

On the Matching Spectrum of Rotagraphs

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The matching polynomial of the rotagraph U_M with M monomer units and one linking edge between the units is considered, with particular attention paid to its zeros. It has been found that the matching spectrum of an infinite rotagraph has, like its characteristic spectrum, a band-like structure. The factorization of the matching polynomial of U_M has been derived, the result being fully analogous to the factorization of the corresponding characteristic polynomial. These results can be used for quick and easy evaluation of the matching spectrum of infinite and finite U_M of any size. For a certain class of U_M , having an acyclic monomer unit, the matching and the characteristic bands coincide. The matching and the characteristic bands of some particular rotagraphs are evaluated.

Introduction

A rotagraph U_M is a convenient mathematical object to represent a regular conjugated polymer closed on itself [1]. It consists of M repeating units which are pairwise connected in the same manner.

The electronic HMO-energies of U_M are determined by the zeros of the characteristic polynomial $\bar{U}_M(x)$. They form the characteristic spectrum $\text{Sp}(U_M)$ of U_M . The cyclic symmetry of U_M enables the factorization of $\bar{U}_M(x)$ into M polynomials of the order n , where n stands for the number of vertices (conjugated centers) of the monomer unit. The j -th factor is associated with the irreducible representation Γ_j of the cyclic group C_M and contains parametrically the character $\bar{\omega}_j = \exp(i\bar{\theta}_j)$ of Γ_j , where $\bar{\theta}_j = 2j\pi/M$, $j = 0, 1, 2, \dots, M-1$, and $i = \sqrt{-1}$. The zeros of the j -factor of $\bar{U}_M(x)$ are denoted by $\bar{x}_1(\bar{\theta}_j), \bar{x}_2(\bar{\theta}_j), \dots, \bar{x}_n(\bar{\theta}_j)$.

When M goes to infinity, $\bar{\theta}_j$ is no longer a discrete parameter but a continuous variable $\bar{\theta}$ within the range $0 \leq \bar{\theta} < 2\pi$. Consequently the zeros $\bar{x}_k(\bar{\theta}_j)$, with a given k , merge to the k -th electronic (or characteristic) band $\bar{x}_k = \bar{x}_k(\bar{\theta})$.

The method is well known in solid state physics and has been already used in the study of conjugated polymers [2, 3].

Another polynomial of interest in chemistry is the matching polynomial [4]. The term acyclic polynomial is also used by some authors [4]. The set of zeros of the matching polynomial $U_M(x)$ is denoted by $\text{Sp}(U_M)$. Some particular results on the matching spectrum $\text{Sp}(U_M)$ of rotagraphs have been presented in the literature [5–7]. Until now no systematical effort has been made to treat $\text{Sp}(U_M)$. Namely, the cyclic symmetry of the Hamiltonian matrix of the rotagraph, which enables the factorization of $\bar{U}_M(x)$, cannot be used in the treatment of the matching polynomial $U_M(x)$ because the matching polynomial is not the characteristic polynomial of any interaction matrix, but is rather defined as a purely combinatorial object. Regardless of this fact, we show in the present paper that the matching polynomial of a rotagraph with $l = 1$, where l denotes the number of linking edges (bonds) between the monomer units, can also be factorized into M factors.

The method is based on the recently established recurrence relations for the matching polynomial of rotagraphs [8]. All of these M factors are of the same form which depends on the matching polynomials of the monomer unit and its certain subgraphs. The factors include the parameter $\theta_j = (2j+1)\pi/2M$, $j = 0, 1, \dots, M-1$, which formally resembles $\bar{\theta}_j$. The zeros of the j -th factor are denoted by $x_1(\theta_j), x_2(\theta_j), \dots, x_n(\theta_j)$.

When M goes to infinity, θ_j becomes a continuous variable θ within the range $0 < \theta < \pi$. Therefore the zeros $x_k(\theta_j)$, with a given k , give rise to a conti-

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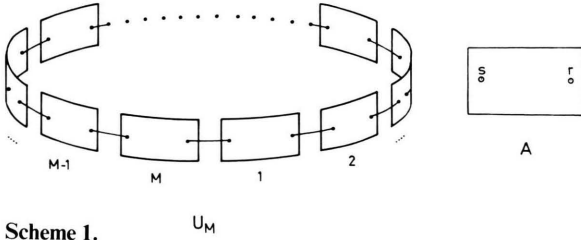
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nuous function $x_k = x_k(\theta)$. We call it, by an analogy with the previous considerations, the k -th matching band of an infinite rotagraph U_M . Note that the θ -range is the half of the $\bar{\theta}$ -range.

Method

The rotagraph U_M with $l=1$ and its repeating monomer unit A is schematically depicted below. The vertices s and r denote the linking sites. Further, we introduce the notation:



Scheme 1.

$\alpha \equiv A$, $\varrho \equiv A^r$, $\sigma \equiv A^s$, and $\delta \equiv A^{s,r}$, where $A^{u,v,\dots}$ denotes the subgraph obtained by deletion of the vertices u, v, \dots (together with their incident edges) out from A . The characteristic and matching polynomials of any graph G are denoted by $\bar{G}(x)$ and $G(x)$, respectively.

The matching polynomial $U_M(x)$ can be expressed as [8]

$$U_M(x) = \text{tr}(T^M), \quad (1)$$

where tr stands for the trace, and the polynomial matrix T is given by

$$T = \begin{bmatrix} \alpha(x) & -\sigma(x) \\ \varrho(x) & -\delta(x) \end{bmatrix}. \quad (2)$$

The characteristic polynomial $\Phi(T, \lambda)$ of T is defined by

$$\Phi(T, \lambda) = \det(\lambda I - T) = \lambda^2 - s_1 \lambda + s_2, \quad (3)$$

where I is the unit matrix of the order 2. The coefficients of $\Phi(T, \lambda)$ are easily evaluated:

$$s_1 = \alpha(x) - \delta(x), \quad s_2 = \varrho(x) \sigma(x) - \alpha(x) \delta(x); \quad (4)$$

they are real functions for all x .

By applying the Cayley-Hamilton theorem: $\Phi(T, T) = 0$, the following recursion formula for $U_M(x)$ has been derived [8]:

$$U_M(x) - s_1 U_{M-1}(x) + s_2 U_{M-2}(x) = 0, \quad M \geq 2. \quad (5)$$

The initial conditions read as follows:

$$U_0(x) = 2, \quad U_1(x) = s_1. \quad (6)$$

As it is known from linear algebra, a relationship exists between the trace of a power of a matrix and the zeros of its characteristic polynomial [9]. Having this in mind, (1) can be rewritten as

$$U_M(x) = \lambda_1^M + \lambda_2^M, \quad (7)$$

where

$$\lambda_{1,2} = \frac{s_1 \pm \sqrt{s_1^2 - 4s_2}}{2} \quad (8)$$

are the zeros of $\Phi(T, \lambda)$, (3). Let us remind that λ_1 and λ_2 are functions of x .

Equations (7) and (8) could be also derived by using the theory of linear recursions [10], but the presented derivation appears to be simpler.

Owing to the recently established inequality [11]

$$s_2 = \varrho(x) \sigma(x) - \alpha(x) \delta(x) = \sum_{P(s,r)} [A^{P(s,r)}(x)]^2 \geq 0, \quad (9)$$

values which λ_1 and λ_2 may assume have a particular property. $P(s, r)$ denotes a path (not walk!) starting in the vertex s and ending in the vertex r of the monomer unit graph A , while the symbol in square brackets means the matching polynomial of the subgraph obtained by deletion of the path $P(s, r)$ out from A . A simple consideration of the parabola on the r.h.s. of (3), taking into account $s_2 \geq 0$, shows that the real values of λ_1 and λ_2 are both non-negative or both non-positive. This property allows us to treat $\lambda_{1,2}$ in a very convenient way.

Taking $s_2 > 0$, three possibilities arise: a) $s_1^2 < 4s_2$, $\lambda_{1,2}$ are complex conjugate numbers; b) $s_1^2 > 4s_2$ and $s_1 > 0$, $\lambda_{1,2}$ are both real and positive; c) $s_1^2 > 4s_2$ and $s_1 < 0$, $\lambda_{1,2}$ are both real and negative numbers. One can easily verify that in all three cases $\lambda_{1,2}$ can be expressed as

$$\lambda_{1,2} = R e^{\pm i\theta}, \quad R = \sqrt{s_2}, \quad \cos \theta = \frac{s_1}{2\sqrt{s_2}} \quad (10)$$

with the following values for

$$a) \theta \in R, \quad \cos \theta = \frac{s_1}{2\sqrt{s_2}}, \quad (11)$$

$$b) \theta = i\psi, \quad \psi \in R, \quad \cos \theta = \text{ch } \psi = \frac{s_1}{2\sqrt{s_2}}, \quad (12)$$

$$c) \theta = \pi + i\psi, \quad \psi \in R, \quad \cos \theta = -\text{ch } \psi = \frac{s_1}{2\sqrt{s_2}}. \quad (13)$$

Equation (7) can be now rewritten as

$$U_M(x) = \lambda_1^M + \lambda_2^M = 2 \cdot R^M \cos M\theta. \quad (14)$$

Using the identity

$$\cos M\theta = 2^{M-1} \sum_{j=0}^{M-1} (\cos \theta - \cos \theta_j), \quad (15)$$

$$\theta_j = (2j+1)\pi/2M$$

we obtain

$$U_M(x) = \sum_{j=0}^{M-1} 2R (\cos \theta - \cos \theta_j). \quad (16)$$

Substitution of R and $\cos \theta$ according to (10) finally gives

$$U_M(x) = \sum_{j=0}^{M-1} (s_1 - 2\sqrt{s_2} \cos \theta_j), \quad (17)$$

$$\theta_j = (2j+1)\pi/2M.$$

Until now we have taken $s_2 > 0$. Putting $s_2 = 0$ in (8) gives $\lambda_1 = s_1$ and $\lambda_2 = 0$, and from (7) $U_M(x) = s_1^M$. Because the same result is reproduced by (17), we conclude that the factorized expression (17) for $U_M(x)$ holds generally, in full formal analogy with the factorization of $\bar{U}_M(x)$. Namely, following [1], $\bar{U}_M(x)$ can be factorized also:

$$\bar{U}_M(x) = \sum_{j=0}^{M-1} [\bar{\alpha}(x) - \bar{\delta}(x) - 2\sqrt{\bar{q}(x)\bar{\sigma}(x) - \bar{\alpha}(x)\bar{\delta}(x)} \cos \bar{\theta}_j], \quad (18)$$

where $\bar{\theta}_j = 2j\pi/M$. Taking by analogy

$$\bar{s}_1 \equiv \bar{\alpha}(x) - \bar{\delta}(x) \quad \text{and} \quad (19)$$

$$\bar{s}_2 \equiv \bar{q}(x)\bar{\sigma}(x) - \bar{\alpha}(x)\bar{\delta}(x),$$

where \bar{s}_2 is a non-negative quantity [8] too, one obtains the factorization for $\bar{U}_M(x)$:

$$\bar{U}_M(x) = \sum_{j=0}^{M-1} (\bar{s}_1 - 2\sqrt{\bar{s}_2} \cos \bar{\theta}_j) \quad (20)$$

having completely the same form as one derived for $U_M(x)$ in (17).

By equating each of the factors in (17) with zero:

$$s_1 - 2\sqrt{s_2} \cos \theta_j = 0, \quad j = 0, 1, \dots, M-1 \quad (21)$$

and solving them in x , one obtains the matching spectrum $\text{Sp}(U_M)$ of a rotagraph U_M .

Some particular zeros of the $\text{Sp}(U_M)$ should be noted from the above equation. x_0 , which is zero of

both s_1 and s_2 appears in the $\text{Sp}(U_M)$ with M -fold degeneracy, for any M . Further, for $M = 2m + 1$, $\theta_m = \pi/2$, the cosine term in (21) vanishes, and all the zeros of s_1 appear in $\text{Sp}(U_M)$. Because $s_1 = U_1(x)$, (6), $\text{Sp}(U_M)$ contains $\text{Sp}(U_1)$ whenever M is odd.

Let us consider an infinite rotagraph. The discrete θ_j parameter becomes a continuous parameter θ and the matching spectrum of U_M , $M \rightarrow \infty$, is obtained by solving in x the equation

$$s_1 - 2\sqrt{s_2} \cos \theta = 0, \quad (22)$$

where the allowed values of θ ($0 < \theta < \pi$) cover half of the first Brillouin zone ($0 \leq \bar{\theta} < 2\pi$). In full analogy with the treatment of the characteristic bands of U_M , $M \rightarrow \infty$, we interpret the k -th zero of (22), $x_k = x_k(\theta)$, $0 < \theta < \pi$, as the k -th matching band of an infinite rotagraph.

Before proceeding to the next section, where some examples are calculated, let us note that the matching bands of a given rotagraph generally differ from its characteristic bands. However, there exists a class of rotagraphs, we denote it by W , such that both the matching and the characteristic bands of $U_M \in W$ have the same functional dependence on the θ -parameter. The class W contains rotagraphs with $l=1$ for which the repeating unit A is represented by an acyclic graph, i.e. by a graph having no cycles. Consequently, the matching and the characteristic polynomials of A and its subgraphs coincide: $\alpha \equiv A(x) \equiv \bar{A}(x)$, $\varrho \equiv A^r(x) \equiv \bar{A}^r(x)$, $\sigma \equiv A^s(x) \equiv \bar{A}^s(x)$, and $\delta \equiv A^{s,r}(x) \equiv \bar{A}^{s,r}(x)$. Taking (4) and (19) into account, expressions (17), for $U_M(x)$, and (20), for $\bar{U}_M(x)$, coincide up to the θ_j and $\bar{\theta}_j$ values. In the case of an infinite rotagraph $U_M \in W$, $M \rightarrow \infty$, both the matching and the characteristic bands are determined by the same equation (22), i.e. both have the same functional dependence on the θ -parameter. The earlier comments on the range of this parameter apply also here, but one should note that the characteristic bands in the interval $\pi < \bar{\theta} < 2\pi$ have the same values as in the interval $0 < \bar{\theta} < \pi$, owing to the periodicity of the cosine function. Because the matching bands represent the same number of spectral values in the interval which is half of the $\bar{\theta}$ interval, their density is doubled in comparison with the density of the characteristic bands, which applies not only to $U_M \in W$ but to any U_M . As the result, the matching and the characteristic spectra of the infinite rotagraphs, having acyclic monomer units and with

$l=1$, fully coincide. This result should not be strange, because due to the presence of only one cycle in such an U_M , the corresponding polynomials $\bar{U}_M(x)$ and $U_M(x)$ differ always only by 2. Obviously, this difference becomes meaningless for an infinite M .

Calculations

Example 1. Let us illustrate the procedure on the simple example of $[M]$ -annulene, where the monomer unit is an isolated vertex. As $\alpha(x) = x$, $\varrho(x) = \sigma(x) = 1$ and $\delta(x) = 0$ in this case, the application of (17) and (21) straightforwardly yields the known results for the matching spectrum of $[M]$ -annulene [5, 7]:

$$x_j = 2 \cdot \cos \frac{(2j+1)\pi}{2M}, \quad j = 0, 1, \dots, M-1. \quad (23)$$

For an infinite annulene only one matching band appears, and it follows (22) that

$$x_1(\theta) = 2 \cdot \cos \theta, \quad 0 < \theta < \pi. \quad (24)$$

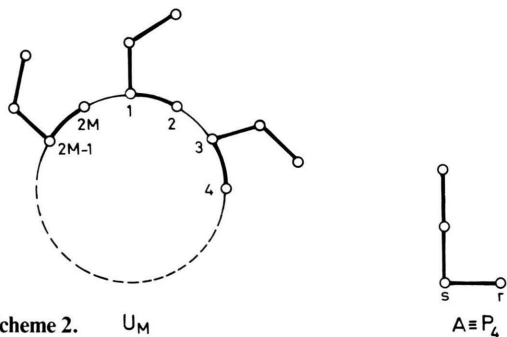
As $[M]$ -annulene belongs to the class W of rotagraphs, (21) and (22) apply again, and the known results for the characteristic spectrum of $[M]$ -annulene are reproduced [12]:

$$\bar{x}_j = 2 \cdot \cos \frac{2j\pi}{M}, \quad j = 0, 1, \dots, M-1. \quad (25)$$

Only one characteristic band exists for $M \rightarrow \infty$, and it is given by

$$\bar{x}_1(\bar{\theta}) = 2 \cdot \cos \bar{\theta}, \quad 0 \leq \bar{\theta} < 2\pi. \quad (26)$$

Example 2. Let U_M represents s -vinyl $[2M]$ -annulene [6]. It is depicted below together with its monomer unit A .



Scheme 2. U_M

The polynomials we need are:

$$\begin{aligned} \alpha(x) &= P_4(x) = \bar{P}_4(x), \quad \varrho(x) = P_3(x) = \bar{P}_3(x), \\ \sigma(x) &= P_2(x) P_1(x) = \bar{P}_2(x) \bar{P}_1(x) \quad \text{and} \\ \delta(x) &= P_2(x) = \bar{P}_2(x), \end{aligned}$$

where P_n denotes the chain with n vertices. Accordingly, one obtains $s_1 = x^4 - 4x^2 + 2$, $s_2 = (x^2 - 1)^2$, and the application of (17) yields

$$\begin{aligned} x^4 - 2(2 + \cos \theta_j) x^2 + 2(1 + \cos \theta_j) &= 0, \\ \theta_j &= \frac{(2j+1)\pi}{2M}, \quad j = 0, 1, \dots, M-1. \end{aligned} \quad (27)$$

The matching spectrum is therefore given by

$$\begin{aligned} \text{Sp}(U_M) &= \{\pm [2 + \cos \theta_j \\ &\quad \pm (\cos^2 \theta_j + 2 \cos \theta_j + 2)^{1/2}]^{1/2} \\ &\quad | \theta_j = (2j+1)\pi/2M, j = 0, 1, \dots, M-1\}. \end{aligned} \quad (28)$$

The above result has already been derived in the literature [6, 13], but by use of a completely different argumentation.

Because $U_M \in W$, the characteristic spectrum $\bar{\text{Sp}}(U_M)$ is also given by (28), but θ_j has to be substituted by $\bar{\theta}_j = 2j\pi/M$, $j = 0, 1, \dots, M-1$. The result is also known in the literature [6, 14].

For an infinite s -vinyl $[2M]$ -annulene the following four matching bands appear:

$$\begin{aligned} x_1(\theta) &= [2 + \cos \theta + (\cos^2 \theta + 2 \cos \theta + 2)^{1/2}]^{1/2}, \\ x_2(\theta) &= [2 + \cos \theta - (\cos^2 \theta + 2 \cos \theta + 2)^{1/2}]^{1/2}, \\ x_3(\theta) &= -x_2(\theta), \quad x_4(\theta) = -x_1(\theta), \quad 0 < \theta < \pi. \end{aligned} \quad (29)$$

Four characteristic bands of an infinite s -vinyl $[2M]$ -annulene are also given by (29), but θ has to be replaced by $\bar{\theta}$, $0 \leq \bar{\theta} < 2\pi$.

In the following examples $U_M \notin W$ and the matching and the characteristic bands do not coincide. In each example the zeros of (22) are evaluated and depicted vs. θ . For the comparison the characteristic bands are drawn on the same figures. The widths of the matching and the characteristic bands are marked by the dashed areas on the left and the right side of the drawings, respectively. The numerical values of the bounds of bands are indicated too.

Example 3. Let U_M represent poly- p -cyclobutadiene. Equation (22) reads now as follows:

$$(x^4 - 5x^2 + 2) - 2\sqrt{2}x \cos \theta = 0. \quad (30)$$

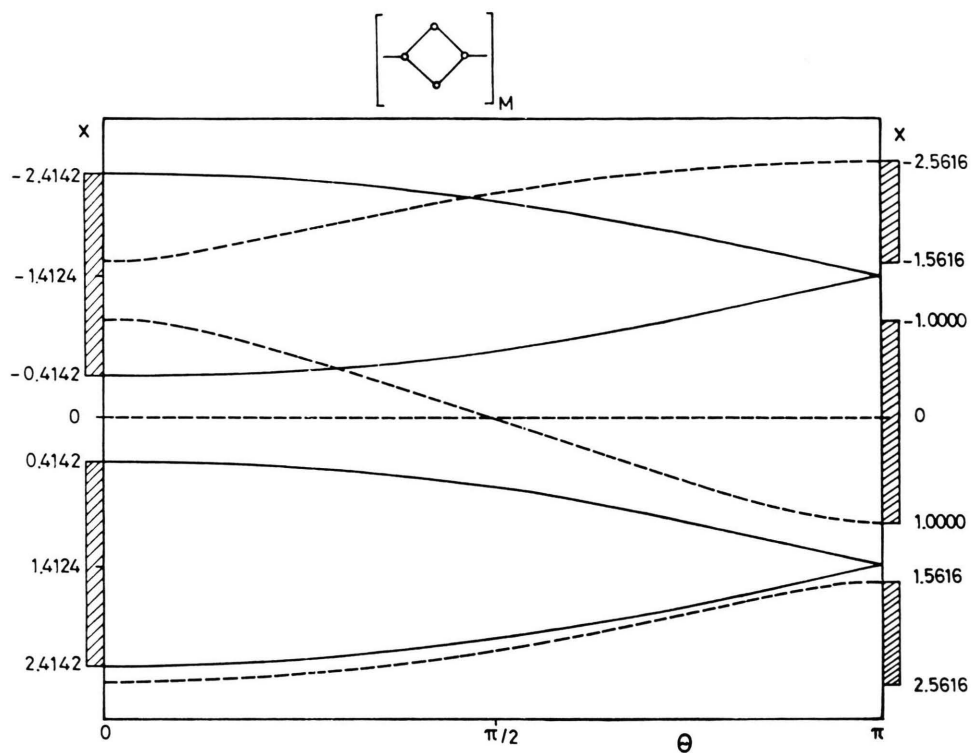


Fig. 1. The matching (full line) and the characteristic (dashed line) bands of poly-p-cyclobutadiene.

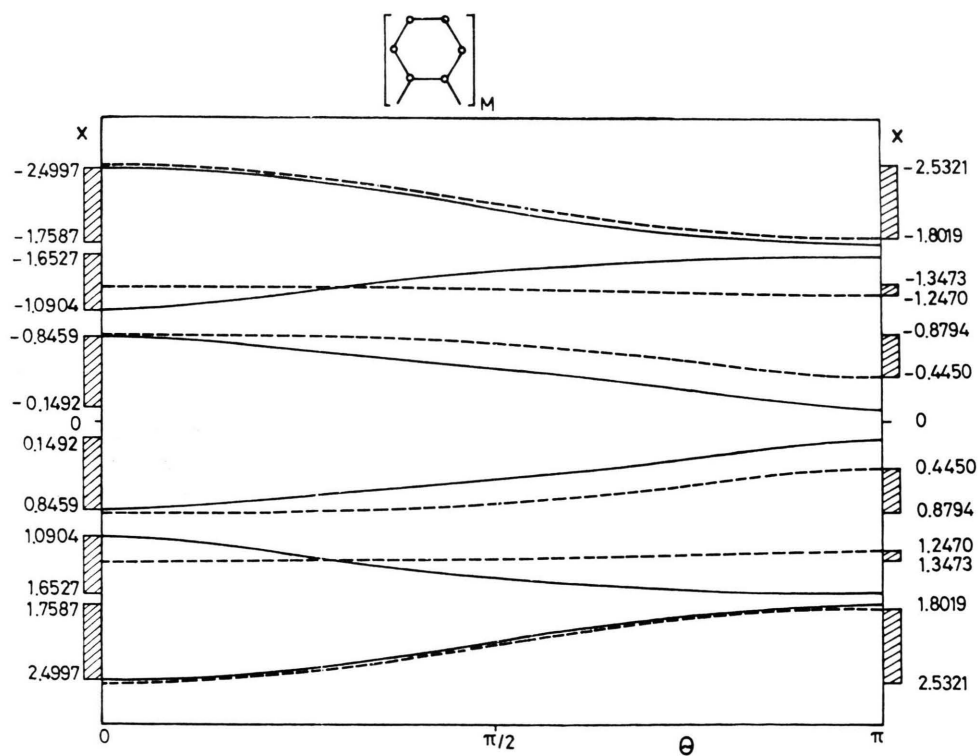


Fig. 2. The matching (full line) and the characteristic (dashed line) bands of poly-o-phenylene.

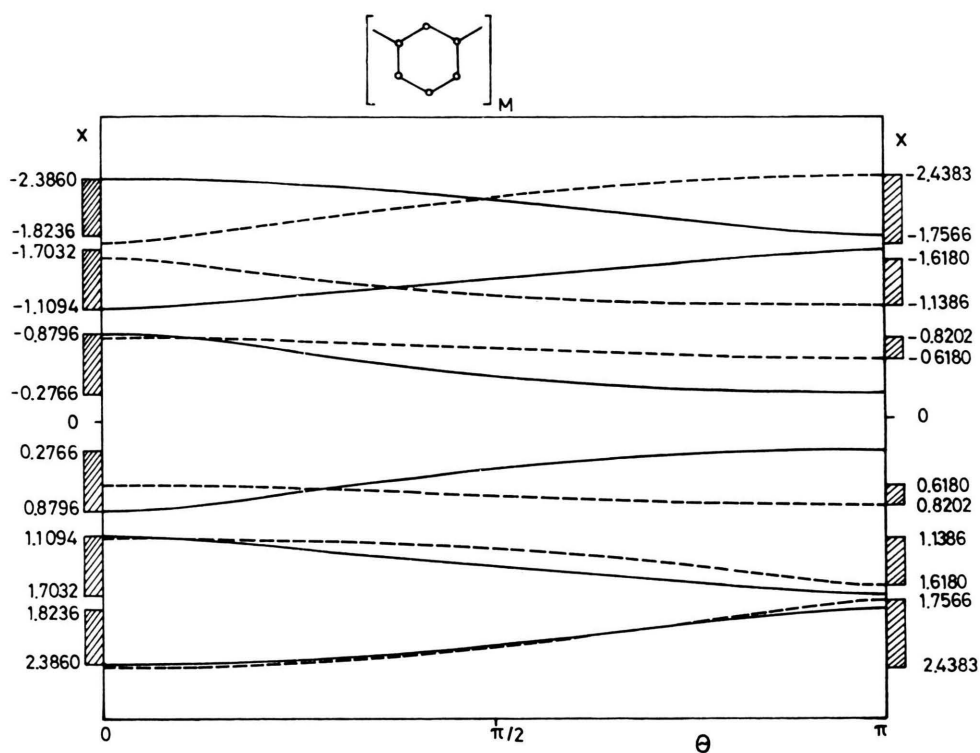


Fig. 3. The matching (full line) and the characteristic (dashed line) bands of poly-m-phenylene.

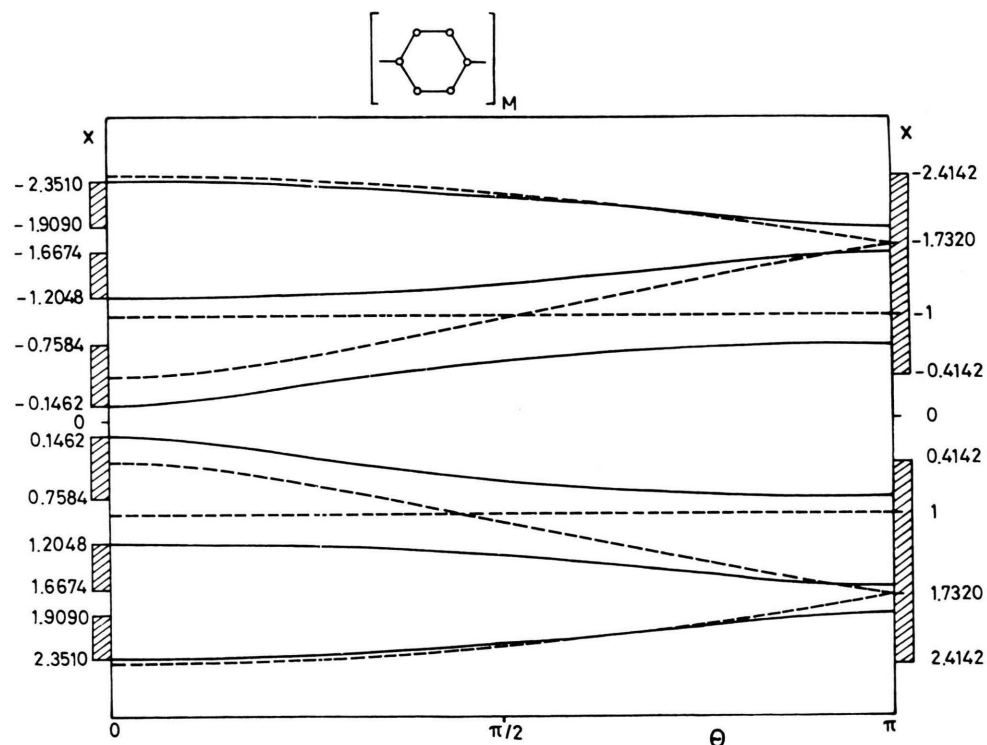


Fig. 4. The matching (full line) and the characteristic (dashed line) bands of poly-p-phenylene.

It enables the evaluation of the matching bands of U_M . They are shown on Fig. 1 together with the characteristic bands of U_M .

Examples 4, 5 and 6. In these examples the matching bands for poly-o-phenylene (Fig. 2), poly-m-phenylene (Fig. 3), and poly-p-phenylene (Fig. 4) are evaluated by the calculation of x -zeros of the respective equations:

poly-o-phenylene:

$$x^6 - 7x^4 + 12x^2 - 3 - 2\sqrt{(x^4 - 3x^2 + 1)^2 + 1} \cos \theta = 0, \quad (31)$$

poly-m-phenylene:

$$x^6 - 7x^4 + 11x^2 - 2 - 2x\sqrt{(x^2 - 2)^2 + 1} \cos \theta = 0, \quad (32)$$

poly-p-phenylene:

$$x^6 - 7x^4 + 11x^2 - 3 - 2\sqrt{2}(x^2 - 1) \cos \theta = 0. \quad (33)$$

Conclusion

In this paper we have shown that the matching spectrum of an infinite rotagraph, with $l = 1$, has a

band-like structure as is the case with its characteristic spectrum. Moreover, the matching polynomial of U_M can be factorized in full analogy with the factorization of the characteristic polynomial of U_M . These results can be used for the evaluation of the matching spectrum of both finite and infinite rotagraphs.

Although we considered rotagraphs with only one linking edge between the monomer units ($l = 1$), the matching band-like structures are expected also for the rotagraphs with higher l . Some preliminary calculations on systems with $l = 2$ support this expectation, but the factorization of the matching polynomial appears to be much more difficult to derive. Work on this subject is in progress.

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- [12] See for example: C. A. Coulson and A. Streitwieser, *Dictionary of pi-Electron Calculations*, Pergamon, Oxford 1955.
- [13] By rewriting the (28) of the present paper with the argument $\theta/2$, it coincides with (17) of [6], where the term $2 \cos^2[(2j+1)\pi/4a]$ has to be corrected and should read as $1 + 2 \cos^2[(2j+1)\pi/4a]$, $a = M$.
- [14] The characteristic spectrum expressed in the argument $\theta/2$ coincides with Eqn. (8) of [6] where the term $2 \cos^2(j\pi/a)$ has to be corrected and should read as $1 + 2 \cos^2(j\pi/a)$, $a = M$.