of $P_{n-1}(x)$, which are given according to eq. (8) as follows:

$$x_k = 2.\cos k\pi/n \quad , \qquad (16)$$
$$k = 1,2,\ldots,n-1;$$

they represent the (n-1) touchings of the boundaries of the interval mentioned above in (iii). From this and eq. (11) the extremal values of $Q_n(x)$ are given by

$$Q_n(x_k) = 2.\cos k\pi = 2.(-1)^k \; . \qquad (17)$$

By comparison with eq. (6), one easily recognizes that eq. (17) represents all the doubly degenerate eigenvalues of the n-membered Hückel and Möbius cycle; for even n, k has to be even for Hückel, but odd for Möbius cycles whilst the opposite is true for odd values of n.

All this leads to the well known expressions for the roots of the acyclic (x_j^A) and the characteristic polynomials of the Hückel (x_k^H) and the Möbius (x_k^M) cycles:

$$x_j^A = 2.\cos\frac{2j+1}{n}\,\frac{\pi}{2} \; , \qquad 0 \leqq j \leqq n-1 \; ;$$
$$x_k^H = 2.\cos\frac{2k}{n}\,\pi \; , \qquad 0 \leqq k \leqq n-1 \; ; \qquad (18)$$
$$x_k^M = 2.\cos\frac{2k+1}{n}\,\pi \; , \qquad 0 \leqq k \leqq n-1 \; .$$

In Fig. 1 the functions $Q_9(x)$ and $Q_{10}(x)$ are depicted; these nicely illustrate the relations between the different sets of roots denoted in eq. (18): The mutual interlacing of the eigenvalues of Hückel and Möbius cycles results from $Q_n(x)$ being a single-valued continous function. The mirror-image relation between the eigenvalue spectra of these two types of odd membered cycles is a consequence of the fact that $Q_n(x)$ is an odd function for odd n. Figure 1 further shows that all the roots of the acyclic polynomial lie in intervals of minimal range which are each bounded by an eigenvalue of the Hückel and the Möbius cycle.

Figure 2 shows the energy band for an infinite annulene; the roots of the acyclic and the characteristic polynomial of the Hückel and the Möbius form of the 18-annulene, $C_{18}H_{18}$, are indicated by crosses, full, and open circles, respectively. These all belong to the band. It can be shown quite generally [14] that this must be essentially the case for the x_k^H's and the x_k^M's; of course, in the case of annulenes considered here, the x_j^A's are forced to belong also to the band because they have the same analytical expression as is valid for x_k^H and x_k^M, but this relationship seems to be accidential.

5. Alternant heteronuclear Hückel and Möbius cycles

We now consider cycles of the general type $(AB)_n$. Their secular determinant may be written as follows:

$$\det \underline{D}((AB)_n) = \begin{vmatrix} y & 1 & 0 & 0 & \dots & 0 & \rho \\ 1 & z & 1 & 0 & \dots & 0 & 0 \\ 0 & 1 & y & 1 & \dots & 0 & 0 \\ 0 & 0 & 1 & z & \dots & 0 & 0 \\ \cdot & \cdot & \cdot & \cdot & & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & & \cdot & \cdot \\ 0 & 0 & 0 & 0 & \dots & y & 1 \\ \rho & 0 & 0 & 0 & \dots & 1 & x \end{vmatrix} = \chi_{2n}(y,z,\rho) \qquad (19)$$

where $y = (\alpha_A-\varepsilon)/\beta_{AB}$, $z = (\alpha_B-\varepsilon)/\beta_{AB}$, and $\rho \in \{+1,-1\}$; both variables, y and z, are linear functions of x, say, y = x + a and

$z = x + b$. In the same manner as the determinant of eq. (1) has been expanded and the resulting terms have been identified, one obtains from eq. (19) the following expression for the characteristic polynomial of the cycles $(AB)_n$:

$$\chi_{2n}(y,z,\rho) = B_{2n}(yz) - B_{2n-2}(yz) - 2.\rho \ , \qquad (20)$$

where $B_{2n}(yz)$ denotes the characteristic and/or acyclic polynomial of an unbranched alternant heteronuclear chain.

It can be shown that $B_{2m}(yz)$ has the following analytical form:

$$B_{2m}(yz) = \sum_{\mu=0}^{m} (-1)^{\mu} \binom{2m-\mu}{\mu} (yz)^{m-\mu} \ . \qquad (21)$$

Let us now define another variable

$$\xi^2 = y \cdot z \qquad (22)$$

which we substitute into eq. (21). Taking $2m = n$ and $\mu = \nu$, one easily sees that by the substitution of eq. (22), the function $B_{2n}(yz)$ is transformed into $P_{2n}(\xi)$ given by eq. (7):

$$B_{2n}(yz) = P_{2n}(\xi) \ . \qquad (23)$$

Hence, on recalling the definition (4), we can rewrite eq. (20) as follows

$$\chi_{2n}(y,z,\rho) = Q_{2n}(\xi) - 2.\rho \ ; \qquad (24)$$

the treatment performed in section 4 may now be applied analogously to the problem of alternant heteronuclear Hückel and Möbius cycles. Bearing in mind that the cycles considered here have a total of 2n centers, one obtains from the eqs. (18) and (22),

$$y_j^A \cdot z_j^A = 4.\cos^2(\frac{2j+1}{2n}\frac{\pi}{2}) , \qquad 0 \leq j \leq n-1 ;$$
$$y_k^H \cdot z_k^H = 4.\cos^2(\frac{2k}{2n}\cdot\pi) , \qquad 0 \leq k \leq n-1 ; \qquad (25)$$
$$y_k^M \cdot z_k^M = 4.\cos^2(\frac{2k+1}{2n}\cdot\pi) , \qquad 0 \leq k \leq n-1 .$$

Since the variables y and z are linear functions [15] of x, say $y = x + a$ and $z = x + b$, the roots of the three polynomials have the general form

$$(x_\ell^S)_{1,2} = -[(a+b) \pm \sqrt{(a-b)^2 + 16.\cos^2\theta_\ell^S}]/2 , \qquad (26)$$

where S denotes either A, H, or M, ℓ either j or k, and θ_ℓ^S the corresponding argument given in eq. (25). The roots are symmetrically located about $x = -(a+b)/2$. All the roots x_k^H and x_k^M are doubly degenerate except the root $(x_0^H)_{1,2}$ and for even n, $(x_{n/2}^H)_{1,2}$ also.

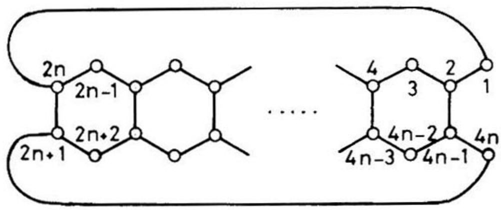
The alternant heteronuclear Hückel and Möbius cycles exhibit the same general properties as the homonuclear cycles, so one may dispense with a detailed discussion. The function $Q_{2n}(\xi)$, however, requires further consideration:

If one replaces x formally by ξ in $Q_{2n}(x)$, only those real values of ξ are realizable which belong to [-2,+2], i.e. $0 \leq \xi^2 \leq 4$. but, by eq. (22), ξ^2 is defined as $\xi^2 = (x+a)(x+b)$; hence, if $x \in (-a,-b)$, one of these factors is positive the other negative and, consequently, $\xi^2 < 0$. Of course, the function $Q_{2n}(\xi)$ is always defined since it is an even function which has real values when $\xi^2 < 0$, but these lie out of the range [-2,+2]. It may be shown that for $\xi^2 < 0$, the function $Q_{2n}(\xi) > 2$ if n is even, and $Q_{2n}(\xi) < -2$ if n is odd, respectively. All this implies: (i) the interval (-a,-b) specifies a gap to which no roots of the polynomials can belong; (ii) the extremum of $Q_{2m}(x)$ at x=0 in the homonuclear case does not occur for $Q_{2m}(\xi)$, the double root at x=0 generated by that extremum is split into two single roots the one at x=-a, $\xi(-a)=0$, and the other at x=-b, $\xi(-b)=0$. As an illustration, in Fig. 3 there are depicted $Q_{16}(\xi)$ and $Q_{18}(\xi)$ for a=1, b=0, i.e., $\xi^2=x^2+x$. The gap interval is (-1,0). In this interval one finds $Q_{16}>2$ and $Q_{18}<-2$, the extrema amounts to $Q_{16}(-1/2) = 52,448257$ and $Q_{18}(-1/2) = -86,015842$, respectively.

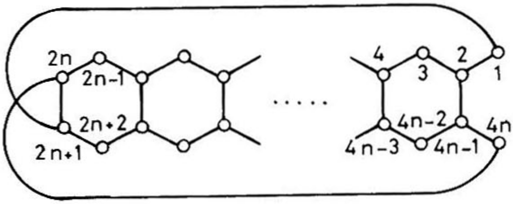
6. Cylindrical (Hückel) and Möbius polyacenes.

As a special example of a polycyclic Hückel and Möbius system, we consider certain forms of polyacene. A planar strip of this material can be thought of as being closed in two different ways, one leading to a cyclindrical form, termed earlier [16] the rota polymer, R, and the other resulting in a Möbius band, M. The structure of these two forms of polyacene is as follows:

R=



M=



The AO's of the centers r and 4n+1-r may be combined symmetrically or antimetrically. Using these linear combinations as basis functions, the problem is factorized. As well for the symmetric as for the antimetric factor, we obtain a secular determinant of exactly the same form as given in eq. (19). This directly shows the applicability of the results of the preceeding section to the problem treated here. The entries of the secular determinants have the following meaning:

	polyacene	
	rota form (Hückel)	Möbius form
symmetric	$y = x$	$y = x$
factor	$z = x + 1$	$z = x + 1$
$\xi^2 = x^2 + x$	$\rho = 1$	$\rho = -1$
antimetric	$y = x$	$y = x$
factor	$z = x-1$	$z = x-1$
$\xi^2 = x^2-x$	$\rho = 1$	$\rho = 1$

As a consequence of these specifications, the antimetric factor does not differ for the Hückel and the Möbius polymer, provided they have the same degree of polymerisation, n. Differences appear only in the symmetric factors of the two forms. This is illustrated by Fig. 4 showing the eigenvalues of R and M for n = 6. Although the formation of these compounds cannot be really anticipated for such a low value of n, this value is chosen as it illustrates the situation with optimal clarity due to the small number of eigenvalues.

The function $Q_{2n}(\xi)$ depicted in Fig. 3 corresponds to the symmetric factor; the function for the antimetric factor is its mirror image reflected at x=0.

A more general treatment of Möbius polymers will be published elsewhere [9]; the treatment by means of $Q_m(x)$ functions can be applied only to those polymers which exhibit symmetries allowing the construction of secular determinants of the type of eq. (19) or a similar type.

To our knowledge, our treatment of the Möbius polyacenes is the first time that the π electron system of a polycyclic Möbius system has been considered.

Appendix A: The differential quotient of $P_n(x)$

The function $P_n(x)$ is defined by eq. (7), hence,

$$dP_n(x)/dx = \sum_{\nu=0}^{n/2} (-1)^{\nu}(n-2\nu)\binom{n-\nu}{\nu}x^{n-1-2\nu} \qquad (A.1)$$

The coefficients appearing in this equation may be expressed alternatively as follows:

$$(n-2\nu)\binom{n-\nu}{\nu} = (n-2\nu)\frac{(n-\nu)!}{\nu!(n-2\nu)!} = (n-\nu)\frac{(n-1-\nu)!}{\nu!\ (n-1-2\nu)!} =$$

$$= (n-\nu)\binom{n-1-\nu}{\nu} \qquad (A.2)$$

Via eq. (A.2), eq. (A.1) may be brought into the following form:

$$dP_n(x)/dx = n\cdot\sum(-1)^{\nu}\binom{n-1-\nu}{\nu}x^{n-1-2\nu} + \sum(-1)^{\nu-1}\cdot\nu\cdot\binom{n-1-\nu}{\nu}x^{n-1-2\nu}$$

$$(A.3)$$

The first term in eq. (A.3) is obviously equal to $n\cdot P_{n-1}(x)$. The coefficients of the second term are treated as follows (where $k = n-1$ is introduced for convenience):

$$\nu\binom{k-\nu}{\nu} = \nu\frac{(k-\nu)!}{\nu!\ (k-2\nu)!} = (k-\nu)\frac{(k-1-\nu)!}{(\nu-1)!(k-2\nu)!} =$$

$$= [(k-1)-(\nu-1)]\binom{(k-2)-(\nu-1)}{(\nu-1)} \ . \qquad (A.4)$$

Using this result, from eq. (A.3) the following expression is derived ($\mu=\nu-1$):

$$dP_n(x)/dx = n\cdot P_{n-1}(x) + (n-2)\sum(-1)^{\mu}\binom{(n-3)-\mu}{\mu}x^{(n-3)-2\mu} +$$

$$+ \sum(-1)^{\mu-1}\cdot\mu\binom{(n-3)-\mu}{\mu}x^{(n-3)-2\mu} \qquad (A.5)$$

The second term in this equation may be identified with $(n-2)P_{n-3}(x)$; the third term has the same form as the last term of eq. (A.3). Hence, repeated application of eq. (A.4) leads to

$$dP_n(x)/dx = n\cdot P_{n-1}(x) + (n-2)\cdot P_{n-3}(x) + \\ + (n-4)\cdot P_{n-5}(x) + (n-6)\cdot P_{n-7}(x) + \ldots \tag{A.6}$$

which may be written compactly as follows:

$$dP_n(x)/dx = \sum_{\kappa=0}^{n/2} (n-2\kappa)\cdot P_{n-1-2\kappa}(x) \tag{A.7}$$

This expression may be verified by means of the recurrence formula

$$P_{n+1}(x) = x\cdot P_n(x) - P_{n-1}(x) \ . \tag{A.8}$$

Differentiating both sides, one obtains

$$dP_{n+1}(x)/dx = P_n(x) + x\cdot dP_n(x)/dx - dP_{n-1}(x)/dx.$$

Introducing (A.7) into this expression, one obtains

$$\sum(n+1-2\kappa)P_{n-2\kappa}(x) = P_n(x) + x\sum(n-2\lambda)P_{n-1-2\lambda}(x) - \\ - \sum(n-1-2\mu)P_{n-2-2\mu}(x).$$

As a consequence of (A.8), the following terms cancel ($\kappa=\lambda=\mu$):

$$\sum(n-2\kappa)P_{n-2\kappa}(x) = x\sum(n-2\lambda)P_{n-1-2\lambda}(x) - \sum(n-2\mu)P_{n-2-2\mu}(x).$$

In this manner, the remaining terms of eq. (A.9) express the trivial identity,

$$\sum_{\kappa=0}^{n/2} P_{n-2\kappa}(x) = P_n(x) + \sum_{\lambda=0}^{(n-2)/2} P_{n-2-2\lambda}(x) \ .$$

This result verifies eq. (A.7).

Appendix B: Generalized recurrence relation of the polynomials $P_n(x)$

It will be shown here, that the function $Q_n(x)$, defined in eq. (4), plays some role in the generalized recurrence relation of the polynomials $P_n(x)$. The well-known recurrence relation

$$P_{n+1}(x) = x \cdot P_n(x) - P_{n-1}(x)$$

has already been given in Eq. (A.8).

The repeated application of this equation results in

$$P_{n+2}(x) = (x^2 - 2) \cdot P_n(x) - P_{n-2}(x) \ ,$$

$$P_{n+3}(x) = (x^3 - 3x) \cdot P_n(x) - P_{n-3}(x) \ ,$$

etc.

In general, one may write

$$P_{n+m}(x) = f_m(x) \cdot P_n(x) - P_{n-m}(x) \qquad \text{(B.1)}$$

where $f_m(x)$ denotes a polynomial of degree m, $m \leq n$. On substituting eq. (10) into this expression, one obtains

$$\sin(n+1+m)\Theta = f_m(\Theta) \cdot \sin(n+1)\Theta - \sin(n+1-m)\Theta \ .$$

On expanding these terms into goniometric functions of the arguments either $(n+1)\Theta$ or $m\Theta$, one obtains

$$f_m(\Theta) = 2\cos m\Theta \ .$$

By comparison with eq. (11), $f_m(\Theta)$ is identified as $Q_m(\Theta)$. Hence, eq. (B.1) may be written as follows:

$$P_{n+m}(x) = Q_m(x)\cdot P_n(x) - P_{n-m}(x) \ . \qquad \text{(B.2)}$$

Obviously, eq. (B.2) is a generalized recurrence relation for the polynomials $P_n(x)$. The combination of eqs. (4) and (B.2) results in the following identity:

$$P_{n+m}(x) + P_{n-m}(x) = P_m(x)\cdot P_n(x) - P_{m-2}(x)\cdot P_n(x) \ . \qquad \text{(B.3)}$$

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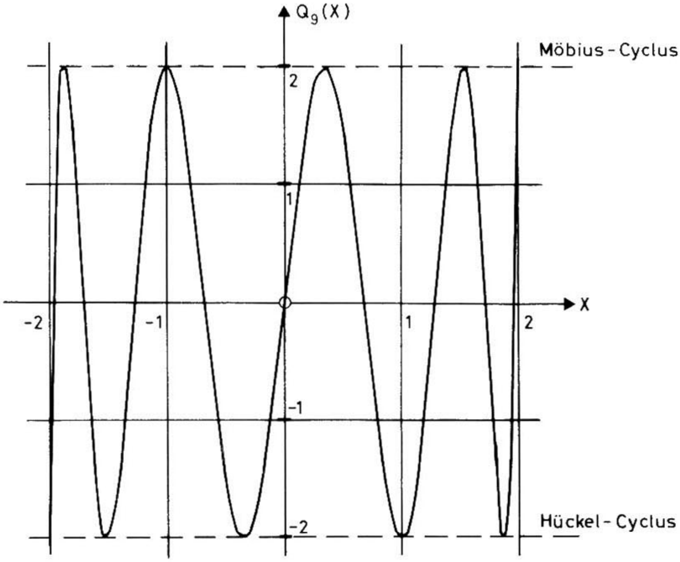
Figure captions:

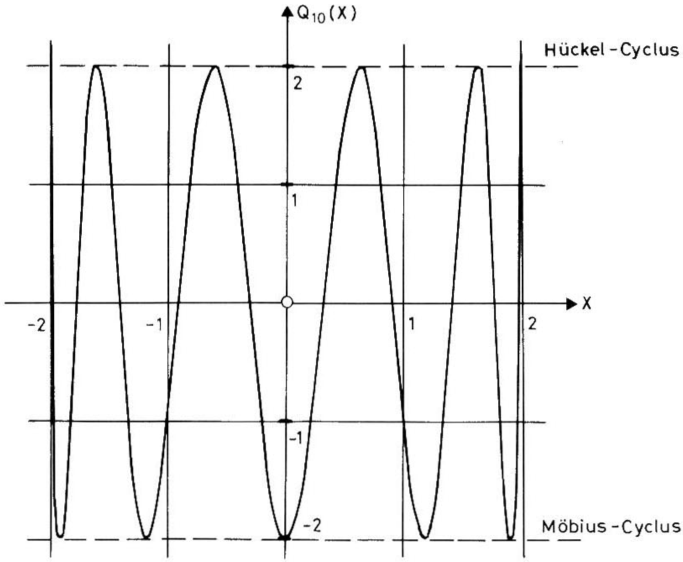
Fig. 1. The functions $Q_9(x)$ and $Q_{10}(x)$. The intersections with the straight lines $g_{1,2}(x) = \pm 2$ represent the eigenvalues of the 9 and 10 membered Hückel (H) and Möbius (M) cycles respectively.

Fig. 2. Band of the eigenvalues of an infinite annulene. The roots of the acyclic (+) and the characteristic polynomials of the Hückel (●) and the Möbius (o) form of the annulene $C_{18}H_{18}$ belong to the band.

Fig. 3. The functions $Q_{16}(\xi)$ and $Q_{18}(\xi)$ as functions of the variable x with $\xi^2 = x^2 + x$.

Fig. 4. Spectra of the eigenvalues of rota-(Hückel)- and Möbius-hexacene $C_{24}H_{12}$. The symmetric functions lead to different level(s), the antimetric functions to the same level(a) for both compounds.


Q9 (X)
Möbius-Cyclus
2
1
X
-2
-1
1
2
-1
-2
Hückel-Cyclus


Q10 (X)
Hückel-Cyclus
2
1
X
-2
-1
1
2
-1
-2
Möbius-Cyclus

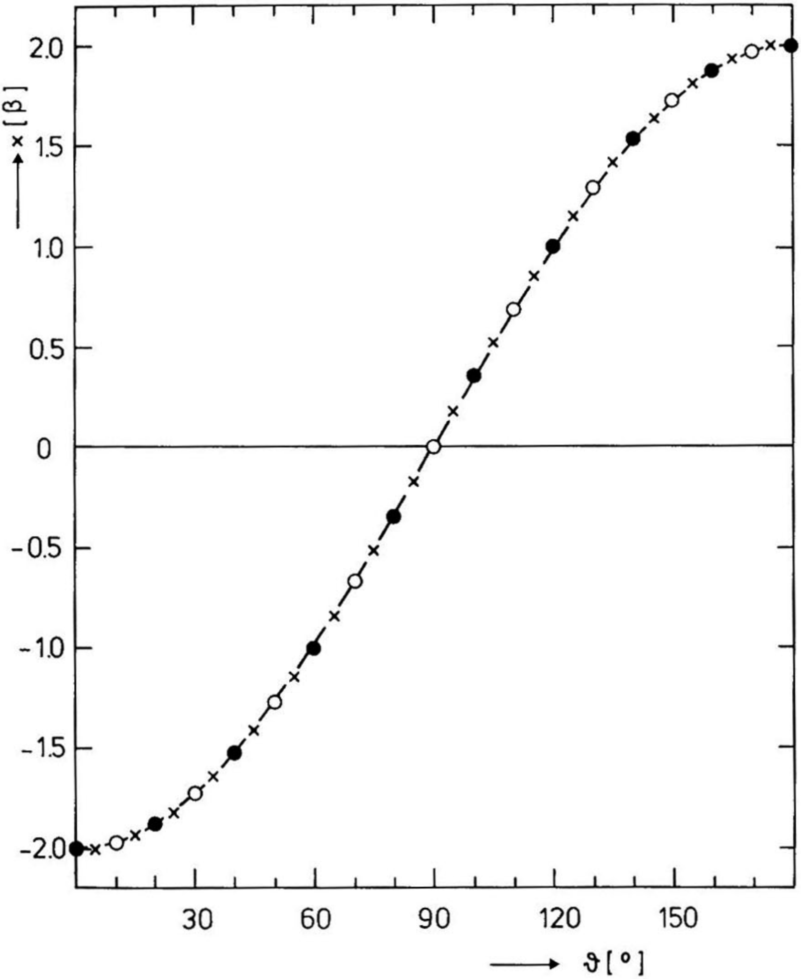


Fig.: 2

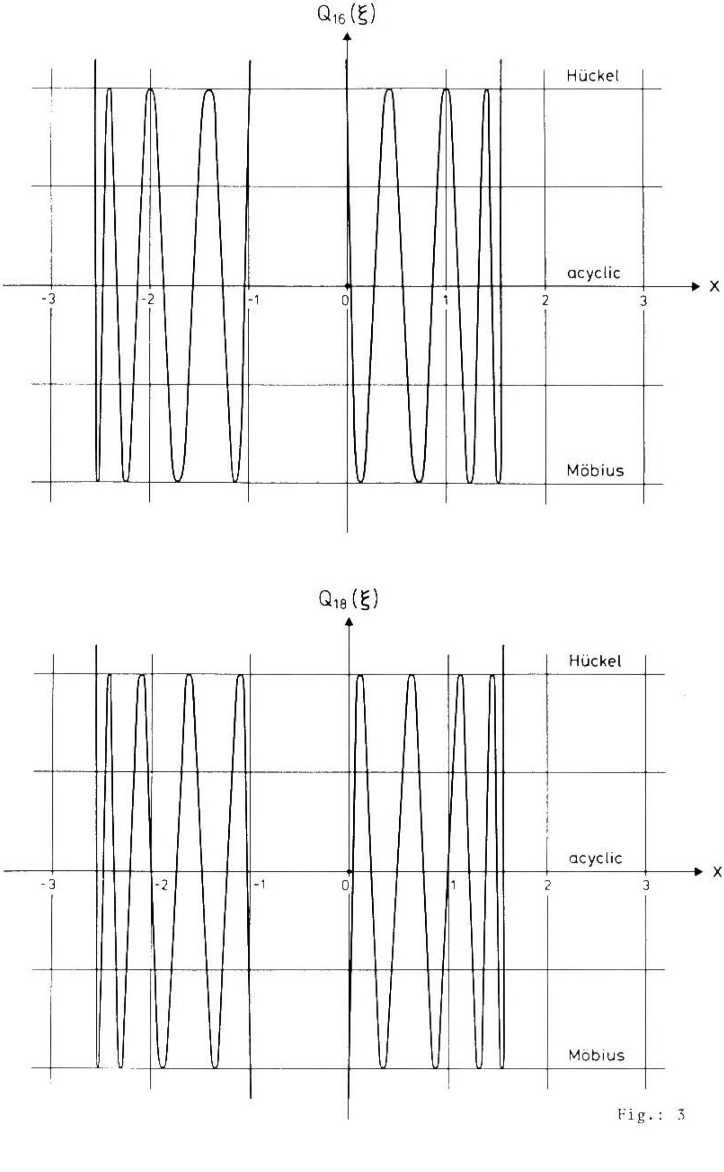

Q16(ξ)
Hückel
acyclic
Möbius
X
-3
-2
-1
0
1
2
3
Q18(ξ)
Hückel
acyclic
Möbius
X
-3
-2
-1
0
1
2
3

Fig.: 3

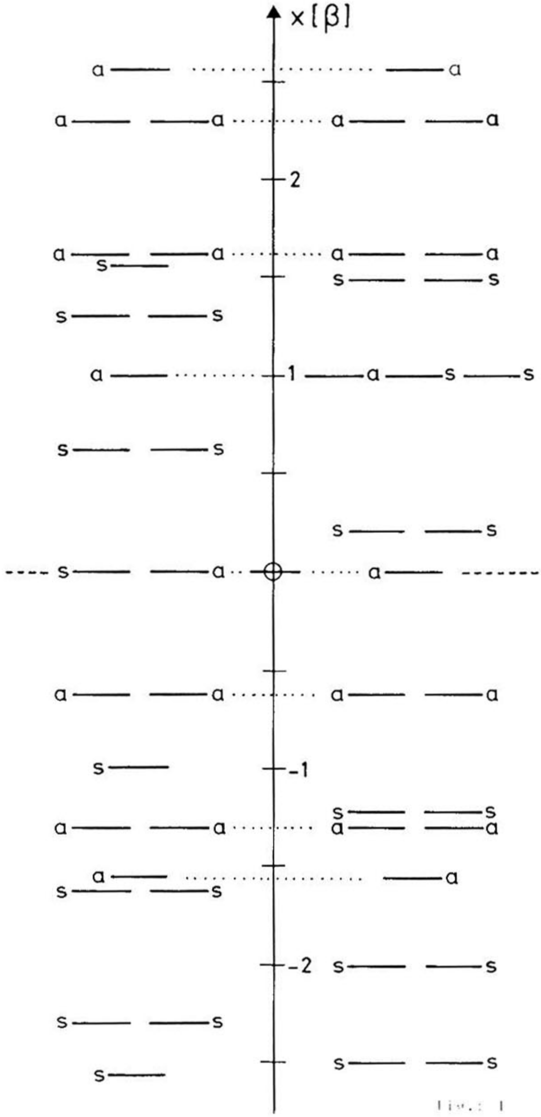


Fig. 1