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STRUCTURAL GRAPHS OF REGULAR POLYMERS AND THEIR PROPERTIES*

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ABSTRACT

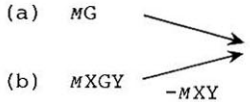
For polymers with regular structure ...-G-G-... two graphs are defined: the ratograph, R, and the fascia graph, F. Using the rough structure of the automorphism group, $A(R)$, of the rotagraph a procedure is developed to determine the eigenvalues and eigenfunctions of R. Using these sets the eigenvalues and eigenfunctions of F are obtained by means of perturbation theory.

The band structure of the eigenvalues of the infinite graphs is investigated. The mathematical conditions for the existence of forbidden zones and gaps within the band strucuture are given. A way to determine the overlapping and self overlapping of bands is outlined.

The use of the procedure presented is discusssed briefly.

(1) Introduction

From a number of molecules, G or XGY, undergoing a polymerisation reaction the polymer, G_M, is formed where M is a number of the order 10 to 10^4. For our purposes it makes no difference if the polymerisation considered has to be classified either as a polyaddition, (a), or as a polycondensation (b), in which M molecules



$$G_M = \ldots\text{-G-G-G-G-G-}\ldots \qquad (1)$$

XY have to be eliminated. In both cases we call G the monomeric unit of the polymer. The structure of G is represented by the simple connected graph G

$$G = [U,K], \qquad (2)$$

where U represents the set of vertices, K the set of edges. The cardinalities of these sets are n and m respectively. The automorphism groups of the G are denoted by $A(G)$. - Polymers are of great interest not least because important natural products as well as synthetics belong to this class of compounds [2].

We shall restrict our considerations to those polymers only which have a regular structure as indicated in (1). There are two types of polymers to be considered:

(1) The polymeric chain is closed on itself: Each monomeric unit is connected to two neighbouring units by the bonds formed during the polymerisation. The polymer has a wheel-like structure; its structural graph we call a rotagraph, R.

(2) The polymeric chain is open: There are two terminal monomeric units, which are connected to only one neigbouring unit each, but the others to two as above. The polymer has a band-like structure; its structural graph we call a fasciagraph, F.

Certainly the band-like polymers corresponding with F are favoured statistically in the chemical reaction but mathematically R can be handled more extensively than F. Further, in the limit of infinite polymers, the eigenvalues of both graphs, R and F, coincide as shown in section 6 and appendix 1.

In this paper we will define both graphs, R and F.

Using the rough structure of $A(R)$ we will outline a certain way to detect the exact eigenvalues of R and the approximate eigenvalues of F. The main purpose of this paper, however, will be a discussion of the band structure of polymers if $M \to \infty$; the origins of the overlapping and the self-overlapping of bands as well as their separation by forbidden zones will also be treated.

(2) Rotagraph R and Fasciagraph F

We start with the union (MG) of M equal components $G_J | J \in M = \{1,2,\ldots,M\}$ as investigated by Harary and Palmer [3]. Its automorphism groups are given by $A(MG) = S_M[A(G)]$. The vertices of each component G_J are labelled by an index $\nu \in n = \{1,2,\ldots,n\}$ in such a way that the bijection

$$U_\nu^J \longleftrightarrow U_\nu^K \quad \forall \nu \in n \text{ and } \forall J,K \in M$$
$$U_\nu^J \in G_J;\ U_\nu^K \in G_K$$

represents an automorphism of (MG). It is obvious that (MG) represents the starting material of the polymerisation on the left side of (1).

To construct R from (MG) one has to add an edge set, K_ν^R, which represents all the bonds formed during

the polymerisation. If l bonds are formed between two monomeric units we have to define l edges in R connecting two neighbours, say G_J and G_{J+1}. In consequence of this we have to partition the vertex sets U_J into three subsets, U_1^J, U_2^J and U_3^J respectively: (i) to U_1^J belong those vertices of G_J which are incident with the edges connecting G_{J-1} and G_J; (ii) to U_2^J belong those vertices of G_J which are incident with the edges connecting G_J and G_{J+1}; (iii) to U_3^J belong those vertices of G_J which are not incident with these edges:

$$U_J = U_1^J \bigcup U_2^J \bigcup U_3^J, \qquad (3)$$

where U_3^J is a disjoint subset by definition. For simplicity we assume that U_1^J and U_2^J are disjoint too[*]). Then the cardinalities of these three subsets are l,l, and $k = n-2l$ respectively. Referring to the partition (3) we may label the vertices beside the supercript $J \in M$ by a pair of indices such as $U_{j,\lambda}^J$, where $j = 1,2$ and $\lambda \in \ell = \{1,2,\ldots,l\}$ or $j = 3$ and $\lambda \in k = \{1,2,\ldots,k\}$. This alternative labelling of the vertices of U_J must be unambiguous; therefore it

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[*] there are only a few polymers, e.g.: polymethylene $(-CH_2-)_M-$, for which U_1^J and U_2^J are not disjoint. It will be seen later that this assumption does not lead to loss of generality.

requires a bijective relation, $r \longleftrightarrow (j,\lambda)$, for each $r \in n$ and for each (j,λ) belonging to $(1,\ell)$, $(2,\ell)$, or $(3,k)$ respectively. With this notation the edges connecting G_J and G_{J+1} in R are defined as follows:

$$K_v^J = \bigcup_{\lambda \in \ell} \{ U_{1,\lambda}^J, U_{2,\lambda}^{J+1} \mid U_{1,\lambda}^J \in G_J; U_{2,\lambda}^{J+1} \in G_{J+1} \}. \qquad (\underline{4})$$

The difference $R \backslash (MG)$ is then given by the union

$$K_v^R = \bigcup_M K_v^J \qquad (\underline{5})$$

which immediately leads to the

Definition of R:

$$R = R(G,M,K^V) = (MG) \bigcup K_v^R. \qquad (\underline{6})$$

It is obvious that the structure of R is uniquely defined by the following three elements: (i) the graph G of the monomeric unit; (ii) the number M of the monomeric units; and (iii) the edge set K^V connecting a pair of neighbouring units.

The fasicagraph F differs from R in the point that in F the monomer units G_1 and G_M are not connected directly.

Therefore

$$K_v^F = K_v^R \setminus K_v^M = \bigcup_{1 \leq J \leq (M-1)} K_v^J. \qquad (7)$$

This leads immediately to the

Definition of F:

$$F = F(G, M, K^V) = (MG) \bigcup K_v^F, \qquad (8)$$

where G, M, and K^V have the same meaning as in (6).

(3) Some properties of the automorphism group $A(R)$ of the rotagraph R

The addition of the edge set K_v^R to (MG) qualifies the equivalence relations established in (MG) in two respects: (i) the automorphic mapping of the monomeric units onto each other cannot further form the symmetric group S_M; (ii) the incidence of the vertices of U_1^J and U_2^J with the edges of K_v^{J-1} and K_v^J respectively may distort some equivalence relations established ultimately in the monomeric units. - Although we may conclude that the automorphism group $A(R)$ of the rotagraph has to be a subgroup of $A(MG)$, actually

$$A(R) \subset S_M[A(G)], \qquad (9)$$

we have to notice too that the symmetry of both factors of the wreath product will be reduced in general. As the example given in fig. 1 shows, $A(R)$ has not always the general structure of a simple wreath product at all. Fortunately for our further purposes we do not need the detailed structure of $A(R)$; the structure of the automorphic mapping of the monomeric units onto each other is sufficient.

Let us suppose firstly U_1^J and U_2^J introduced by (3) are inequivalent subsets so that they cannot be mapped bijectively onto each other. If we now map G_J onto G_K this means in detail

$$G_J \longleftrightarrow G_K = \{U_j^J \longleftrightarrow U_j^K | j \in \{1,2,3\}\} \qquad (10)$$

or, still more detailed: $U_{1,1}^J \longleftrightarrow U_{1,1}^K$, $U_{1,2}^J \longleftrightarrow U_{1,2}^K$, ... etc. Since one vertex, $U_{1,1}^J$, incident with the edge $\{U_{2,1}^{J-1}, U_{1,1}^J\} \in K_v^{J-1}$ has been mapped onto $U_{1,1}^K$, incident with the edge $\{U_{2,1}^{K-1}, U_{1,1}^K\} \in K_v^{K-1}$, the other one has to be mapped onto $U_{2,1}^{K-1} \in G_{K-1}$. Generalized, (10) implies the mapping

$$G_{J+L} \longleftrightarrow G_{K+L} \qquad \forall L \in M. \qquad (11)$$

Because K represents any member of M, (11) obviously corresponds with the set of the cyclic permutations of the indices $J \in M$ forming the cyclic group C_M. We may summarize the results to give

Proposition 1: If U_1^J and U_2^J are inequivalent subsets the automorphic mapping of the monomeric units G_J onto each other forms the cyclic group C_M operating on the index set M.

From this follows immediately

Proposition 2: If each vertex $U_\nu^J \in G_J$ forms an equivalence class by itself the automorphism group of R is given by

$$A(R) = C_M[E_n]. \qquad (12)$$

Proof: (i) If each vertex $U_\nu^J \in G_J$ forms its own equivalence class the internal automorphism $G_J \longleftrightarrow G_J$ consists only of the identical mapping, forming the group E_n. (ii) From proposition 1 follows that the outer factor is given by C_M.

The order of the wreath product $C_M[E_n]$ equals M.

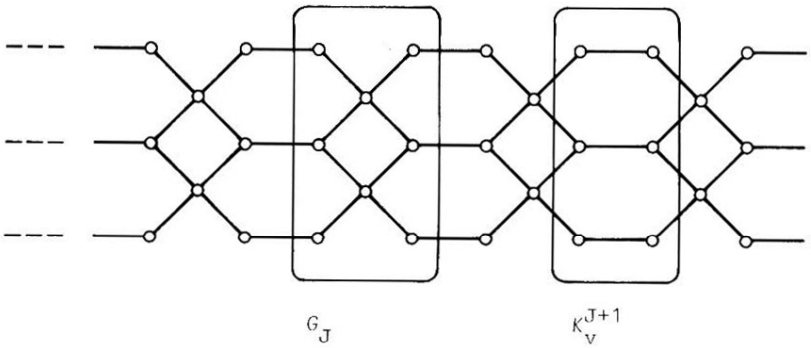


Figure 1: Part of a rotagraph $R(G,M,K^V)$. The degree of $A(R)$ obviously is $8M$, its order equals $4M$. This order cannot be realized for all integral values of M by a wreath product of the general from $C_M[B]$ or $D_M[B']$ respectively.

It should be mentioned that M is the minimal value of the order of $A(R)$ because the mappings $G_J \longleftrightarrow G_K$ are always feasible in R. Any increase of the internal symmetry of the monomeric units is followed by an increase of the order $A(R)$.

Let us now suppose that U_1^J and U_2^J are equivalent subsets such that the internal automorphism $G_J \longleftrightarrow G_J$ contains the bijections

$$U_{1,\lambda}^J \longleftrightarrow U_{2,\lambda}^J \quad \forall\ \lambda \in \ell. \tag{13}$$

Then $G_J \longleftrightarrow G_K$ means in detail:

$$G_J \longleftrightarrow G_J = \{[U_1^J \longleftrightarrow U_1^J;\ U_2^J \longleftrightarrow U_2^J;\ U_3^J \longleftrightarrow U_3^J];$$

$$[U_1^J \longleftrightarrow U_2^J;\ U_3^J \longleftrightarrow U_3^J]\}, \tag{14}$$

where $U_1^J \longleftrightarrow U_2^J$ stands for $\{U_{1,\lambda}^J \longleftrightarrow U_{2,\lambda}^J \mid \lambda \in \ell\}$. Then the vertex $U_{1,\lambda}^J$ can be mapped either onto the vertex $U_{1,\lambda}^K$ or onto $U_{2,\lambda}^K$; this means in detail an alternative mapping of the edge $\{U_{2,\lambda}^{J-1},\ U_{1,\lambda}^J\}$ onto $\{U_{2,\lambda}^{K-1},\ U_{1,\lambda}^K\} \in K_v^{K-1}$ as discussed above or onto $\{U_{2,\lambda}^K,\ U_{1,\lambda}^{K+1}\} \in K_v^K$. The second option may be generalized to

$$G_{J+L} \longleftrightarrow G_{K-L} \quad \forall\ L \in M. \tag{15}$$

It is obvious that (15) corresponds with the set of the permutation of the following type

$$\begin{pmatrix} \ldots J-2 & J-1 & J & J+1 & J+2\ldots \\ \ldots K+2 & K+1 & K & K-1 & K-2\ldots \end{pmatrix}$$

Together with the set of cyclic permutations they form the dihedral group $\mathcal{D}_M$. Hence we may formulate

Proposition 3: If by the equivalence of the subsets U_1^J and U_2^J the bijections $U_{1,\lambda}^J \longleftrightarrow U_{2,\lambda}^J$ are feasible for all $\lambda \in \ell$ then the automorphic mapping of the monomeric units G_J onto each other forms the the dihedral group $\mathcal{D}_M$ operating on the index set M.

The bijections (14) do not necessarily imply that $A(R)$ has the form $\mathcal{D}_M[B]$; figure 1 illustrates the point.

The changes in the equivalence relations within a monomeric unit of R by the addition of K_v^R to (MG) are simulated by a graph, $G' = G \bigcup (\bigcup_{\ell} \{U_{1,\lambda}, U_{2,\lambda}\})$. It is obvious that $G' = R(G, M=1, K^V)$, but this graph has no chemical meaning (see sect. 7.9).

(4) Eigenvalues, eigenvectors and eigenfunctions of $R(G,M,K^V)$

The adjacency matrix R of the rotagraph $\mathcal{R}$ consists of $M \times M$ quadratic blocks each of the size $n \times n$:

$$
\begin{aligned}
R &= (R_{JK}) \mid J,K \in M \\
R_{JK} =: &= G \;\ldots\ldots\; K = J \\
&= V \;\ldots\ldots\; K = (J+1) \bmod M \\
&= V^T \;\ldots\ldots\; K = (J-1) \bmod M \\
&= O \;\ldots\ldots\; \text{otherwise}
\end{aligned}
\qquad (16)
$$

G represents the adjacency matrix of the monomer graph $\mathcal{G}$, V the adjacency matrix of K^V. According to these definitions, the elements of both these matrices are either O or 1. From (16) it is obvious, that $\mathcal{R}$ has cyclic block form ($R_{1M} = V^T$ and $R_{M1} = V$). If C_μ^j represents an eigenvector of $\mathcal{R}$, the indices will be discussed below, the eigenvalue problem is given as follows:

$$(R + x_\mu^j I)\; C_\mu^j = H^R \cdot C_\mu^j = O. \qquad (17)$$

The matrix H^R, defined by $(R + xI)$, has the same cyclic form as R; both matrices differ only in the diagonal blocks

$$H_{JJ}^R = D = G + xI; \quad \forall\, J \in M. \qquad (18)$$

There are $(n \times M)$ eigenvectors $c_\mu^j \mid \mu \in n,\ j \in M$ satisfying (17). They all together form the matrix of eigenvectors C which may be split into M blocks $C_j \mid j \in M$ each of them consisting of (nM) rows and n columns:

$$\begin{aligned} C &= (C_1\ C_2\ \ldots\ C_j\ \ldots\ C_M), \\ C_j &= (c_1^j\ c_2^j\ \ldots\ c_\mu^j\ \ldots\ c_n^j). \end{aligned} \tag{19}$$

For the sake of simplicity we suppose that in R only the minimum of equivalency is realized. Then according to (12) the automorphism group of R is given by $A(R) = C_M[E_n]$. From this it is to be expected that the block C_j corresponds exactly with the j-th irreducible representation Γ_j of the general cyclic group C_M formed by the set of the operations $\{S^r\}$. The characters of Γ_j are given [4] by the row $\chi(\Gamma_j) = (\omega_j^r)$, where $0 \leqq r \leqq (M-1)$ and $\omega_j = \exp(2ij\pi/M)$. Under these circumstances C_j and c_μ^j should have the following respective forms:

$$C_j = \begin{pmatrix} c_j \\ \omega_j c_j \\ \omega_j^2 c_j \\ \cdot \\ \cdot \\ \cdot \\ \omega_j^{M-1} c_j \end{pmatrix} \qquad \text{and} \qquad c_\mu^j = \begin{pmatrix} c_\mu^j \\ \omega_j c_\mu^j \\ \omega_j^2 c_\mu^j \\ \cdot \\ \cdot \\ \cdot \\ \omega_j^{M-1} c_\mu^j \end{pmatrix} \tag{20}$$

where c_j stands for a nxn matrix and c_μ^j for a column vector consisting of n elements. Introducing this form into (17) and using (18) one obtains for the k-th row of H^R the following:

$$\omega_j^{k-1} \cdot [\omega_j^{\times} V^T + D + \omega_j V] \cdot c_\mu^j = 0$$

or

$$[\omega_j^{\times} V^T + D + \omega_j V] \cdot c_\mu^j = 0, \qquad (\underline{\underline{21}})$$

where 0 stands for an nx1 column vector. The fact that (21) does not depend on the row index k, reflects the generality of (20). Further by (21) the original (nM)x(nM) dimensional problem (17) is reduced to M problems $(0 \leq j \leq (M-1))$ of the dimension nxn. If $A(R)$ is of a higher order than $C_M[E_n]$, there are internal equivalence relations in the monomeric units G_J which allow some further factorisations of (21). In section (7.8) we shall discuss briefly some aspects of such a factorisation, but in what follows we shall assume that the automorphism group is represented properly by $C_M[E_n]$.

Now let us define the matrix E_j by

$$E_j = [\omega_j^{\times} V^T + D + \omega_j V]. \qquad (22)$$

It is evident that

(i) E_j is hermitian;

(ii) E_j has an even number of complex elements;

(iii) the maximal number of complex elements of E_j equals $2l$, since $|K^V| = l$;

(iv) E_j is a (real) symmetric matrix if and only if $V = V^T$.

The reduced eigenvalue problem (21) may be rewritten now as follows

$$E_j \cdot c_\mu^j = 0. \qquad (23)$$

This demands that the determinant of E_j has zero value:

$$\det E_j = E_j = |E_{rs}^j| = 0. \qquad (24)$$

For the sake of clarity in what follows we summarize the non-zero elements of E_j. By dropping the supposition $U_1^J \bigcap U_2^J = \phi$ introduced in the text following (3), we obtain:

(i) diagonal elements: $E_{rr}^j =$

$$= x \qquad \text{if } U_r^J \notin (U_1^J \bigcap U_2^J);$$
$$= x + z_j \quad \text{if } U_r^J \in (U_1^J \bigcap U_2^J);$$

(ii) off diagonal elements: $E^{j}_{rs} =$

$$
\begin{aligned}
&= 1 && \text{if } \{U^J_r, U^J_s\} \in G_J;\\
&= \omega_j && \text{if } \{U^J_r, U^{J+1}_s\} \in K^J_v;\\
&= \omega_j^{::} && \text{if } \{U^{J-1}_r, U^J_s\} \in K^{J-1}_v;\\
&= z_j && \text{if } \{U^{J-1}_r, U^J_s\} \in K^{J-1}_v \wedge \{U^J_r, U^{J+1}_s\} \in K^J_v;\\
&= 1+\omega_j && \text{if } \{U^J_r, U^J_s\} \in G_J \wedge \{U^J_r, U^{J+1}_s\} \in K^J_v;\\
&= 1+\omega_j^{::} && \text{if } \{U^J_r, U^J_s\} \in G_J \wedge \{U^{J-1}_r, U^J_s\} \in K^{J-1}_v;\\
&= 1+z_j && \text{if } \{U^J_r, U^J_s\} \in G_J \wedge \{U^{J-1}_r, U^J_s\} \in K^{J-1}_v \wedge \{U^J_r, U^{J+1}_s\} \in K^J_v.
\end{aligned}
$$

wherein z_j stands for $z_j = \omega_j + \omega_j^{::} = 2\cos\delta_j$ with $\delta_j = 2j\pi/M$.

Concerning (24) we may state the following

Proposition 4: The expansion of $E_j = 0$ leads to a polynominal, $E(x,\delta_j)$ in x of degree n with real coefficients, $A_\nu(\cos\delta_j)$, as follows:

$$E_j = E(x,\delta_j) = \sum_{\nu=0}^{n} A_\nu(\cos\delta_j) \cdot x^\nu = 0. \qquad (25)$$

The coefficients $A_\nu(\cos\delta_j)$ represent polynominals in $2\cos\delta_j$ of maximal degree l with integral coefficients, $B_{\nu\lambda}$, as follows:

$$A_\nu(\cos\delta_j) = \sum_{\lambda=0}^{h_\nu} B_{\nu\lambda}\cdot(2\cos\delta_j)^\lambda; \quad h \leqq \min(n-\nu,l) \qquad (26)$$

Proof: (i) Because the diagonal elements, E^j_{rr}, equal either x or $(x + 2\cos\delta_j)$ it is obvious that $E(x,\delta_j)$ represents a polynomial in x of degree n. - (ii) Since E_j is hermitian the coefficients of this polynomial, A_ν, have to be real. Therefore their dependence upon δ_j is expressed by the real argument $\cos\delta_j$, but not by the complex ones, ω_j and ω_j^*. - (iii) Since $|K^\nu| = 1$, E_j has maximal l pairs of complex conjugated elements, $E^j_{rs} = E^{j*}_{sr}$. Therefore the exponent of the highest power of ω_j and ω_j^* respectively, occurring in the expansion of E_j, cannot exceed the value of l; (in this the sums $\omega^g + \omega^{*g} = 2\cos g\delta_j$ obtained directly are transformed into polynomials in $\cos\delta_j$ of degree g). - (iv) The factor of x^ν in (25) represents a sum to which all the possible products of $(n-\nu)$ off-diagonal elements contribute. If $E^j_{rr} = x$ for all r, these are the sole contributions to $A_\nu(\cos\delta)$; however, if some of the diagonal elements are given by $E^j_{ss} = (x + 2\cos\delta_j)$, contributions of the type $(2\cos\delta)^\mu$ times all the possible products of $(n-\nu-\mu)$ of diagonal elements also occur. In no case the exponent, λ, of $(2\cos\delta_j)^\lambda$ in (26) exceed $(n-\nu)$. Therefore: $\lambda \leqq \min(n-\nu,l)$. - (v) If in the product of the off-

diagonal elements the factor $\omega_j \overset{\ast\ast}{\omega}_j = 1$ occurs, λ cannot reach that maximal value. Therefore the summation in (26) runs actually up to $h_\nu \leqq \min\,(n-\nu, l)$. - (vi) Apart from x, ω_j and $\overset{\ast\ast}{\omega}_j$, the elements of E_j consists of integers only; consequently the $B_{\nu\lambda}$ are integers also.

It should be noted that $E(x,\delta_j)$ is a function of a single variable, x, whilst δ_j plays the rôle of a discrete parameter referring to the irreducible representation Γ_j of $\mathcal{C}_M$. The n roots of (25) represent the eigenvalues, $x_\nu^j = x_\nu\,(\cos\delta_j)$, of (23). Upon inserting them into (23) the eigenvectors c_j are obtained. Thus the eigenfunctions, ψ_μ^j, are given by

$$\psi_\mu^j = \sum_{\gamma=1}^{n} c_{r\mu}^j \phi_r^j; \qquad (27)$$

$$\phi_r^j = \frac{1}{\sqrt{M}} \sum_{J=1}^{M} \omega_j^{J-1} \phi_r^J;$$

where ϕ_r^J stands for the orthonormal basic function correlated to the vertex $U_r^J \in G_j$ whilst ϕ_r^j represents one of the symmetry adapted functions belonging to the irreducible presentation Γ_j of $\mathcal{C}_M$. There is no need for any specification concerning the basis functions ϕ_r^J; but in what

follows it is assumed that the ϕ_r^J are real orthonormal functions.

Proposition 5: If $j \neq 0$ and $j \neq M/2$ the eigenfunctions ψ_μ^j and $\psi_\mu^{(M-j)}$ are degenerate each other pairwise, that is :

$$\psi_\mu^{(M-j)} = \psi_\mu^{j*}, \qquad (28)$$

$$x_\mu^{(M-j)} = x_\mu^j.$$

$\psi_\mu^{(M-j)}$ and $x_\mu^{(M-j)}$ are abbreviated by $\psi_\mu^{\bar{j}}$ and $x_\mu^{\bar{j}}$ respectively.

Proof: (i) From the definition of ω_j it follows that $\omega_{(M-j)} = \omega_j^*$. Since the basis functions are assumed to be real, therefore the equality holds

$$\phi_r^{(M-j)} = \phi_r^{j*}.$$

(ii) As a consequence of this, $E_{(M-j)} = E_j^*$ and hence, from (23) it follows that

$$c_{(M-j)} = c_j^*.$$

(iii) Upon inserting these results into (27) $\psi_\mu^{(M-j)} = \psi_\mu^{j*}$ is immediately obtained. - (iv) Since $x_\mu^j = x_\mu(\cos\delta_j)$ and $\cos\delta_j = \cos\delta_{M-j}$ the other equality in (28) follows at once.

(5) Eigenvalues of the infinite rotagraph $R(G,\infty,K^V)$ - Band structure and density of eigenvalues

As pointed out above, $\delta_j = 2j\pi/M$ represents a discrete parameter referring to $\Gamma_j \in C_M$. Consequently the difference $(\delta_{j+1}-\delta_j) = 2\pi/M$ is non-zero. However, if M tends to become infinite, this difference tends to zero

$$\lim_{M\to\infty} (\delta_{j+1}-\delta_j) = \lim_{M\to\infty} \frac{2\pi}{M} = 0. \qquad (29)$$

This means δ_j is no longer a discrete parameter but a continuous variable within the range $0 \leq \delta < 2\pi$. In the same way as δ_j refers to $\Gamma_j \in C_M$ any distinct value of δ refers to exactly one distinct irreducible representation $\Gamma(\delta) \in C_\infty$.

The form of (25) is not altered by $M\to\infty$ but $E(x,\delta) = 0$ represents now an implicite function of the two variables x and δ. When interpreted as a polynomial in x of degree n

with real coefficients which are continous functions of $\cos\delta$, $E(x,\delta) = 0$ produces for each value of δ a set of n roots depending on δ, $\{x_r^\delta = x_r(\cos\delta) \,|\, r\in n\}$, which belongs to $\Gamma(\delta)\in C_\infty$. Therein the indices are used such, that $x_r^\delta < x_{r+1}^\delta$ for all $r\in n$. A differential increase of δ, say from δ to $(\delta+d\delta)$, causes a differential change of the roots, say from x_r^δ to $(x_r^\delta+dx_r^\delta)$; the set of these roots belong to $\Gamma(\delta+d\delta)\in C_\infty$.

Let us consider now what happens to the root x_r^δ if δ runs continuously over the whole intervall $0\leqq\delta<2\pi$: The set $\{x_r^\delta=x_r(\cos\delta) \,|\, 0\leqq\delta<2\pi\}$ forms a continuous band of eigenvalues. It is obvious that each eigenvalue of this band corresponds to another irreducible representation $\Gamma(\delta)\in C_\infty$. Therefore each irreducible representation $\Gamma(\delta)\in C_\infty$ contributes exactly one eigenvalue to the band. Since $r\in n$ a total of n such bands are formed. These results are summarized to

Proposition 6: The spectrum of the eigenvalues of the infinite rotagraph $R(G,\infty,K^V)$ consists of n continous bands

$$\{\{x_r^\delta = x_r(\cos\delta) \;|\; 0\leqq\delta<2\pi\} \,|\, r\in n\}. \qquad (30)$$

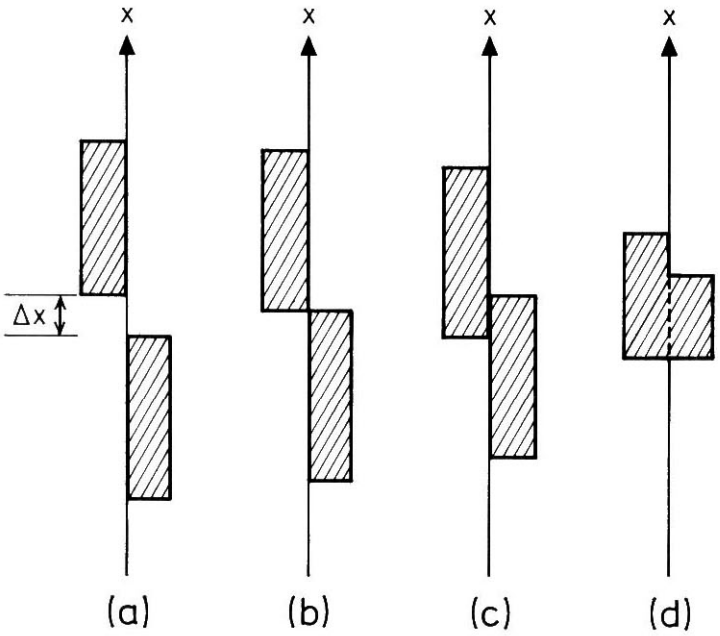


Figure 2: Continuous bands of eigenvalues: (a) well separated by a gap $\Delta x>0$; (b) mutually adjoint each other; (c) overlapping each other; (d) self overlapping of a single band.

Each eigenvalue of such a band belongs to a different irreducible representation of C_∞ and vice versa each irreducible representation of C_∞ contributes exactly one eigenvalue to each band.

In the band structure of the spectrum some typical details may appear which are sketched in figure 2: A pair of bands may be well separated by a *forbidden zone* or a *gap*, $\Delta x>0$ (a); two bands may be *mutually adjoined* to each other (b) or may *overlap* each other (c); the bands may be either *smooth* (a,b,c) or they may show *self-overlapping* (d). A wide variety of band patterns arises from the combination of these elements. In this section we will draw attention to the origins of these details.

Alternative to the interpretation of $E(x,\delta)$ as a polynomial in x it may be understood also as a polynomial in $(2\cos\delta)$ with real coefficients which are functions of x, say $f_\lambda(x)$. Both these alternatives are expressed as follows:

$$E(x,\delta) = \sum_{\nu=0}^{n} A_\nu(\cos\delta)\cdot x^\nu = \sum_{\lambda=0}^{h} f_\lambda(x)\cdot(2\cos\delta)^\lambda = 0;$$

$$A_\nu(\cos\delta) = \sum_{\lambda=0}^{h_\nu} B_{\nu\lambda}\cdot(2\cos\delta)^\lambda; \quad f_\lambda(x) = \sum_{\nu=0}^{n-\lambda} B_{\nu\lambda}\cdot x^\nu; \qquad (31)$$

$$h = \max(\{h_\nu\}) \leq 1.$$

By solving $E(x,\delta) = 0$ in respect to $(2\cos\delta)$ one obtains h roots denoted as follows:

$$2\cos\delta_s = \Theta_s(x); \qquad s\in\{1,2,\ldots,h\} \tag{32}$$

Due to the properties of $2\cos\delta$, $\Theta_s(x)$ has to be real and its absolute numerical value must not exceed the number 2. This means

$$\begin{aligned} &Im\,[\Theta_s(x)] = 0, \\ &-2 \leqq \Theta_s(x) \leqq +2. \end{aligned} \tag{33}$$

Suppose at $x = x_1$ as well as at $x = x_2 > x_1$ there is at least one function $\Theta_s(x)$ accomplishing (33), but in the open range $x_1 < x < x_2$ one of the conditions (33) or both are failed for all $s\in\{1,2,\ldots,h\}$. No eigenvalue x_1^{δ} belonging to a band can then be realized within this range. Consequently the range $x_1 < x < x_2$ represents a *forbidden zone* of eigenvalues. Therefore we may state in

Proposition 7: A forbidden zone of eigenvalues, $\Delta x = x_2 - x_1$, appears if for each value of x within the open range $x_1 < x < x_2$ all the functions $\Theta_s(x)\,|\,s\in\{1, 2,\ldots,h\}$ do not satisfy the condition (33).

Suppose, for a given value $x = x_k$ all the h functions $0_s(x)|s\in\{1,2,\ldots,h\}$ satisfy (33). Then x_k corresponds with h distinct values of $2\cos\delta_s|s\in\{1,2,\ldots,h\}$. Because the range of δ is given by $0\leqq\delta<2\pi$ but $\cos\delta$ is uniquely determined only within the range $0\leqq\delta<\pi$, x_k corresponds with $2h$ distinct values of δ, which may be ordered to h pairs $\{\delta,2\pi-\delta\}$ or more briefly indicated by $\{\delta, -\delta\}$. We therefore may state

Proposition 8: The maximal multiplicity (degeneracy) of eigenvalues occurring in the band spectrum of the infinite rotagraph is given by $2h \leqq 2l$; h being defined in (31).

The both eigenvalues, $x_k = x_k(\cos\delta_s)$ and $x_{\bar{k}} = x_k(\cos(-\delta_s))$, are indeed equal but they belong to the different irreducible representations $\Gamma(\delta_s)$ and $\Gamma(-\delta_s)$ respectively. Except when $\delta=0$ and $\delta=\pi$ all the other values of δ have a pair of irreducible representations, $\Gamma(\delta)$ and $\Gamma(-\delta)$, the eigenvalues of which are degenerate. This leads to the intermediate

Conclusion 1: Each band $\{x_r^\delta|0\leqq\delta<2\pi\}$ consists of two

single eigenvalues, x_r^0 and x_r^π, and an infinite number of pairs of doubly degenerated eigenvalues, $x_r^\delta = x_r^{-\delta}$.

Before going ahead it should be noted in which way the topological parameters, n, l and M, of the rotagraph determine its spectrum of eigenvalues: the number of bands is given by n, the cardinality of the vertex set U_J; the cardinality, l, of the edge set K_J^ν bounds the maximal multiplicity; the number of eigenvalues within a band equals, M, the number of monomeric units forming R.

We now treat the question if within a band there are extremal eigenvalues. For that purpose we have to consider $dx/d\delta = -(\partial E/\partial\delta)/(\partial E/\partial x) = 0$. From (31) one obtains

$$\frac{dx}{d\delta} = \frac{2\sin\delta \cdot \sum (\lambda \cdot f_\lambda(x)) \cdot (2\cos\delta)^{\lambda-1}}{\sum (df_\lambda(x)/dx) \cdot (2\cos\delta)^{\lambda}} = 0 \qquad (34)$$

Since the denominator of this fraction is finite for finite x, (34) requires

$$\sin\delta \cdot \sum_{\lambda=0}^{n} (\lambda \cdot f_\lambda(x)) \cdot (2\cos\delta)^{\lambda-1} = 0. \qquad (35)$$

From the first factor of (35), $\sin\delta=0$, one obtains two sets of extremal eigenvalues, namely

$$\{x_r^0 | r\in n\}\in \Gamma(0), \qquad (36)$$
$$\{x_r^\pi | r\in n\}\in \Gamma(\pi).$$

These are the single eigenvalues mentioned in conclusion 1. Since they are extremal eigenvalues corresponding with the bounds of $\cos 0 \geqq \cos\delta \geqq \cos\pi$ we call them the *natural bounds of the bands*.

The other factor of (35) represents an algebraic equation in $(2\cos\delta)$ of degree $(h-1)$:

$$\sum_{\lambda=0}^{h} (\lambda \cdot f_\lambda(x)) \cdot (2\cos\delta)^{\lambda-1} = 0.$$

Solving this equation one obtains $(h-1)$ functions

$$2\cos\delta_t^{extr} = \Theta_t'(x), \qquad (37)$$

corresponding generally with extremal eigenvalues $x(\cos\delta_t^{extr})$. Certainly these eigenvalues are realized only if $\Theta_t'(x)$ attain the conditions given in (33) for $\Theta(x)$.

Proposition 9: Self-overlapping of a band take place if at least one extremal eigenvalue, $x_r(\cos\delta_t^{extr})$, belongs to the band which lies outside the interval determined by the natural bounds of the band considered.

Proof: (i) Suppose there exist only one extremal eigenvalue, x_r^δ, related to the natural bounds as follows: $x_r^o < x_r^\delta < x_r^\pi$. As a consequence of the continuity within the band as well as of the fact that $dx/d\delta = 0$ as $x = x_r^o$, $x = x_r^\delta$, and $x = x_r^\pi$, no overlapping can take place and a smooth band (fig. 3a) results. - (ii) But if the relation is given by $x_r^\delta < x_r^o < x_r^\pi$, the same arguments leads to a self overlapping band (fig. 3b).- (iii) These results can be generalized as in proposition 9.

If in the band $\{x_r^\delta | 0 \leq \delta < 2\pi\}$ there are h_r extremal eigenvalues corresponding neither to $\delta=0$ nor $\delta=\pi$, i.e.: $\{x_r^\delta = x_r(\cos\delta_{extr}) | \delta_{extr} \neq 0,\pi\}$, then obviously the highest multiplicity which may occur in the band is given by $2h_r$. We call h_r the order of the self-overlapping of band r. The upper and the lower bound of a self-overlapping band need not to coincide with the natural bounds of the band; they are given by $\sup\{x_r^\delta\}$ and $\inf\{x_r^\delta\}$ respectively.

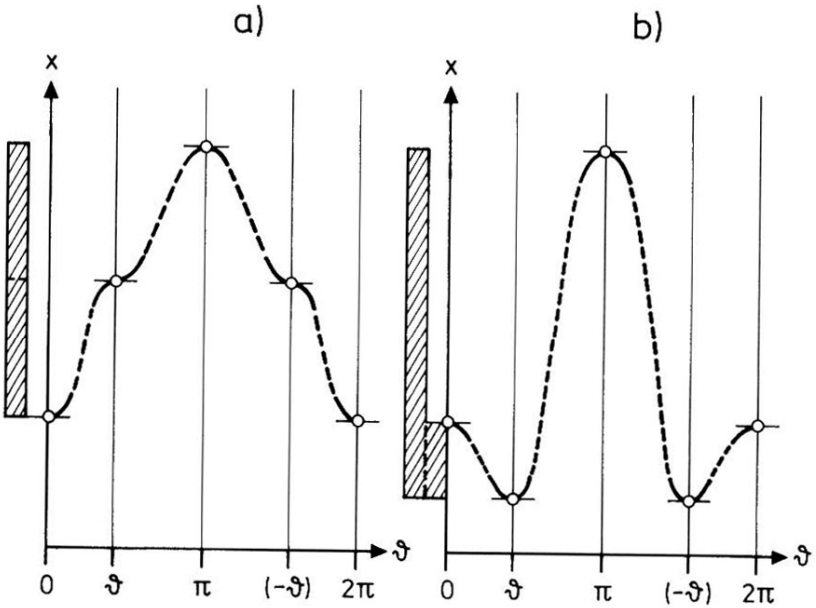


Figure 3: Illustration to proposition 9 concerning the self overlapping of bands (see text).

Turning now to the condition under which bands become mutually adjoined we recall that the indices of the bands, $r \in n$, are used such that the relation $x_r^\delta < x_{r+1}^\delta$ holds for all $r \in n$ and all values of δ.

Proposition 10: The bands $\{x_r^\delta | 0 \leq \delta < 2\pi\}$ and $\{x_s^\delta | 0 \leq \delta < 2\pi\}$, $r \neq s$, are mutually adjoined to each other if the union of the natural bounds, i.e.: $\{x_r^o | r \in n\} \bigcup \{x_r^\pi | r \in n\}$, contains a pair of degenerate eigenvalues with different indices, $r \neq s$.

Corollary: If the automorphism group of $R(G, \infty, K^V)$ is properly described by $C_\infty[\mathcal{B}_n]$, where $\mathcal{B}_n \supseteq E_n$ is a permutation group operating on the vertices of the monomeric unit, then the degenerate eigenvalues belong to different irreducible representations, i.e.: $x_r^o = x_s^\pi$.

Proof: (i) The indices of the degenerate eigenvalues must be different, because $x_r^o = x_r^\pi$ indicates either an infinite sharp band, $x_r^o = x_r^\delta = x_r^\pi$ for all values of δ, or an self-overlapping band (like fig. 3b with $x_r^o = x_r^\pi$). - (ii) Since $\Gamma(0) \in C_\infty$ is a one-dimensional representation no degeneracy occurs in the set of its eigenvalues $\{x_r^o | r \in n\}$. The same is true for $\Gamma(\pi) \in C_\infty$ and $\{x_r^\pi | r \in n\}$. Therefore in the case of $A(R) = C_\infty[\mathcal{B}_n]$ the degeneracy must occur

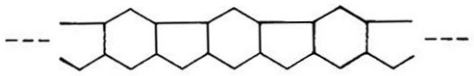
between these two sets expressed by $x_r^0 = x_s^\pi$. - (iii) But in the case that $A(R)$ maps the indices $J \in M$ as $\mathcal{D}_\infty$, each representation $\Gamma(\delta) \in C_\infty$ is split into two representations, say $\Gamma_1(\delta) \in \mathcal{D}_\infty$ and $\Gamma_2(\delta) \in \mathcal{D}_\infty$. Although the eigenvalues of these representations are not degenerate within its representation, degeneracy between the two sets may occur. Therefore the condition $x_r^0 = x_s^\pi$ holds only in the case that $A(R)$ exhibits no higher symmetry as indicated by $C_\infty[\mathcal{B}_n]$.

Proposition 11: If the automorphism group of the infinite rotagraph is properly given by $A(R) = C_\infty[\mathcal{B}_n]$ no crossing of bands can occur.

Proof: (i) If the bands r and s cross each other there would be at least one value of δ for which $x_r^\delta = x_s^\delta$ would hold. Because both eigenvalues belong to the same one-dimensional representation, $\Gamma(\delta)$, the relation $x_r^\delta = x_s^\delta$ stands in contradiction to the group-theoretical theorem that the eigenvalues of a one-dimensional representation are non degenerate. - (ii) Therefore we have $x_r^\delta \neq x_s^\delta$ for all $\delta \in [0, 2\pi)$ indicating the non-crossing of the bands r and s.

The band structure may be represented graphically

in one of the two ways sketched in fig. 4a and b for the polymer [5]



(38)

for which n=7 and l=2. $E(x,\delta)$ is quadratic in $(2\cos\delta)$ and of degree 7 in x. In fig. 4a all the bounds of the bands are marked and self overlapping is indicated by drawing the overlapping parts of the bands side by side. Fig. 4b is a drawing of $E(x,\delta)=0$ in the $(x-\delta)$-plane; the range of δ is shortened to $0\leq\delta\leq\pi$ in fig. 4b, taking into account the symmetry caused by $E(x,\delta)=$ $=E(x,(2\pi-\delta))$. Since fig. 4b illustrates the slope $dx/d\delta$ it is also more informative than fig. 4a; the latter may be understood as a projection of the curves of fig. 4b onto the x-axis. Further in fig. 4b the function δ_{extr} = $= \delta_{extr}(x)$ corresponding to (37) is drawn also.

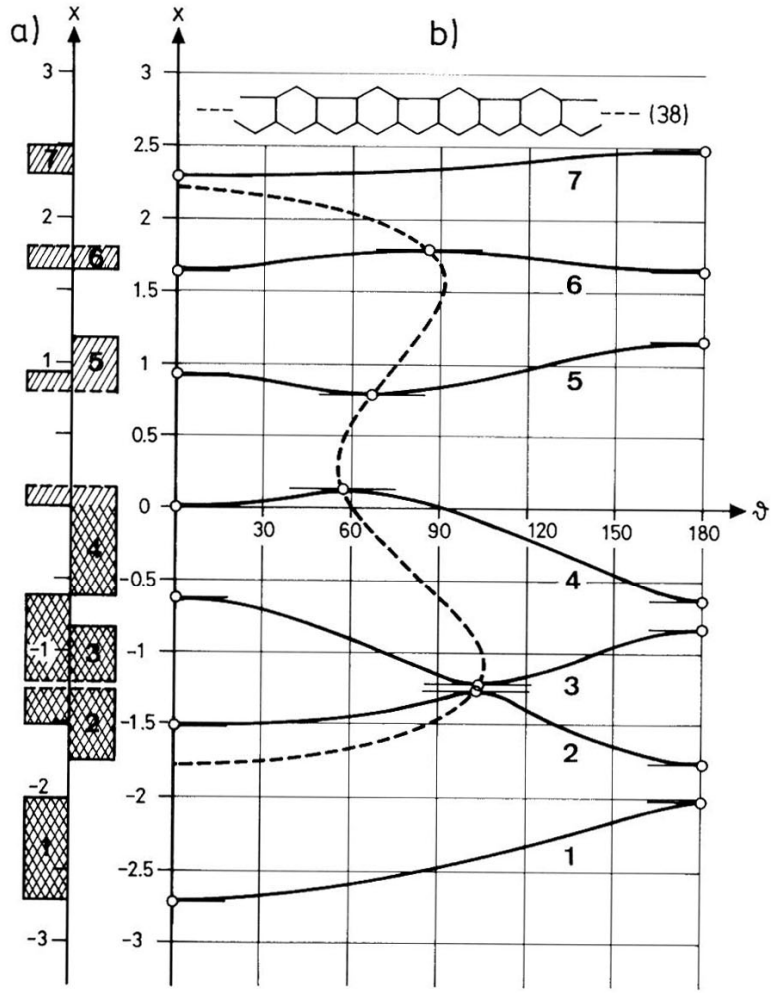


Figure 4: Band structure of the infinite polymer (38).

a) ▨ empty bands; ▩ full bands; —— natural bounds; ---- other bounds.

b) —— bands; .... δ_{extr}.

Band numbers are indicated by r. Please note: the bands 3 and 4 are annexed; all bands beside band 1 and 7 are self overlapping.

It should be noted that for the infinite polymer (38) the automorphism group is properly described by $A(R)=C_{\infty}[E_7]$. Therefore no crossing of bands can occur according to proposition 10. The gap between the bands 2 and 3 may be understood group theoretically as a consequence of the non-crossing rule; from the stand point of (33) it is produced by the complexity of $\theta(x)$ within the forebidden zone. It is to be supposed that all the forbiiden zones produced by $Im[\theta(x)]\neq 0$ satisfy the demands arising from the non-crossing rule.

We now discuss briefly the density of the eigenvalues, $\rho_r(x)$, within a band r. From the definition of δ_j for finite M, $\delta_j=2j\pi/M$, and (29) in case of $M\to\infty$, it follows immediately that a differential increase of δ, $d\delta$, causes a differential increase of the number, N, of eigenvalues, dN, which has to be proportional to $d\delta$; hence:

$$dN = k_r \cdot d\delta.$$

These dN eigenvalues form an interval dx within a band, say within the band r. Then we obtain:

$$dN = \rho_r(x) \cdot dx \qquad (39)$$

and eliminating dN, the density of eigenvalues in the band r results to be the following function of x

$$\rho_r(x) = k_r \cdot \frac{d\delta}{dx} \quad . \qquad (40)$$

The expression of the reciprocal of $(d\delta/dx)$ is given by (34). The value of k_r is determined such that the integral over each band results in the same number of eigenvalues within the band. For a finite rotagraph this number equals M.

The proportionality (39) attempts to indicate which eigenvalues are occupied within a partially filled band. Let us take the HMO approximation for the polymer (38) as an example. Because each monomeric unit contributes 7 π-electrons, the bands 1, 2 and 3 will be full but half of the band 4 will be empty. From fig. 4b and (39) one may conclude that the subset $\{x_4^\delta \mid \pi/2 \leq \delta < 3\pi/2\}$ represents the occupied levels of that band but the subset $\{x_4^\delta \mid 0 \leq \delta < \pi/2;\ 3\pi/2 \leq \delta < 2\pi\}$ the empty ones. Therefore the occupation indicated in fig. 4a results. It should just mentioned that due to partial filling of band 4 the polymer (38) should exhibit conductivity [6].

(6) Eigenvalues and eigenfunctions of the fascia graph $F(G,M,K^V)$

The adjacency matrix F of the fasciagraph $\bar{F}$ consists of $M \times M$ quadratic blocks of size $n \times n$ each:

$$
\begin{aligned}
F &= (F_{JK}) \mid J, K \in M \\
F_{JK} =: &= G \qquad \text{if } K = J \\
&= V \qquad \text{if } K = (J+1) \leqq M \\
&= V^T \qquad \text{if } K = (J-1) \geqq 1
\end{aligned}
\tag{41}
$$

G and V having the same meaning as in (16). Hence, the adjacency matrices of these two polymer graphs differ only in two blocks:
We have now

$$F_{1M} = F_{M1} = O$$

whilst

$$R_{1M} = V^T; \quad R_{M1} = V.$$

Let us define this difference by

$$
\begin{aligned}
&F - R = H^{(1)} = (H^{(1)}_{JK}) \\
&H^{(1)}_{1M} = -V^T; \quad H^{(1)}_{M1} = -V \\
&H^{(1)}_{JK} = O \ \ldots \text{ otherwise.}
\end{aligned}
\tag{42}
$$

The eigenvalue problem of F may be formulated analogously to (17) as follows

$$(F+yI)\cdot C_\mu^j = H^F\cdot C_\mu^j = 0,\ \forall\ j \in M \qquad (\underline{\underline{43}})$$

y_μ^j and C_μ^j having a similar meaning as in (17). Splitting C again into M blocks, C_j, each of the dimmension $(nM)xn$ and consisting of the n eigenvectors $C_\mu^j|\mu\epsilon n$, one obtains

$$\begin{aligned} C &= (C_j\ C_2\ \ldots\ C_j\ \ldots\ C_M), \\ C_j &= (C_1^j\ C_2^j\ \ldots\ C_\mu^j\ \ldots\ C_n^j). \end{aligned} \qquad (\underline{\underline{44}})$$

It should be noted that the C of (19) and (44) are different. From (42) it is seen that (43) may be written as

$$H^F\cdot C_\mu^j = (H^R + H^{(1)})\cdot C_\mu^j = H^R\cdot C_\mu^j + H^{(1)}\cdot C_\mu^j = 0. \qquad (\underline{\underline{45}})$$

In the case that (43) cannot be directly solved a perturbational treatment is offered in (45) in which $H^R\cdot C_\mu^j = 0$ represents the unperturbed system solved in both the foregoing sections and $H^{(1)}$ is the perturbation operating on it. This offer is taken up in Appendix 1.

At first we discuss the direct solution of (43) and state the

Proposition 12: If H^F is a real symmetric matrix due to $V = V^T$, the eigenvectors C_j are of the form

$$C_\mu^j = \begin{pmatrix} \sin\delta_j \cdot c_\mu^j \\ \sin 2\delta_j \cdot c_\mu^j \\ \cdot \\ \cdot \\ \cdot \\ \sin M\delta_j \cdot c_\mu^j \end{pmatrix} \qquad (\underline{\underline{46}})$$

wherein c_μ^j is a column matrix consisting of n elements and $\delta_j = j\pi/(M+1)$. It should be noted that δ_j in this case differs from that the in case of R. The eigenvalues $\{y_r^j = y_r(\cos\delta_j) \mid r \in n\}$ and the square matrix $c_j = (c_1^j\ c_2^j \ \ldots\ c_\mu^j \ \ldots\ c_n^j)$ are determined by

$$\det|D + 2V \cdot \cos\delta_j| = 0. \qquad (\underline{\underline{47}})$$

Proof: (i) From (43) using the J-th row of H^F one obtains

$$[V^T \cdot \sin(J-1)\delta_j + D \cdot \sin J\delta_j + V \cdot \sin(J+1)\delta_j]\, c_\mu^j = 0.$$

Using the expansion theorem

$$\sin(J \pm 1)\delta_j = \sin J\delta_j \cdot \cos\delta_j \pm \cos J\delta_j \cdot \sin\delta_j$$

this leads to

$$\{\sin J\delta_j[D+(V^T+V)\cos\delta_j] - \cos J\delta_j[V^T - V]\sin\delta_j\}\cdot c_\mu^j = 0.$$

If $V=V^T$ as supposed, this gives

$$\sin J\delta_j\cdot[D + 2V\cdot\cos\delta_j]\cdot c_\mu^j = 0$$

and finally - because $\sin J\delta_j \neq 0$ - one obtains

$$[D + 2V\cdot\cos\delta_j]\cdot c_\mu^j = 0. \qquad (48)$$

Because (48) does not depend on the row index it should be true for each row $J\in M$. - (ii) Although in the first and in the last row of H^F there are only blocks different from zero, (48) is obtained from these rows also, because the respective equations may be completed by $\sin(1-1)\delta_j\cdot V^T\cdot c_\mu^j$ in the case of $J=1$ and by $\sin(M+1)\delta_j\cdot V\cdot c_\mu^j$ in the case of $J=M$. - (iii) From (48) it immediately follows that the eigenvalues and the square matrix c_j is determined by (47).

In the case $V = V^T$ considered here, the eigenfunctions χ_μ^j, are given by

$$\chi_{\mu}^{j} = \sum_{r=1}^{n} c_{r\mu}^{j} \, \phi_{r}^{j}; \qquad (49)$$

$$\phi_{r}^{j} = \sqrt{\frac{2}{M+1}} \sum_{J=1}^{M} \phi_{r}^{J} \cdot \sin J\delta_{j}$$

Unfortunately the structural requirements of $V=V^{T}$ are only satisfied very rarely by polymers. Therefore in nearly all cases of fasciagraphs one has either to solve the $(nM)x(nM)$ problem (43) or to use the perturbational treatment offered by (45). For the direct solution of (43) there is no generalisation possible if $V \neq V^{T}$; hence, we cannot discuss this case further. Using the Rayleigh-Schrödering-formalism of perturbation theory [7] the utilisation of (45) is briefly outlined in appendix 1. The perturbational expansions of the eigenvalues, $-y_{\mu}^{j}$, and the eigenfunctions, χ_{μ}^{j}, of the fasciagraph $F(G,M,K^{V})$ are given in table (A:1); in the last section of the appendix they are discussed briefly. From (A:29) it is shown that the corresponding infinite graphs, $F(G,\infty,K^{V})$ and $R(G,\infty,K)$ have congruent spectra. This and some other details discussed in the last section of the appendix leads to the following

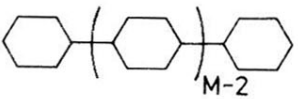
Supposition 1: If the internal automorphic mapping, $G_{J} \longleftrightarrow G_{J}$, is congruous for terminal monomeric units

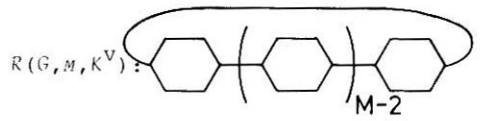
(J=1,M) and the non-terminal ones, then the eigenvalues of $F(G,M,K^V)$ lie within the bands of $R(G,\infty,K^V)$; if the terminal monomeric units, G_1 and G_M, exhibit some further internal automorphic mapping not feasible for the non-terminal units, some eigenvalues of $F(G,M,K^V)$ could lie between the bands of $R(G,\infty,K^V)$. It is supposed that the number of those eigenvalues does not exceed the number of additional automorphisms induced by the terminal groups.

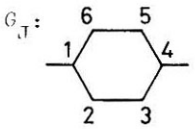
Comment: The additional automorphisms induced by the terminal monomeric units may cause some irreducible representations in $A(F)$ which have no correspondence in $A(R)$. Eigenvalues belonging to these representations need not lie within the bands of $R(G,\infty,K^V)$. Because each additional automorphism can generate only one additional representation at most the number of eigenvalues lying within the gaps of $R(G,\infty,K^V)$ cannot exceed the number of additional automorphisms.

The example of p- and m-polyphenyls may illustrate supposition 1. In the case of p-polyphenyls

$F(G,M,K^V)$:







the internal automorphism consists of the two permutations

$$\begin{pmatrix}1&2&3&4&5&6\\1&2&3&4&5&6\end{pmatrix}, \begin{pmatrix}1&2&3&4&5&6\\1&6&5&4&3&2\end{pmatrix}$$

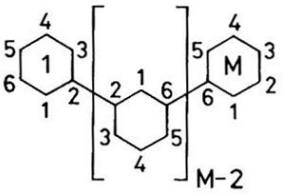
They are feasible in each monomeric unit, G_J, of $F(G,M,K^V)$ and $R(G,M,K^V)$. Therefore the automorphism group of F is a subgroup of that of R

$$A(F(G,M,K^V)) \subset A(R(G,M,K^V))$$

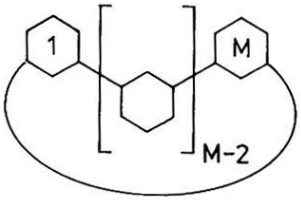
and the eigenvalues of F should lie within the bands of $R(G,\infty,K^V)$. Fig. 5a confirms that for M = 2,3,...,10.

However, in the case of m-polyphenyls

$F(G,M,K^V)$:



$R(G,M,K^V)$:



the terminal units, G_1 and G_M, of the fasciagraph exhibit an internal automorphic mapping, that is

$$\begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 3 & 2 & 1 & 6 & 5 & 4 \end{pmatrix} \qquad (5\underline{\underline{Q}})$$

which is feasible neither in the non-terminal units of F nor in any unit of R. The representations induced by this permutation in $A(F)$ have no correspondence in $A(R)$ therefore $A(F)$ is not a subgroup of $A(R)$. This permutation generates the following eigenvalues and eigenfunctions:

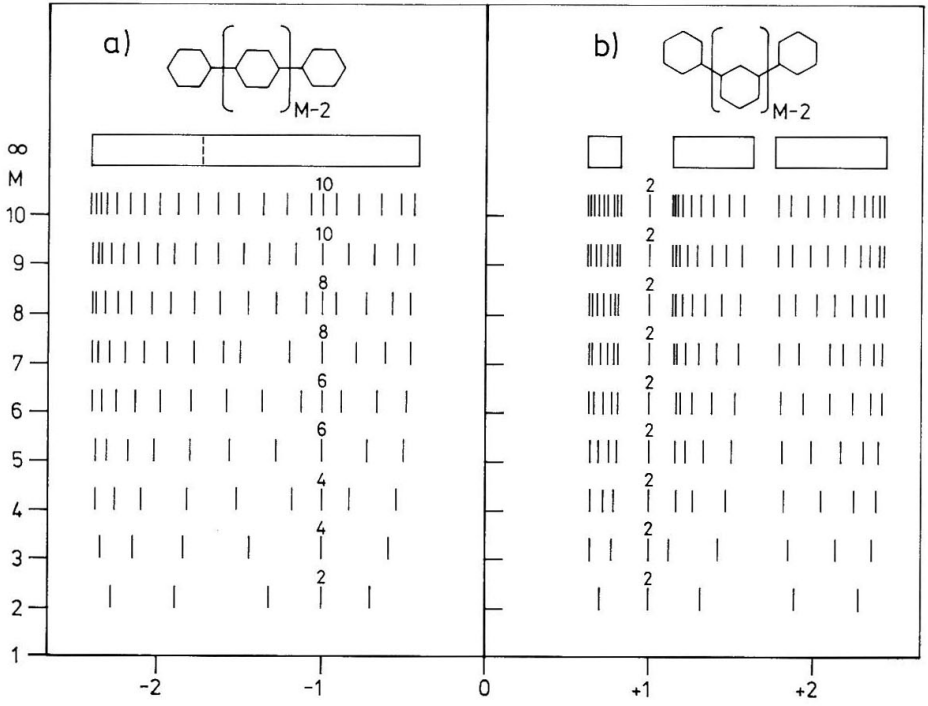


Figure 5: Eigenvalues of oligo-p-phenyls (a) and oligo-m-phenyls (b), M = 1,2,3,...,10, and the band spectra of the corresponding rotagraphs (only the half of the respective spectra are shown, which are symmetric in respect to x=0.

y	x
-1	$\frac{1}{2}\ (\phi^1_1-\phi^1_3-\phi^1_4+\phi^1_6)$
+1	$\frac{1}{2}\ (\phi^1_1-\phi^1_3+\phi^1_4-\phi^1_6)$
-1	$\frac{1}{2}\ (\phi^M_1-\phi^M_3-\phi^M_4+\phi^M_6)$
+1	$\frac{1}{2}\ (\phi^M_1-\phi^M_3+\phi^M_4-\phi^N_6)$

These have no correspondence to the eigenvalues and eigenfunctions of R. As fig. 5b confirms, they lie within the forbidden zones of $R(G,\infty,K^V)$.

(7) Discussion

(7.1) The band structure of the eigenvalues of infinite polymers presented in this paper assumes physical significance if the topological results are identified as those produced by means of a one-electron Hamiltonian; but then the occupation of the bands with maximal $2M$ electron has to be taken into account. If there is a forebidden zone between the fully occupied bands and the empty ones, the material should behave as an insulator or semiconductor. But the gaps are determined by three factors representing the topology, the geometry, and the electron correlation [8-12]. In this paper we have discussed only the topological

factor. However, the geometric factor can be handled in exactly the same way if the topologically unweighted graph is replaced by an appropriately weighted one [13-16]. The results obtained in either of these two ways may be used for the estimation of the electron correlation independent of the method. Therefore, in spite of the restriction to topological considerations, the results reported here have a broader significance. As a consequence of its transparency the procedure outlined here allows some interesting new insights.

(7.2) However, an unsolved problem concerns the ways in which the existence of gaps in the band spectra of infinite rotagraphs depends on the internal structure of the monomeric unit, G, and the edge set K^V. Sufficient but not necessary structural conditions to cause such a gap are given in another paper [17]. Of course, if for a given structure the implicit function, $E(x,\delta)=0$, of (31) is evaluated, it is readily proved from (33) whether there is a forbidden zone at $x=0$ or not.

(7.3) In (33) the origins of the appearance of forbidden zones are given. It is obvious that (33) retains its significance if the geometric factor is taken into account by starting from a weighted graph. However, the consideration of the electronic correlation

will also lead to an implicit function, like $E(x,\delta)=0$ in (31), if the eigenvectors depend on the characters of the irreducible representation of $C_{M;}$ under this condition the statements of (33) are independent of the methods used. Perhaps (33) loses its significance if the regular structure, $-(G)_M-$, of the polymer is distorted by copolymerisation or something else.

(7.4) The procedure outlined here reminds one to some extent of the Bloch formalism used in solid state theory [6]. The greatest similarities arise from the formal idenity of the symmetry group of translation and the infinite cyclic group. Indeed, in the case of the rotagraphs the Born-von Karman condition

$$\hat{T}^n f(\vec{r}) = f(\vec{r}+n\cdot\vec{a})$$

is achieved to some extent. However, in the case of the fasciagraphs our results differ noticeably from those which are to be expected from the application of the Bloch formalism. A typical difference represents the degeneracy of the bands: Using the Born-von Karman conditions the eigenvalues of an infinite band-like polymer should form doubly degenerate bands; using the

procedure outlined here no such degeneracy of the eigenvalues occurs (see appendix 1).

(7.5) Isolated states, as mentioned in connection with supposition 1, are frequently found in solid state calculations due to a distortion of the translational symmetry. Because we are not using this symmetry we cannot explain the isolated eigenvalues shown in fig. 5b in such terms. But it seems to be obvious that the increase of the internal symmetry of the terminal monomeric units in poly-m-phenyls is an analogous distortion of symmetry too.

The number of eigenvalues, $n \cdot M$, is a constant and independent of the fact whether there is such a distortion or not. Therefore the isolated eigenvalues found in the forbidden zones represent only eigenvalues which in the case of rotagraphs lie within the bands. Figure 6 illustrates this: In figure 6a the isolated eigenvalue coincides with the bounds of the lowest bands but in figure 6b it lies within the gap.

(7.6) Functions like those set up in (46) are frequently used in the course of the application of the Bloch method to polymers [18-21]. To our knowledge,

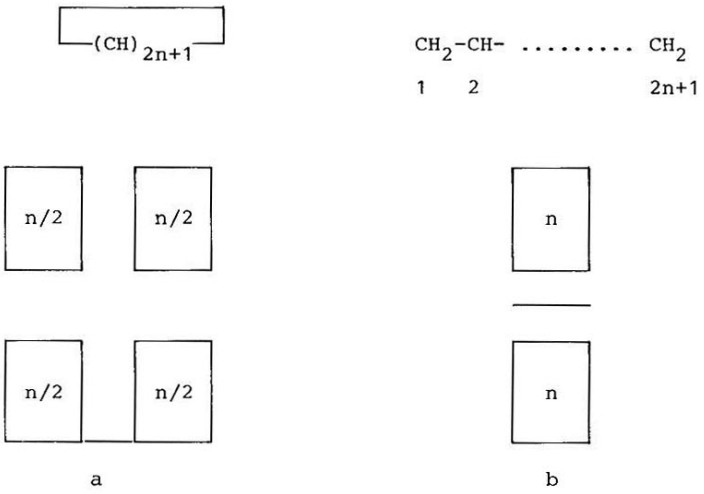


Figure 6: Band structure [12] of polymethines with an odd number, 2n+1, of centres:

a) rings: the Born-von Karman condition is simulated by

$$c_{r\mu} = c_{s\mu} \qquad \text{if: } (r-s)\mu = 0 \bmod(2n+1)$$

b) chains: the Born-von Karman condition is cancelled by the boundary condition

$$c_{o\mu} = c_{(2n+2)\mu} = 0.$$

in this paper for the first time a criterion is presented which allow us to classify these functions as "approximate" or "exact" solutions within the framework of the method used (see Proposition 12).

(7.7) The use of permutations groups instead of point groups is consistent with the ideas of graph theory. In some cases there is a real advantage in using permutation groups: local symmetries may be used independently of each other in the permutation groups whilst the point groups do not contain symmetry elements corresponding to such local symmetries. Let us take the fascia form of poly-m-phenyl (section 6) as an example: supposing, the configuration of the molecule is such that the highest possible symmetry is realized, then the point group of this polymer is either C_{2v} (if M is odd) or C_{2h} (if M is even). In these groups there is no symmetry element corresponding to the automorphic mapping (50). These phenomena have been discussed earlier by different authors [22-24].

Another but related question is under which conditions the spectrum of a polymer contains the spectrum of its monomeric units. This problem has been discussed recently [25].

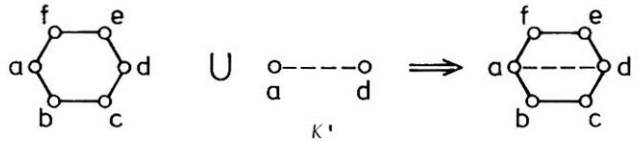
(7.8) For simplicity throughout this paper it has been assumed that there is a maximum, n, of equivalence classes in the monomeric unit G; this means two things: (i) each vertex of G forms an equivalence class for itself; (ii) the automorphism group of the rotagraph is represented by $A(R) = C_M[E_n]$ properly. This assumption is not attained in each concrete structure, of course. If, for instance, the fine group representing the internal automorphisms of the monomeric units within the rotagraph is of a higher order than 1, the nxn dimensional problems (21) and (48) respectively may be decomposed into a number of problems of reduced size.

Beside this reduction there is another important consequence of the increase of the order of the automorphism group. If this group is given properly as $A(R) = C_M[E_n]$ the non-crossing rule determines the pattern of band structure: all the eigenvalues $\{x_\mu^\delta \mid \mu \in n\}$ correspond to the same value of δ and they all belong to one and the same one-dimensional irreducible representation $\Gamma(\delta)$; hence they cannot be degenerate and no crossings of bands can occur therefore. However, if $A(R) \supset C_M[E_n]$ is of higher order, then each irreducible representation

$\Gamma(\delta)$ of $C_M[E_n]$ is split into two or more irreducible representations which for this reason differ in respect to some of the additional group elements but they all are related to the same value of δ. Then an accidental degeneracy of two eigenvalues, say $x_\mu^\delta = x_\nu^\delta$, each belonging to another representation may occur indicating the crossing of the two respective bands.

(7.9) One might expect that the automorphism group, $A(R)$, is determined by that, $A(G)$, of the monomer graph and the reduction of its equivalence relations caused by the edge set K^V. This problem is more complicated than it seems and is not solved in detail; therefore we cannot go into detail. However, it is obvious that a general solution of this problem is not needed for the performance of the procedure outlined here.

It hav· been noted (see the text following Proposition 3) that the reduction of the original equivalence relations established in G by the edge set K^V is simulated by the addition of the edge set $K' = \bigcup_\ell \{U_{1\lambda}, U_{2\lambda}\}$ to G producing $G' = G \cup K'$; for instance, in the case of the poly-p-phenyl-structure one obtains:

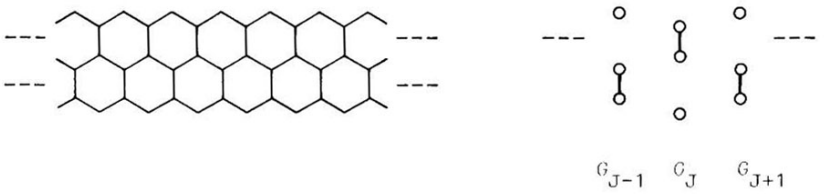


G G'

$(U_{11} = a;\ U_{21} = d)$

Whilst in G all the six vertices are equivalent to each other in G' they form two equivalence classes. If G' is used in deriving the automorphism group of the polymer graph, one has to observe that no edge of G can be mapped onto any edge of K' and vice versa.

(7.10) A few words should be said upon the term "monomeric unit". Chemists like to refer to the starting material in reaction (1) as this. In connection with the symmetry properties of polymer graphs it is more convenient, however, to understand by this term the smallest aggregate of vertices and edges which is repeated regularly in the graph; it need not be connected. In the case of



the monomeric units it is a disconnected graph consisting of 3 vertices and 1 edge.

This polymer is a supplementary example to the foot note relating to equation (3). It is obvious that in this case assumption (3) is dropped by $u_1^J = u_2^J = u_J$. Nevertheless, the procedure outlined here can be applied to this polymer structure without any difficulties [5]. This shows that (3) fascilitates the considerations to some extent but has not the rank of a necessary condition.

(7.11) The procedure reported here has been applied to more than twenty concrete structures. The results obtained thereby will be reported elsewhere [5].

Acknowledgements:

We wish to thank Dr. H. Barentzen, Mülheim, for helpful discussions. The eigenvalues of poly-p- and poly-m-phenyls (M = 5,6,7,8,9,10) have been calculated by Mr. W. Beisiegel using a current computer program written by Dr. F. Mark; the figures have been drawn by Mrs. I. Schneider and the typing was done by Mrs. L. Heidemann. Here we also thank them for their help.

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Appendix:

Perturbational treatment of $F(G,M,K^V)$

This appendix takes up the offer given by (45) to develop the eigenvalues and eigenvectors of $F(G,M,K^V)$ in terms of the eigenvalues and eigenfunctions of $R(G,M,K^V)$ using Rayleigh-Schrödinger perturbation theory [7].

The matrices R and F, introduced in (16) and (41) respectively, may be understood as the representations of two respective hermitian operators, $\hat{R_H}$ and $\hat{F_H}$, in the set of orthonormal basis functions, $\{\phi_r^J | r\in n,\ J\in M\}$, introduced in (27):

$$R = \langle \underline{\phi} | \hat{R_H} | \underline{\phi} \rangle,$$
$$F = \langle \underline{\phi} | \hat{R_H} | \underline{\phi} \rangle, \qquad (\underline{\underline{A}}:1)$$

where $|\underline{\phi}\rangle$ denotes a row vector formed from the basis functions as follows:

$$|\underline{\phi}> = (|\underline{\phi}^1> \; |\underline{\phi}^2> \; \ldots \; |\underline{\phi}^J> \; \ldots \; |\underline{\phi}^M>)$$
$$|\underline{\phi}^J>= (|\phi_1^J> \; |\phi_2^J> \; \ldots \; |\phi_\gamma^J> \; \ldots \; |\phi_n^J> \qquad (\underline{A;2})$$

It should be noted that both $R(G,M,K^V)$ and $F(G,M,K^V)$ have the same set of basis functions if G, M, and K^V agree with each other in these graphs.

The matrix $H^{(1)}$ introduced in (42) may be understood analogously as the representation of an effective hermitian opertor $\hat{H}^{(1)}$ in the basis set:

$$H^{(1)} = <\underline{\phi}|\hat{H}^{(1)}|\underline{\phi}>. \qquad (\underline{A;3})$$

Then the definition (42) of $H^{(1)}$ = F-R corresponds with the operator relation $H^{(1)} = {}^F\hat{H} - {}^R\hat{H}$ which may be rewritten as follows

$$\hat{H} = \hat{H}^{(o)} + \hat{H}^{(1)} \qquad (\underline{A;4})$$

if according to [7] one recognizes:

$\hat{H} = {}^F\hat{H}$ ... the effective operator of the problem which is to be solved;

$\hat{H}^o = {}^R\hat{H}$ ... the effective operator of the solved problem

$$\hat{H}^{o}\ \psi_{\mu}^{j} = -\ x_{\mu}^{j}\ \psi_{\mu}^{j}; \qquad (\underline{\underline{A:5}})$$

$\hat{H}^{(1)}$ ... the effective operator of a perturbation acting on the problem (A:5) producing solutions of the problem

$$\hat{H}\ \chi_{\mu}^{J} = -y_{\mu}^{j}\ \chi_{\mu}^{j} \qquad (\underline{\underline{A:6}})$$

where $\{-y_{\mu}^{j}\}$ and $\{\chi_{\mu}^{j}\}$ represents the sets of eigenvalues and eigenfunctions of $F(G,M,K^{V})$ respectively.

These eigenvalues and eigenfunctions are now expanded [7] as follows

$$-y_{\mu}^{j} = (-y_{\mu}^{j})^{(o)} + \lambda(-y_{\mu}^{j})^{(1)} + \lambda^{2}(-y_{\mu}^{j})^{(2)} + \ldots =$$

$$= \sum_{\kappa=o}^{\infty} \lambda^{\kappa}(-y_{\mu}^{j})^{(\kappa)}, \qquad (\underline{\underline{A:7}})$$

$$\chi_{\mu}^{j} = (\chi_{\mu}^{j})^{(o)} + \lambda(\chi_{\mu}^{j})^{(1)} + \lambda^{2}(\chi_{\mu}^{j})^{(2)} + \ldots =$$

$$= \sum_{\kappa=o}^{\infty} \lambda^{\kappa}(\chi_{\mu}^{j})^{(\kappa)}.$$

Here the parameter λ is introduced only for formal reasons; it serves as an expansion parameter and will be put equal to 1 later on. Inserting (A:4) and (A:7) into (A:6) and

collecting the terms of the same power λ^{ν} one obtains for

$\underline{\nu = 0:}$

$$\left(\hat{H}^{(0)} - (-y_{\mu}^{j})^{(0)}\right)(\chi_{\mu}^{j})^{(0)} = 0 \qquad (\underline{A:8})$$

$\underline{\nu = 1:}$

$$\left(\hat{H}^{(0)} - (-y_{\mu}^{j})^{(0)}\right)(\chi_{\mu}^{j})^{(1)} + \left(\hat{H}^{(1)} - (-y_{\mu}^{j})^{(1)}\right)(\chi_{\mu}^{j})^{(0)} = 0 \qquad (\underline{A:9})$$

$\underline{\nu \geq 2:}$

$$\left(\hat{H}^{(0)} - (-y_{\mu}^{j})^{(0)}\right)(\chi_{\mu}^{j})^{(\nu)} + \left(\hat{H}^{(1)} - (-y_{\mu}^{j})^{(1)}\right)(\chi_{\mu}^{j})^{(\nu-1)} +$$

$$+ \sum_{\xi=2}^{\nu} - (-y_{\mu}^{j})^{(\xi)}(\chi_{\mu}^{j})^{(\nu-\xi)} = 0 \qquad (\underline{A:10})$$

According to perturbation theory [7] one recognizes the identity of (A:8) and (A:5); this means that

$$(-y_{\mu}^{j})^{(0)} = -x_{\mu}^{j} \qquad (\underline{A:11})$$

for each possible pair (μ,j). But it does not mean a similar equality between $(\chi_{\mu}^{j})^{(0)}$ and ψ_{μ}^{j} because the latter functions are doubly degenerate if $j \neq 0$ and $j \neq M/2$, as shown in proposition 6. Hence, first of all we have to find those linear combinations of the degenerated functions,

$$\Xi_{\mu}^{j} = \alpha\, \psi_{\mu}^{j} + \beta\, \psi_{\mu}^{j^{*}} \qquad (\underline{A:12})$$

which are invariant under the action of $\hat{H}^{(1)}$. This leads to the following two dimensional secular problem for each pair of degenerate functions

$$\begin{vmatrix} (h^{jj}_{\mu\mu} - E_1) & h^{j\bar{j}}_{\mu\mu} \\ h^{\bar{j}j}_{\mu\mu} & (h^{\bar{j}\bar{j}}_{\mu\mu} - E_1) \end{vmatrix} = 0 \qquad (\underline{\underline{A:13}})$$

where the $h^{jk}_{\mu\nu}$ denote the integrals $\langle\psi^j_\mu|\hat{H}|\psi^k_\nu\rangle$ and $E_1 = (-y^j_\mu)^{(1)}$. The solution of (A:13) results in the following pair of "zeroth-order" functions

$$\begin{aligned} \Xi^j_\mu &= \eta^j_\mu\,\psi^j_\mu + \eta^{j*}_\mu\,\psi^{j*}_\mu, \\ \Xi^{\bar{j}}_\mu &= \bar{\eta}^j_\mu\,\psi^j_\mu + \bar{\eta}^{j*}_\mu\,\psi^{j*}_\mu; \end{aligned} \qquad (\underline{\underline{A:14}})$$

$$\eta^j_\mu = \frac{1}{\sqrt{2}}\,e^{i\tau^j_\mu/2} \qquad \bar{\eta}^j_\mu = \frac{1}{\sqrt{2}}\,e^{i(\pi+\tau^j_\mu)/2};$$

$$tg\ \tau^j_\mu = \frac{Im\ h^{j\bar{j}}_{\mu\mu}}{Re\ h^{j\bar{j}}_{\mu\mu}} = \frac{Im\ \langle\psi^j_\mu|\hat{H}^{(1)}|\psi^{j*}_\mu\rangle}{Re\ \langle\psi^j_\mu|\hat{H}^{(1)}|\psi^{j*}_\mu\rangle}.$$

From this result it is readily concluded that both the Ξ^j_μ

and $\Xi_\mu^{\bar{j}}$ are real functions. They represents the zeroth-order approximations of the eigenfunctions of $F(G,M,K^V)$:

$$(\chi_\mu^j)^{(o)} = \Xi_\mu^j$$
$$(\chi_\mu^{M-j})^{(o)} = \Xi_\mu^{\bar{j}} \qquad (A:15)$$

If in addition to (A:14) one puts

$$\psi_\mu^o = \Xi_\mu^o \text{ and } \psi_\mu^{M/2} = \Xi_\mu^{M/2},$$

the set $\{\psi_\mu^j\}$ is totally transformed* into the set $\{\Xi_\mu^j\}$. It is more convenient to use the latter set than the former as the set of unperturbed functions satisfying (A:8).

Ther perturbation functions $(\chi_\mu^j)^{(\nu-\xi)}$ are then expanded as follows

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* The functions Ξ_μ^j and Ξ_μ^j are eigenfunctions of $\hat{H}^o$, i.e.:

$$\hat{H}^o \Xi_\mu^j = -x_\mu^j \Xi_\mu^j.$$

In ψ_μ^j the superscript j refers to the representation $\Gamma_j \epsilon C_M$; but in Ξ_μ^j and $\Xi_\mu^{\bar{j}}$ this meaning of the superscript is lost.

$$(\chi_\mu^j)^{(\nu-\xi)} = \sum_{\substack{(\kappa,k)\\ \neq(\mu,j)}}' \left((\nu-\xi) A_{\kappa\mu}^{kj} \cdot \Xi_\kappa^k + (\nu-\xi) A_{\kappa\mu}^{\bar{k}j} \cdot \Xi_\kappa^{\bar{k}} \right) \qquad (\underline{\underline{A:16}})$$

Inserting this expansion into (A:9) and (A:10) one obtains after the mulitplication from the left with Ξ_μ^{j*}, Ξ_κ^{k*}, and $\Xi_\kappa^{\bar{k}*}$ respectively and integration the following expressions in straight-forward calculations:

$\underline{\nu = 1:}$

$$(-y_\mu^j)^{(1)} = H_{\mu\mu}^{jj}; \quad {}^{(1)}A_{\kappa\mu}^{kj} = -\frac{H_{\kappa\mu}^{kj}}{x_\mu^j - x_\kappa^k}, \quad {}^{(1)}A_{\kappa\mu}^{\bar{k}j} = -\frac{H_{\kappa\mu}^{\bar{k}j}}{x_\mu^j - x_\lambda^k};$$

$\underline{\nu \geq 2:}$

$$(-y_\mu^j)^{(\nu)} = \sum_{\substack{(\kappa,k)\neq\\ \neq(\mu,j)}}' \left(H_{\mu\kappa}^{jk} \cdot {}^{(\nu-1)}A_{\kappa\mu}^{kj} + H_{\mu\kappa}^{j\bar{k}} \cdot {}^{(\nu-1)}A_{\kappa\mu}^{\bar{k}j} \right);$$

$$(\nu)A_{\kappa\mu}^{kj} = \frac{1}{x_\mu^j - x_\kappa^k} \left[\sum_{\xi=1}^{\nu-1} (\nu-\xi) A_{\kappa\mu}^{kj} \cdot (-y_\mu^j)^{(\xi)} - \right.$$

$$\left. - \sum_{\substack{(\lambda,\bar{l})\neq\\ \neq(\mu,j)}}' \left(H_{\kappa\lambda}^{k\bar{l}} \cdot {}^{(\nu-1)}A_{\lambda\mu}^{lj} + H_{\kappa\lambda}^{k\bar{l}} \cdot {}^{(\nu-1)}A_{\lambda\mu}^{\bar{l}j} \right) \right], \qquad (\underline{\underline{A:17}})$$

$$ {}^{(\nu)}A^{\bar{k}j}_{\kappa\mu} = \frac{1}{x^j_\mu - x^k_\kappa} \left[\sum_{\xi=1}^{\nu-1} {}^{(\nu-\xi)}A^{\bar{k}j}_{\kappa\mu} \cdot (-y^j_\mu)^{(\xi)} - \right. $$

$$ \left. - \sum_{\substack{(\lambda,l)\neq \\ \neq(\mu,j)}}{}' \left(H^{\bar{k}l}_{\kappa\lambda} \cdot {}^{(\nu-1)}A^{lj}_{\lambda\mu} + H^{\bar{k}\bar{l}}_{\kappa\lambda} \cdot {}^{(\nu-1)}A^{\bar{l}j}_{\lambda\mu} \right) \right] . $$

Here $H^{kj}_{\kappa\mu}$ indicates the integral

$$ H^{kj}_{\kappa\mu} = \langle \Xi^k_\kappa | \hat{H}^{(1)} | \Xi^j_\mu \rangle . \qquad (\underline{\underline{A:18}}) $$

Inserting (A:14) into this definition a straightforward calculation leads to

$$ H^{kj}_{\kappa\mu} = \eta^{k*}_\kappa \cdot \eta^j_\mu \cdot h^{kj}_{\kappa\mu} + \eta^k_\kappa \cdot \eta^j_\mu \cdot h^{\bar{k}j}_{\kappa\mu} + \eta^{k*}_\kappa \cdot \eta^{j*}_\mu \cdot h^{k\bar{j}}_{\kappa\mu} + \eta^k_\kappa \cdot \eta^{j*}_\mu \cdot h^{\bar{k}\bar{j}}_{\kappa\mu} = $$

$$ = 2 \cdot Re[\eta^{k*}_\kappa \cdot \eta^j_\mu \cdot h^{kj}_{\kappa\mu} + \eta^k_\kappa \cdot \eta^j_\mu \cdot h^{\bar{k}\bar{j}}_{\kappa\mu}] = \qquad (\underline{\underline{A:19}}) $$

$$ = Re[e^{i(\tau^j_\mu - \tau^k_\kappa)/2} \cdot h^{kj}_{\kappa\mu} + e^{i(\tau^j_\mu + \tau^k_\kappa)/2} \cdot h^{\bar{k}j}_{\kappa\mu}] . $$

The definitions of τ^j_μ and τ^k_κ are given by (A:14). From this general formula the following especial expressions are easily derived:

$$H^{jj}_{\mu\mu} = h^{jj}_{\mu\mu} - |h^{j\bar{j}}_{\mu\mu}| \; ; \qquad H^{\bar{j}\bar{j}}_{\mu\mu} = h^{jj}_{\mu\mu} + |h^{j\bar{j}}_{\mu\mu}|$$

$$H^{j\bar{j}}_{\mu\mu} = H^{\bar{j}j^{\ast\ast}}_{\mu\mu} = 0. \qquad (A.20)$$

Inserting (27) into the definition of $h^{jk}_{\mu\kappa}$ one obtains

$$h^{jk}_{\mu\kappa} = \langle\psi^{j}_{\mu}|\hat{H}^{(1)}|\psi^{k}_{\kappa}\rangle =$$

$$= \frac{1}{M}\sum_{J,k;r,s}\sum\langle\omega^{(J-1)}_{j}c^{j}_{r\mu}\cdot\phi^{J}_{r}|\hat{H}^{(1)}|\omega^{(K-1)}_{k}c^{k}_{s\kappa}\cdot\phi^{K}_{s}\rangle =$$

$$= \frac{1}{M}\sum_{J,K;r,s}\sum\omega^{\ast\ast(J-1)}_{j}\cdot c^{j^{\ast\ast}}_{r\mu}\cdot\omega^{(K-1)}_{k}\cdot c^{k}_{s\kappa}\cdot\langle\phi^{J}_{r}|\hat{H}^{(1)}|\phi^{K}_{s}\rangle.$$

According to (42) there are only two pairs of superscripts, that are (J=1, K=M) and (J=M, K=1), for which the integrals $\langle\phi^{J}_{r}|\hat{H}^{(1)}|\phi^{K}_{s}\rangle$ do not vanish totally. Therefore the independent summations over J$\in M$ and K$\in M$ may be replaced by the introduction of these two pairs; this leads to

$$h^{jk}_{\mu\kappa} = \frac{1}{M}\sum_{r,s}\sum\{\omega^{\ast\ast}_{k}\cdot c^{j^{\ast\ast}}_{r\mu}\cdot c^{k}_{s\kappa}\cdot\langle\phi^{1}_{r}|\hat{H}^{(1)}|\phi^{M}_{s}\rangle +$$

$$+ \omega_{j}\cdot c^{j^{\ast\ast}}_{r\mu}\cdot c^{k}_{s\kappa}\cdot\langle\phi^{M}_{r}|\hat{H}^{(1)}|\phi^{1}_{s}\rangle\}. \qquad (A.21)$$

The first integral in (A:21) does not vanish only if $U^1_r = U^1_{1\lambda} \epsilon u^1_1$ and $U^M_s = U^M_{2\lambda'} \epsilon u^M_2$ and then according to (42) one obtains

$$<\phi^1_{1\lambda} | \hat{H}^{(1)} | \phi^M_{2\lambda'}> = - \delta_{\lambda\lambda'}. \qquad (A:22a)$$

The second integral in (A:21) does not vanish only if $U^M_r = U^M_{2\lambda} \epsilon u^M_2$ and $U^1_s = U^1_{1\lambda'} \epsilon u^1_1$; and then in accordance to (42) one obtains

$$<\phi^M_{2\lambda} | \hat{H}^{(1)} | \phi^1_{1\lambda'}> = - \delta_{\lambda\lambda'}. \qquad (A:22b)$$

The independent summations over $r \in n$ and $s \in n$ may be replaced therefore by the summation over $\lambda \epsilon \ell$. Using (A:22a) and (A:22b) one finally obtains

$$h^{jk}_{\mu\kappa} = - \frac{1}{M} \sum_{\lambda \epsilon \ell} \{\omega^{\ddot{x}}_k \cdot c^{j\ddot{x}}_{(1\lambda)\mu} c^k_{(2\lambda)\kappa} + \omega_j \cdot c^k_{(1\lambda)\kappa} c^{j\ddot{x}}_{(2\lambda)\mu}\} \qquad (A:23)$$

In an analogous way one further obtains

$$h^{j\bar{k}}_{\mu\kappa} = <\psi^j_\mu | \hat{H}^{(1)} | \psi^{k\ddot{x}}_\kappa> =$$

$$= - \frac{1}{M} \sum_{\lambda \epsilon \ell} \{\omega_k \cdot c^{j\ddot{x}}_{(1\lambda)\mu} \cdot c^{k\ddot{x}}_{(2\lambda)\kappa} + \omega_j \cdot c^{k\ddot{x}}_{(1\lambda)\kappa} \cdot c^{j\ddot{x}}_{(2\lambda)\mu}\}. \qquad (A:24)$$

From their definitions it follows that

$$h^{\bar{j}k}_{\mu\kappa} = \langle \psi^{j*}_{\mu} | \hat{H}^{(1)} | \psi^{k}_{\kappa} \rangle = h^{j\bar{k}*}_{\mu\kappa} ,$$

$$h^{\bar{j}\bar{k}}_{\mu\kappa} = \langle \psi^{j*}_{\mu} | \hat{H}^{(1)} | \psi^{k*}_{\kappa} \rangle = h^{jk*}_{\mu\kappa} . \qquad (\underline{\underline{A:25}})$$

From these general formulae the following especial expressions are derived:

$$h^{jj}_{\mu\mu} = h^{\bar{j}\bar{j}}_{\mu\mu} = -\frac{2}{M} Re[\sum_{\lambda \in \ell} \omega_j \cdot c^{j}_{(1\lambda)\mu} \cdot c^{j*}_{(2\lambda)\mu}], \qquad (\underline{\underline{A:26}})$$

$$h^{\bar{j}j}_{\mu\mu} = h^{j\bar{j}*}_{\mu\mu} = -\frac{2}{M} \sum_{\lambda \in \ell} \omega^{*}_{j} \cdot c^{j}_{(1\lambda)\mu} \cdot c^{j}_{(2\lambda)\mu} .$$

It should be noted that $c^{j}_{(1\lambda)\mu}$ and $c^{j}_{(2\lambda)\mu}$ may be equal but they need to be. - By means of these equations the quantities $H^{jk}_{\mu\kappa}$ are traced back to the characters, ω_j, of C_M and some elements, $c^{j}_{r\mu}$, of the eigenvector matrix of R.

For later use it is convenient to introduce the quantities

$$\tilde{h}^{jk}_{\mu\kappa} = M \cdot h^{jk}_{\mu\kappa} \quad \text{and} \quad \tilde{H}^{jk}_{\mu\kappa} = M \cdot H^{jk}_{\mu\kappa} \qquad (\underline{\underline{A:27}})$$

Since $|\omega_j| = 1$ and $|c^j_{r\mu}| \leq 1$, the absolute magnitudes of these quantities follow the respective relations

$$0 \leq |\tilde{h}^{jk}_{\mu\kappa}| \leq 2\,l \text{ and } 0 \leq |\tilde{H}^{jk}_{\mu\kappa}| \leq 4\,l. \qquad (\underline{\underline{A:28}})$$

It should be remembered that l, representing the cardinality of K^v, will be always a small number but M is of the order 10^1 to 10^4. The bigger M is the smaller will be the original quantities $h^{jk}_{\mu\kappa}$ and $H^{jk}_{\mu\kappa}$.

In table (A:1) the eigenvalues and eigenvectors of $F(G,M,K^v)$ are given up to the third order. From these formulae it is readily concluded that:

(1) According to (A:20) the functions χ^j_μ and $\chi^{\bar{j}}_\mu$ corresponding to the eigenvalues $-y^j_\mu$ and $-y^{\bar{j}}_\mu$ respectively are not degenerate. This means at last that the spectrum of $F(G,M,K^v)$ consists of non-degenerate eigenvalues.

(2) Because commonly $M >> 4l$ the first order term in the expansion of $-y^j_\mu$ is the leading term. As shown in (A:26) the sign of $(-y^j_\mu)^{(1)}$ depends on the relative

signs of $c^{j}_{(1\lambda)\mu}$ and $c^{j}_{(2\lambda)\mu}$. It is therefore hard to state generally if the leading term causes either an increase or a decrease of zeroth order eigenvalues $(-y^{j}_{\mu})^{(o)} = -x^{j}_{\mu}$; but in the cases $\mu = 1$ and $\mu = n$ there should be in general $(-y^{j}_{1}) > 0$ and $(-y^{j}_{n}) < 0$ respectively. This presumes that the eigenvalues of $F(G,M,K^{V})$ lie within the bands of the eigenvalues of the corresponding infinite rotagraph $R(G,\infty,K^{V})$.

(3) If M tends to infinity one obtains

$$\lim_{M\to\infty} (-y^{j}_{\mu}) = -x^{j}_{\mu}, \qquad (\underline{\underline{A:29}})$$

although some of the differences $(x^{j}_{\mu} - x^{k}_{\kappa})$ may tend to zero because the ν-th order term $(-y^{j}_{\mu})^{(\nu)}$ contains only $(\nu-1)$ such factors in its demoninators but goes with $M^{-\nu}$. As a consequence of (A:29) the spectra of both infinite graphs, $F(G,\infty,K^{V})$ and $R(G,\infty,K^{V})$, should have equal band structures.

(4) No general limit of the eigenfunctions χ^{j}_{μ} of $F(G,M,K^{V})$ can be given in the case that M tends to become infinite. This is due to the fact that the denominators of the coefficients ${}^{(\nu)}A^{kj}_{\kappa\mu}$ are of the general form $(M\cdot\Delta x)^{\nu}$; if $M\to\infty$ some of the $\Delta x \to 0$ and hence a non zero limit for ${}^{(\nu)}A^{kj}_{\kappa\mu}$ could result.

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TABLE (A:1):

Perturbational expansion of the eigenvalues, $-y_\mu^j$, and eigenfunctions, χ_μ^j, of the fasciagraph $F(G,M,K^V)$

$$-y_\mu^j = -x_\mu^j + \frac{1}{M}\tilde{H}_{\mu\mu}^{jj} - \frac{1}{M^2}\sum_{(\kappa k)}{}' \frac{\tilde{H}_{\mu\kappa}^{jk}\tilde{H}_{\kappa\mu}^{kj} + \tilde{H}_{\mu\kappa}^{j\bar{k}}\tilde{H}_{\kappa\mu}^{\bar{k}j}}{(x_\mu^j - x_\kappa^k)} + \frac{1}{M^3}\sum_{(\kappa,k)}{}'\sum_{(\lambda 1)}{}' \frac{\tilde{H}_{\mu\kappa}^{jk}\tilde{H}_{\kappa\lambda}^{k1}\tilde{H}_{\lambda\mu}^{1j} + \tilde{H}_{\mu\kappa}^{j\bar{k}}\tilde{H}_{\kappa\lambda}^{\bar{k}1}\tilde{H}_{\lambda\mu}^{1j} + \tilde{H}_{\mu\kappa}^{jk}\tilde{H}_{\kappa\lambda}^{k\bar{1}}\tilde{H}_{\lambda\mu}^{\bar{1}j} + \tilde{H}_{\mu\kappa}^{j\bar{k}}\tilde{H}_{\kappa\lambda}^{\bar{k}\bar{1}}\tilde{H}_{\lambda\mu}^{\bar{1}j}}{(x_\mu^j - x_\kappa^k)(x_\mu^j - x_\lambda^1)} -$$

$$- \frac{\tilde{H}_{\mu\kappa}^{jk}\tilde{H}_{\kappa\mu}^{kj}\tilde{H}_{\mu\mu}^{jj} + \tilde{H}_{\mu\kappa}^{j\bar{k}}\tilde{H}_{\kappa\mu}^{\bar{k}j}\tilde{H}_{\mu\mu}^{jj}}{(x_\mu^j - x_\kappa^k)^2} - \frac{1}{M^4} \cdots\cdots + \frac{1}{M^5} \cdots\cdots \pm \cdots\cdots$$

$$\chi_\mu^j = \Xi_\mu^j - \frac{1}{M}\sum_{(\kappa k)}{}' {}_1B_{\kappa\mu}^{kj}\Xi_\kappa^k + {}_1B_{\kappa\mu}^{\bar{k}j}\Xi_\kappa^{\bar{k}} + \frac{1}{M^2}\sum_{(\kappa,k)}{}' {}_2B_{\kappa\mu}^{kj}\Xi_\kappa^k + {}_2B_{\kappa\mu}^{\bar{k}j}\Xi_\kappa^{\bar{k}} - \frac{1}{M^3}\sum_{(\kappa,k)}{}' {}_3B_{\kappa\mu}^{kj}\Xi_\kappa^k + {}_3B_{\kappa\mu}^{\bar{k}j}\Xi_\kappa^{\bar{k}} +$$

$$+ \frac{1}{M^4} \cdots\cdots - \frac{1}{M^5} \cdots\cdots \pm \cdots\cdots$$

$${}_1B_{\kappa\mu}^{kj} = \tilde{H}_{\kappa\mu}^{kj} / (x_\mu^j - x_\kappa^k),$$

$${}_1B_{\kappa\mu}^{\bar{k}j} = \tilde{H}_{\kappa\mu}^{\bar{k}j} / (x_\mu^j - x_\kappa^k);$$

$$ {}^{2}B^{kj}_{\kappa\mu} = - \frac{\tilde{H}^{kj}_{\kappa\mu}\tilde{H}^{jj}_{\mu\mu}}{(x^j_\mu - x^k_\kappa)^2} + \sum'_{(\lambda 1)} \frac{\tilde{H}^{k1}_{\kappa\lambda}\tilde{H}^{1j}_{\lambda\mu} + \tilde{H}^{k\bar{1}}_{\kappa\lambda}\tilde{H}^{\bar{1}j}_{\lambda\mu}}{(x^j_\mu - x^k_\kappa)(x^j_\mu - x^1_\lambda)} $$

$$ {}^{2}B^{\bar{k}j}_{\kappa\mu} = - \frac{\tilde{H}^{\bar{k}j}_{\kappa\mu}H^{jj}_{\mu\mu}}{(x^j_\mu - x^k_\kappa)^2} + \sum'_{(\lambda 1)} \frac{\tilde{H}^{\bar{k}1}_{\kappa\lambda}\tilde{H}^{1j}_{\lambda\mu} + \tilde{H}^{\bar{k}\bar{1}}_{\kappa\lambda}\tilde{H}^{\bar{1}j}_{\lambda\mu}}{(x^j_\mu - x^k_\kappa)(x^j_\mu - x^1_\lambda)} $$

$$ {}^{3}B^{kj}_{\kappa\mu} = \frac{\tilde{H}^{kj}_{\kappa\mu}\tilde{H}^{jj}_{\mu\mu}\tilde{H}^{jj}_{\mu\mu}}{(x^j_\mu - x^k_\kappa)^3} - \sum'_{(\lambda 1)} \frac{\tilde{H}^{k1}_{\kappa\lambda}\tilde{H}^{1j}_{\lambda\mu}\tilde{H}^{jj}_{\mu\mu} + \tilde{H}^{k\bar{1}}_{\kappa\lambda}\tilde{H}^{\bar{1}j}_{\lambda\mu}\tilde{H}^{jj}_{\mu\mu}}{(x^j_\mu - x^k_\kappa)^2 (x^j_\mu - x^1_\lambda)} + \frac{\tilde{H}^{kj}_{\kappa\mu}\tilde{H}^{j1}_{\mu\lambda}\tilde{H}^{1j}_{\lambda\mu} + \tilde{H}^{kj}_{\kappa\mu}\tilde{H}^{j\bar{1}}_{\mu\lambda}\tilde{H}^{\bar{1}j}_{\lambda\mu}}{(x^j_\mu - x^k_\kappa)^2 \cdot (x^j_\mu - x^1_\lambda)} + \frac{\tilde{H}^{k1}_{\kappa\lambda}\tilde{H}^{1j}_{\lambda\mu}\tilde{H}^{jj}_{\mu\mu} + \tilde{H}^{k\bar{1}}_{\kappa\lambda}\tilde{H}^{\bar{1}j}_{\lambda\mu}\tilde{H}^{jj}_{\mu\mu}}{(x^j_\mu - x^k_\kappa) \cdot (x^j_\mu - x^1_\lambda)^2} - $$

$$ - \sum'_{(\nu n)} \frac{\tilde{H}^{k1}_{\kappa\lambda}\tilde{H}^{1n}_{\lambda\nu}\tilde{H}^{nj}_{\nu\mu} + \tilde{H}^{k\bar{1}}_{\kappa\lambda}\tilde{H}^{\bar{1}n}_{\lambda\nu}\tilde{H}^{nj}_{\nu\mu} + \tilde{H}^{k1}_{\kappa\lambda}\tilde{H}^{1\bar{n}}_{\lambda\nu}\tilde{H}^{\bar{n}j}_{\nu\mu} + \tilde{H}^{k\bar{1}}_{\kappa\lambda}\tilde{H}^{\bar{1}\bar{n}}_{\lambda\nu}\tilde{H}^{\bar{n}j}_{\nu\mu}}{(x^j_\mu - x^k_\kappa) \cdot (x^j_\mu - x^1_\lambda) \cdot (x^j_\mu - x^n_\nu)} $$

$$ {}^{3}B^{\bar{k}j}_{\kappa\mu} = \frac{\tilde{H}^{\bar{k}j}_{\kappa\mu}\tilde{H}^{jj}_{\mu\mu}\tilde{H}^{jj}_{\mu\mu}}{(x^j_\mu - x^k_\kappa)^3} - \sum'_{(\lambda 1)} \frac{\tilde{H}^{\bar{k}1}_{\kappa\lambda}\tilde{H}^{1j}_{\lambda\mu}\tilde{H}^{jj}_{\mu\mu} + \tilde{H}^{\bar{k}\bar{1}}_{\kappa\lambda}\tilde{H}^{\bar{1}j}_{\lambda\mu}\tilde{H}^{jj}_{\mu\mu}}{(x^j_\mu - x^k_\kappa)^2 (x^j_\mu - x^1_\lambda)} + \frac{\tilde{H}^{\bar{k}1}_{\kappa\mu}\tilde{H}^{j1}_{\mu\lambda}\tilde{H}^{1j}_{\lambda\mu} + \tilde{H}^{\bar{k}j}_{\kappa\mu}\tilde{H}^{j\bar{1}}_{\mu\lambda}\tilde{H}^{\bar{1}j}_{\lambda\mu}}{(x^j_\mu - x^k_\kappa)^2 \cdot (x^j_\mu - x^1_\lambda)} + \frac{\tilde{H}^{\bar{k}1}_{\kappa\lambda}\tilde{H}^{1j}_{\lambda\mu}\tilde{H}^{jj}_{\mu\mu} + \tilde{H}^{\bar{k}\bar{1}}_{\kappa\lambda}\tilde{H}^{\bar{1}j}_{\lambda\mu}\tilde{H}^{jj}_{\mu\mu}}{(x^3_\mu - x^k_\kappa)(x^j_\mu - x^1_\lambda)^2} - $$

$$ - \sum'_{(\nu n)} \frac{\tilde{H}^{\bar{k}1}_{\kappa\lambda}\tilde{H}^{1n}_{\lambda\nu}\tilde{H}^{nj}_{\nu\mu} + \tilde{H}^{\bar{k}\bar{1}}_{\kappa\lambda}\tilde{H}^{\bar{1}n}_{\lambda\nu}\tilde{H}^{nj}_{\nu\mu} + \tilde{H}^{\bar{k}1}_{\kappa\lambda}\tilde{H}^{1\bar{n}}_{\lambda\nu}\tilde{H}^{\bar{n}j}_{\nu\mu} + \tilde{H}^{\bar{k}\bar{1}}_{\kappa\lambda}\tilde{H}^{\bar{1}\bar{n}}_{\lambda\nu}\tilde{H}^{\bar{n}j}_{\nu\mu}}{(x^j_\mu - x^k_\kappa) \cdot (x^j_\mu - x^1_\lambda)(x^j_\mu - x^n_\nu)} $$