THE USE OF PERTURBATION METHODS
FOR QUANTUM-CHEMICAL INVESTIGATIONS
OF SYSTEMS BUILT UP FROM IDENTICAL UNITS

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(Presented by P. Gombás. — Received 19. III. 1956)

The paper deals with the investigation of molecules built up from n identical units using perturbation considerations. By means of considerations based on a simple variant of the molecular orbital method we succeeded both in the case of energy values and in that of bond orders in separating the results into sums of products in which the one factor contains quantities referring only to the basic unit, and the second depends on the data of the series. The second part of the paper deals with the calculations relating to the polyrylene series in order to illustrate the usefulness of the general method. According to the results of the calculations the method can be successfully applied and by its means it becomes possible to investigate the dependence of the quantities characterizing the series on the strength of the bonds connecting the single units.

Introduction

In theoretical chemical investigations cases frequently occur, in which the members of a series of compounds can be obtained by aid of successive condensation of a given unit. Such problems are met with in the theoretical examination of polymers, further some series of condensed aromatic compounds also belong here ; thus for instance the members of the polyrylene series can be obtained by successive condensation of naphtalene, likewise that of anthracene yields the members of the polyanthene series, etc. For the theoretical investigation of these kinds of problems a simple variant of the molecular-orbital theory (linear combination of atomic orbitals) appears above all suitable. For the present, on account of the complicated molecular structure, there is namely not much hope for the application of the refinements of the method to the higher members of the series, on the other hand according to experiences made so far the main regularities are reproduced quite well also with the above-mentioned version of the molecular-orbital method. Unfortunately, owing to the high order of the determinantal equation occurring, the application of even this simple method becomes very tedious when the higher members of the series are investigated. Therefore it is desirable to work out a treatment in which the calculations relating to the individual members of the series are reduced to those referring to the basic unit. For this purpose the use of the perturbation method seems most appropriate.

The above-mentioned problems were first successfully investigated by COULSON AND RUSHBROKE [1]. Their treatment refers to the case in which

there is a connection between the repeating units only in one place. This results in an equation suitable for the determination of the energy values. In the following the same problem is dealt with using the perturbation method.

The case investigated by us is more general in so far as it also extends to multiple linking of the units, furthermore formulae are developed for the determination of the energy values as well as for the coefficients. On the basis of the latter the computation of the bond order and bond length, resp. becomes feasible.

The paper is divided into two parts. In the first the general method is elaborated. The results obtained here are very general and suitable for wide-ranging application as no special assumption is made regarding the individual units. Hence they are valid even in those cases when not only π-electrons play an important role within the unit (the problems of polymers). In the second part of the paper the treatment of the polyrylene series is presented. This serves on the one hand as an illustration for the use of the method, and on the other allows the investigation of some interesting properties of the series.

I

The perturbation method for the treatment of systems built up from identical units

1. Basic assumptions and notation

The one-electron function extending over the whole molecule (molecular orbital) is assumed to be the linear combination of functions centered on the individual atoms (atomic orbitals)

$$\psi_i = c_{1i} u_1 + c_{2i} u_2 + \ldots + c_{ni} u_n, \tag{1}$$

where ψ_i is the i-th molecular orbital and u_k represents the electron function belonging to atom k. The determination of the coefficients is carried out with the variation method by minimizing the energies of the individual orbitals according to the following secular equations :

$$\sum_k \left(H_{ik} - \varepsilon \, S_{ik} \right) c_{ik} = 0, \qquad i = 1, 2, \ldots, n, \tag{2}$$

where

$$H_{ik} = \int u_i^* H u_k \, d\tau, \qquad S_{ik} = \int u_i^* u_k \, d\tau.$$

H represents the Hamiltonian derived on the basis of the effective potential acting upon the single electrons and ε the energy of the individual molecular orbital.

In each orbital two electrons with opposite spins can be accomodated, the filling up of the orbitals takes place in order of increasing energy.

Regarding the matrix elements the following simplifications are used:

a) $S_{rr} = 1$, $S_{sr} = 0$ (the overlap integral is taken to be 0).

b) H_{ik} differs from zero only in the case when $i = k$, or when i and k are indices belonging to neighbouring atoms.

These simplifications allow an alternative discussion of the problem:

Let us consider the coefficients of the i-th molecular orbital $(c_{1i}, c_{2i}, \ldots, c_{ni})$ to be the components of an n-dimensional vector and denote the corresponding vector with $\mathfrak{r}_i$. In view of the above-mentioned simplifications the secular equations (2) are equivalent to the matrix eigenvalue problem as follows:

$$H\mathfrak{r}_i = \varepsilon_i \mathfrak{r}_i \, . \tag{3}$$

This method of treatment proves to be very useful in the investigation of systems built up from identical units when using perturbation calculation.

2. The perturbation calculation

Consider a series, the members of which can be obtained by the repetition of a given unit. The connection between the single units be as follows:

a) The i-th unit should be joined only to the preceding and the subsequent unit. (As an exception serve the first and the last units which are joined to the second and the last but one, resp.)

b) The connection between the units following each other be of the same structure.

More detailed, the latter means the following. Let us number the atoms of the first unit from 1 to e. In the following units the same numbering is used, the upper index indicating only the unit involved. Connection of identical structure means that the joining between the units following each other is as follows:

$$
\begin{array}{ccc}
f-1 & f & f+1 \\
-\begin{pmatrix} s & r \\ s' & r' \\ s'' & r'' \end{pmatrix}- & -\begin{pmatrix} s & r \\ s' & r' \\ s'' & r'' \end{pmatrix}- & -\begin{pmatrix} s & r \\ s' & r' \\ s'' & r'' \end{pmatrix}-
\end{array} \tag{4}
$$

The matrix of the n-th member of the series occurring in equation (3) has according to the above the following form:

$$H = \begin{vmatrix} A & B & . & . & . & . \\ \tilde{B} & A & B & . & . & . \\ . & \tilde{B} & A & B & . & . \\ . & . & . & \tilde{B} & A & B \\ . & . & . & . & \tilde{B} & A & B \\ . & . & . & . & . & \tilde{B} & A \end{vmatrix}, \tag{5}$$

where, A, $\tilde{B}$, B mean matrices of order e. A represents a matrix of a single unit, B corresponds to the connection between units f and $f + 1$, its non-vanishing elements are : H_{rs}, $H_{r's'}$ $H_{r''s''}$ ... etc. $\tilde{B}$ corresponds to the connection between the units f and $f - 1$. This is the transpose of B, its non-vanishing elements are H_{sr} $H_{s'r'}$ $H_{s''r''}$ etc. The eigenvectors $\mathfrak{a}_i, \ldots, \mathfrak{a}_e$ of the matrix A are vectors of dimension e, their components being $\mathfrak{a}_i \{c_{1i}, c_{2i}, \ldots, c_{ei}\}$ and the corresponding eigenvalues ε_i. In the following only those cases will be investigated in detail in which the basic unit has no degenerate eigenvalue. The calculations can be easily generalized for the case when some eigenvalues are degenerate.

For matrix of the unperturbed problem that matrix should be chosen where B and $\tilde{B}$, resp. are zero matrices. From the physical point of view this means that no connection between the individual units is assumed. The eigenvalues and eigenvectors of this matrix can be given at once : its eigenvalues are identical with those of the basic unit with the difference that each eigenvalue ε_i is n-fold degenerate, n linearly independent eigenvectors belong to it. By choosing the latter we have a high degree of arbitrariness, as, if n linearly independent vectors belong to the i-th eigenvalue, any linear combination of them is an eigenvector as well and belongs to the same eigenvalue. It is appropriate to choose the n linearly independent eigenvectors as follows :

$$\mathfrak{r}^0_{i1} = \begin{pmatrix} \mathfrak{a}_i \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad \mathfrak{r}^0_{i2} = \begin{pmatrix} 0 \\ \mathfrak{a}_i \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad \ldots \mathfrak{r}^0_{in} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ \mathfrak{a}_i \end{pmatrix}, \tag{6}$$

$\mathfrak{r}^0_{i1}, \mathfrak{r}^0_{i2}, \ldots, \mathfrak{r}^0_{in}$ are vectors of dimension n. e. Each "component" occurring in formula (6) represents a vector of dimension e (the corresponding eigenvector of A).

Let us consider the difference between the original matrix and that corresponding to the unperturbed problem to be a perturbation matrix.

$$
P = \begin{vmatrix}
\cdot & B & \cdot & \cdot & \cdot & \cdot \\
\widetilde{B} & \cdot & B & \cdot & \cdot & \cdot \\
\cdot & \widetilde{B} & \cdot & B & \cdot & \cdot \\
\cdot & \cdot & \widetilde{B} & \cdot & B & \cdot \\
\cdot & \cdot & \cdot & \widetilde{B} & \cdot & B \\
\cdot & \cdot & \cdot & \cdot & \widetilde{B} & \cdot
\end{vmatrix},
\tag{7}
$$

In order that this really represents a perturbation it is necessary that the connection between the single units should be looser than those within the single units. Thus the non-vanishing matrix elements of B and $\widetilde{B}$ are smaller regarding their numerical values than the elements of matrix A.

On the basis of (6) and (7) the following relation is easily verified :

$$
(\mathfrak{r}^0_{jh} \, P \mathfrak{r}^0_{ik}) = \begin{cases}
(\mathfrak{a}_j \, B \, \mathfrak{a}_i), & \text{if} & h = k - 1, \\
(\mathfrak{a}_j \, \widetilde{B} \, \mathfrak{a}_i), & \text{if} & h = k + 1, \\
0, & \text{if} & \begin{cases} h \neq k - 1, \\ h \neq k + 1, \end{cases}
\end{cases}
\tag{8}
$$

where

$$
(\mathfrak{a}_i \, B \, \mathfrak{a}_i) = (\mathfrak{a}_i \, \widetilde{B} \, \mathfrak{a}_i) = \sum c_{ri} \, H_{rs} \, c_{si} \equiv \gamma_i,
$$

$$
(\mathfrak{a}_i \, B \, \mathfrak{a}_j) = (\mathfrak{a}_j \, \widetilde{B} \, \mathfrak{a}_i) = \sum c_{ri} \, H_{rs} \, c_{sj} \equiv \vartheta^{ij}_1 \equiv \vartheta^{ji}_2,
\tag{9}
$$

$$
(\mathfrak{a}_j \, B \, \mathfrak{a}_i) = (\mathfrak{a}_i \, \widetilde{B} \, \mathfrak{a}_j) = \sum c_{si} \, H_{sr} \, c_{rj} \equiv \vartheta^{ji}_1 \equiv \vartheta^{ij}_2.
$$

3. The examination of the perturbed eigenvalues

In the first step the exact zero-order coefficients are determined together with the first-order energy correction which is evaluated on the basis of the usual secular equations

$$
\mathfrak{p}^0_{is} = \sum_{l=1}^{n} a^i_{sl} \, \mathfrak{r}^0_{il}, \qquad \sum a^i_{sl} \left[(\mathfrak{r}^0_{is} \, P \mathfrak{r}^0_{il}) - \varepsilon'_i \, \delta_{sl} \right] = 0.
\tag{10}
$$

Using (8) and (9) it follows that $(\mathfrak{r}^0_{is} \, P \mathfrak{r}^0_{il})$ is zero, except when $s = l + 1$ and $s = l - 1$, resp., in which case its value is γ_i. The secular determinant is the following

$$\begin{vmatrix} -\varepsilon_i' & \gamma_i & . & . & . & . \\ \gamma_i & -\varepsilon_i' & \gamma_i & . & . & . \\ . & \gamma_i & -\varepsilon_i' & \gamma_i & . & . \\ . & . & \gamma_i & -\varepsilon_i' & \gamma_i & . \\ . & . & . & \gamma_i & -\varepsilon_i' & \gamma_i \\ . & . & . & . & \gamma_i & -\varepsilon_i' \end{vmatrix} = 0 \,. \tag{11}$$

The secular determinant (11) and the corresponding secular equations resp. are well known (they occur for instance in the problem of the linear chain polyenes). The zeros of the determinant and the coefficients of the system of equations can be given at once:

$$\varepsilon_{ik}' = 2\,\gamma_i \cos ka \,, \tag{12}$$

$$a_{sl}^i = \sqrt{\frac{2}{n+1}} \sin sl\,a \,, \qquad a = \frac{\pi}{n+1} \,. \tag{13}$$

In the first-order approximation the level corresponding to the i-th eigenvalue is split into n levels, the magnitude of the splitting is $2\gamma_i$ (i. e. the distance of the highest and lowest levels originating from the i-th level). It is worth wile to mention that a_{sl}^i does not depend on i, accordingly the upper index is omitted in the following.

The second-order energy correction is as follows:

$$\varepsilon_{ik}'' = \sum_{j \neq i}^{e} \frac{1}{\varepsilon_i - \varepsilon_j} \sum_{l=1}^{n} (\mathfrak{p}_{ik}^0 \, P \mathfrak{p}_{j\,l}^0)^2 \,.$$

Using (10) and (13), further taking (8) and (9) into account

$$(\mathfrak{p}_{ik}^0 \, P \mathfrak{p}_{jl}^0) = \sum_{u=1}^{n} \sum_{v=1}^{n} a_{ku} a_{lv} (\mathfrak{r}_{iu}^0 \, P \mathfrak{r}_{jv}^0) = \vartheta_1^{ij} \sum_{v=2}^{n} a_{k\,v-1}\,a_{lv} +$$

$$+ \vartheta_2^{ij} \sum_{v=1}^{n-1} a_{k\,v+1}\,a_{lv} = \vartheta_1^{ij} \sum_{v=1}^{n} a_{k\,v-1}\,a_{lv} + \vartheta_2^{ij} \sum_{v=1}^{n} a_{k\,v+1}\,a_{lv} \tag{14}$$

is obtained.

(In the last transformation the fact is used that $a_{k0} = a_{k\,n+1} = 0$.) Consequently

$$\sum_{l=1}^{n} (\mathfrak{p}_{ik}^0 \, P \mathfrak{p}_{jl}^0)^2 = \sum_{l=1}^{n} \sum_{v=1}^{n} \sum_{w=1}^{n} \left\{ (\vartheta_1^{ij})^2 \, a_{k\,v-1}\,a_{K\,w-1} + (\vartheta_2^{ij})^2 \, a_{k\,v+1}\,a_{k\,w+1} + \right.$$

$$\left. + \vartheta_1^{ij}\,\vartheta_2^{ij} \, (a_{k\,v-1}\,a_{k\,w+1} + a_{k\,v+1}\,a_{k\,w-1}) \right\} a_{lv}\,a_{lw} \,.$$

Summing over l with given v and w and taking into account that $\sum\limits_{l=1}^{n} a_{lv}\, a_{lw} = \delta_{vw}$ the following is obtained:

$$
\sum_{l=1}^{n} (\mathfrak{p}_{ik}^{0}\, P \mathfrak{p}_{jl}^{0})^{2} = (\vartheta_{1}^{ij})^{2} \sum_{v=1}^{n} a_{kv-1}^{2} + (\vartheta_{2}^{ij})^{2} \sum_{v=1}^{n} a_{kv+1}^{2} + 2\, \vartheta_{1}^{ij}\, \vartheta_{2}^{ij} \sum_{v=1}^{n} a_{k\,v-1}\, a_{k\,v+1} =
$$

$$
= (1 - a_{kn}^{2})\, (\vartheta_{1}^{ij})^{2} + (1 - a_{k1}^{2})\, (\vartheta_{2}^{ij})^{2} + 2\, \vartheta_{1}^{ij}\, \vartheta_{2}^{ij}\, (1 - na_{k1}^{2})\ .
$$

Let us introduce the following notation:

$$
\zeta_{\varkappa\lambda}^{i} = \sum_{j\neq i}^{e} \frac{\vartheta_{\varkappa}^{ij}\, \vartheta_{\lambda}^{ij}}{\varepsilon_{i} - \varepsilon_{j}}\ , \qquad \varkappa, \lambda = \left\{ \begin{array}{l} 1\ , \\ 2\ . \end{array} \right. \tag{15}
$$

In view of the fact that $a_{k1}^{2} = a_{kn}^{2}$ (namely $a_{kf} = -(-1^{k})\, a_{kn+1-f}$), the second-order energy correction is as follows:

$$
\varepsilon_{ik}'' = (1 - a_{k1}^{2})\, (\zeta_{11}^{i} + \zeta_{22}^{i}) + 2\, (1 - na_{k1}^{2})\, \zeta_{12}^{i} =
$$

$$
= \left(1 - \frac{2}{n+1}\, \sin^{2} k\, \frac{\pi}{n+1} \right) (\zeta_{11}^{i} + \zeta_{22}^{i}) + 2 \left(1 - \frac{2n}{n+1}\, \sin^{2} k\, \frac{\pi}{n+1} \right) \zeta_{12}^{i}\ . \tag{16}
$$

In the above results it is essential that both in the first-order and in the second-order eigenvalue correction we succeeded in separating them into factors, in the first of which only quantities referring to the basic unit occur (γ_{i}, $\zeta_{K\lambda}^{i}$), whereas in the second only data characterizing the series.

4. Examination of the perturbed eigenvectors

For the investigation of the bond order and the bond length, resp. the perturbed eigenvectors are needed. For the examination of the bonds connecting the single units it is sufficient to investigate the first-order perturbation, however, for the calculation of the bond orders corresponding to bonds within the units also the second-order perturbation calculation is needed. The perturbed eigenvectors in the second-order approximation are as follows:

$$
\mathfrak{r}_{ik}'' = \mathfrak{p}_{ik}^{0} + \mathfrak{p}_{ik}^{1} + \mathfrak{p}_{ik}^{2}\ , \tag{17}
$$

where

$$
\mathfrak{p}_{ik}^{1} = \sum_{m\neq k}^{n} (im/ik;\ 1)\, \mathfrak{p}_{im}^{0} + \sum_{j\neq i}^{e} \sum_{m=1}^{n} (jm/ik;\ 1)\, \mathfrak{p}_{jm}^{0}\ , \tag{18}
$$

$$
\mathfrak{p}_{iK}^{2} = (ik/ik;\ 2)\, \mathfrak{p}_{ik}^{0} + \sum_{m\neq k}^{n} (im/ik;\ 2)\, \mathfrak{p}_{im}^{0} + \sum_{j\neq i}^{e} \sum_{m=1}^{n} (jm/ik;\ 2)\, \mathfrak{p}_{jm}^{0}\ . \tag{19}
$$

The coefficients occurring in formulae (18) and (19) are according to Corson [2] the following.

$$(im/ik\,;\,1) = \sum_{j \neq i}^{e} \sum_{l=1}^{n} \frac{(\mathfrak{p}_{im}^{0} P \mathfrak{p}_{jl}^{0})\,(\mathfrak{p}_{jl}^{0} P \mathfrak{p}_{ik}^{0})}{(\varepsilon_i - \varepsilon_j)\,(\varepsilon_{ik}' - \varepsilon_{im}')}\,; \tag{20}$$

$$(jm/ik\,;\,1) = \frac{(\mathfrak{p}_{jm}^{0} P \mathfrak{p}_{ik}^{0})}{\varepsilon_i - \varepsilon_j}\,; \tag{21}$$

$$(ik/ik\,;\,2) = -\frac{1}{2} \sum_{\mu \neq i}^{e} \sum_{v=1}^{n} (uv/ik\,;\,1)^2\,; \tag{22}$$

$$(im/ik\,;\,2) = \sum_{j \neq i}^{e} \sum_{v=1}^{n} \frac{(\mathfrak{p}_{im}^{0} P \mathfrak{p}_{jv}^{0})\,(jv/ik\,;\,2)}{\varepsilon_{ik}' - \varepsilon_{im}'} - \frac{\varepsilon_{ik}''\,(im/ik\,;\,1)}{\varepsilon_{ik}' - \varepsilon_{im}'}\,; \tag{23}$$

$$(jm/ik\,;\,2) = -\sum_{u \neq i}^{e} \sum_{v=1}^{n} \frac{(\mathfrak{p}_{jm}^{0} P \mathfrak{p}_{\mu r}^{0})\,(uv/ik\,;\,1)}{\varepsilon_j - \varepsilon_i} - \frac{\varepsilon_{ik}'\,(\mathfrak{p}_{jm}^{0} P \mathfrak{p}_{ik}^{0})}{(\varepsilon_j - \varepsilon_i)^2}\,. \tag{24}$$

Of the vector equations (17)—(19), which correspond to vectors of dimension $n.\ e.$ let us consider those parts which correspond to the f-th components, these will be vector equations of dimension e.

In other words that vector will be investigated the components of which are the coefficients belonging to the atoms of the f-th unit,

$$(\mathfrak{r}_{ik}'')_f = a_{kf}\,\mathfrak{a}_i + (\mathfrak{p}_{ik}^1)_f + (\mathfrak{p}_{ik}^2)_f\,, \tag{25}$$

where

$$(\mathfrak{p}_{ik}^1)_f = \left(\sum_{m \neq k}^{n} (im/ik\,;\,1)\,a_{mf}\right) \mathfrak{a}_i + \sum_{j \neq i}^{e} \left(\sum_{m=1}^{n} (jm/ik\,;\,1)\,a_{mf}\right) \mathfrak{a}_j\,, \tag{26}$$

$$(\mathfrak{p}_{ik}^2)_f = \left[(ik/ik\,;\,2)\,a_{kf} + \sum_{m \neq k}^{n} (im/ik\,;\,2)\,a_{mf}\right] \mathfrak{a}_i + \sum_{j \neq i}^{e} \left(\sum_{m=1}^{n} (jm/ik\,;\,2)\,a_{mf}\right) \mathfrak{a}_j\,. \tag{27}$$

In the evaluation of the sums occurring in formulae (26) and (27) the procedure given in detail in the preceding paragraph for the evaluation of the second-order correction of the eigenvalues is followed. The matrix elements $(\mathfrak{p}_{im}^{0} P \mathfrak{p}_{jl}^{0})$ are given on the basis of equation (14). In the following steps, we succeeded using formulae (20)—(24), in separating the summing of each term into two parts, the first containing only the quantities relating to the basic units, the second those related to the a_{ik}-s

$$a_{ik} = \sqrt{\frac{2}{n+1}}\,\sin ik\,\frac{\pi}{n+1}\,.$$

In the sums referring to the basic unit the following notations are used:

$$a_\varkappa^{ij} = \frac{\vartheta_\varkappa^{ij}}{\varepsilon_i - \varepsilon_j} \tag{28}$$

$$\varrho_{\varkappa\lambda}^i = \sum_{j \neq i}^e a_\varkappa^{ij}\, a_\lambda^{ij}\ , \tag{29}$$

$$\pi_{\varkappa\lambda}^{ij} = \sum_{u \neq i}^e a_\varkappa^{iu}\, \vartheta_\lambda^{uj}\ , \tag{30}$$

$$\tau_{\varkappa\lambda\mu}^{\ i} = \sum_{j \neq i}^e a_\varkappa^{ij}\, \pi_{\lambda\mu}^{ij} \equiv \sum_{j \neq i}^e \sum_{u \neq i}^e \frac{\vartheta_\varkappa^{ij}\, \vartheta_\lambda^{iu}\, \vartheta_\mu^{uj}}{(\varepsilon_i - \varepsilon_j)\,(\varepsilon_i - \varepsilon_u)}\ . \tag{31}$$

Using the definition of $\vartheta_\varkappa^{ij}$-s the following identities are easily verified:

$$\tau_{121}^i = \tau_{212}^i \equiv \varkappa_i\ , \qquad \tau_{122}^i = \tau_{211}^i \equiv \lambda_i, \qquad \tau_{221}^i = \tau_{222}^i \equiv \mu_i\ , \tag{32}$$

$$\tau_{112}^i = \tau_{111}^i \equiv \nu_i\ .$$

The sums relating to the a_{ik}-s can be divided into two groups: the sums occurring in the first group can be evaluated simply by utilizing the orthogonality properties of the a_{ik}-s

$$\left(\sum_{t=1}^n a_{it}\, a_{kt} = \delta_{ik}\right).$$

The sums occurring in the further steps are as follows:

$$\sum_{t=1}^n a_{m,\, t-1}\, a_{k,t-1} = \delta_{mk} - a_{mn}\, a_{kn}\ ; \qquad \sum_{t=1}^n a_{m,\, t+1}\, a_{k,\, t+1} = \delta_{mk} - a_{m_1}\, a_{k_1},$$

$$\sum_{t=1}^n \left(a_{m,\, t-1}\, a_{k,t+1} + a_{m,\, t+1}\, a_{k,\, t-1}\right) = 2\,\cos 2k\alpha \cdot \delta_{mk} + a_{k_1}\, a_{m_1} + a_{mn}\, a_{kn}\ ,$$

$$\sum_{t=1}^n \left(a_{m,\, t-1}\, a_{k,\, t+2} + a_{n,\, t+1}\, a_{k,\, t-2}\right) = 2\cos 3k\alpha\, \delta_{mk} + a_{k2}\, a_{m1} + a_{k,\, n-1}\, a_{mn}\ .$$

The other group consists of the following type of sums:

$$\sum_i^{\lambda\mu f} = \sum_{m \neq k}^n \frac{a_{k\lambda}\, a_{m\mu}\, a_{mf}}{(\cos k\alpha\ - \cos m\alpha)^i}\ . \tag{34}$$

The computation of the latter is given in detail in the Appendix.

All other sums occurring in the computation can be reduced to the above-mentioned ones utilizing the orthogonality properties of the a_{ik}-s and other simple trigonometrical relations.

Concerning the sums occurring in the perturbation calculation of the eigenvectors the following results are obtained by means of the method outlined above:

$$a)\quad \sum_{m \neq k}^n (im/ik;1),\quad a_{nf} = \frac{1}{2\gamma_i}\left\{-\zeta_{11}^i \sum_1^{nnf} - \zeta_{22}^i \sum_1^{11f} + \zeta_{12}^i\left(\sum_1^{11f} + \sum_1^{nnf}\right)\right\}. \tag{35}$$

For the computation the following relation was used :

$$\sum_{l=1}^{n} (\mathfrak{p}_{im}^{0} \ P\mathfrak{p}_{jl}^{0})(\mathfrak{p}_{jl}^{0} \ P\mathfrak{p}_{ik}^{0}) = \sum_{l=1}^{n} \left\{ \vartheta_{1}^{ij} \sum_{t=1}^{n} a_{m\,t-1} \, a_{lt} + \vartheta_{2}^{ij} \sum_{t=1}^{n} a_{m\,t+1} \, a_{lt} \right\} \cdot$$

$$\left\{ \vartheta_{1}^{ji} \sum_{s=1}^{n} a_{ls} \, a_{k\,s+1} + \vartheta_{2}^{ji} \sum_{s=1}^{n} a_{ls} \, a_{k\,s-1} \right\} =$$

$$= \left(\vartheta_{1}^{ij} \right)^2 \sum_{t=1}^{n} a_{mt-1} \, a_{kt-1} + \left(\vartheta_{2}^{ij} \right)^2 \sum_{t=1}^{n} a_{mt+1} \, a_{kt+1} + \vartheta_{1}^{ij} \vartheta_{2}^{ij} \sum_{t=1}^{n} (a_{mt+1} \, a_{kt-1} + a_{mt-1} \, a_{kt+1}) \, .$$

b) $$(jm/ik\,;1) = a_{2}^{ij} \sum_{t=1}^{n} a_{mt} \, a_{kt+1} + a_{1}^{ij} \sum_{t=1}^{n} a_{nt} \, a_{kt-1} \, , \tag{36}$$

$$\sum_{j\neq i}^{e} \left(\sum_{m=1}^{n} (jm/ik\,;1) \, a_{mf} \right) \mathfrak{a}j = a_{kf+1} \, \check{b}_i + a_{kf-1} \, \check{c}_i \, , \tag{37}$$

where

$$\check{b}_i = \sum_{j\neq i}^{e} a_{2}^{ij} \, \mathfrak{a}_j \, , \qquad \check{c}_i = \sum_{j\neq i}^{e} a_{1}^{ij} \, \mathfrak{a}_j \, . \tag{38}$$

where

c) $$(ik/ik\,;2) \, a_{kf} = - \frac{1}{2} \left\{ (1 - a_{k1}^{2})(\varrho_{11}^{i} + \varrho_{22}^{i}) + 2(1-na_{k1}^{2}) \, \varrho_{12}^{i} \right\} a_{kf} \, . \tag{39}$$

The deduction of this part is essentially identical with the procedure outlined for the second-order perturbation calculation of the eigenvalue.

d) $$(jm/ik\,;2) = \frac{1}{\varepsilon_i - \varepsilon_j} \left\{ \delta_{mk} \left(\pi_{12}^{ij} + \pi_{21}^{ij} - \gamma_i [a_{1}^{ij} + a_{2}^{ij}] \right) + \right.$$
$$+ a_{m1} \, a_{k1} \left(\pi_{11}^{ij} - \pi_{21}^{ij} \right) + a_{mn} \, a_{kn} \left(\pi_{22}^{ij} - \pi_{12}^{ij} \right) + \tag{40}$$
$$\left. + \sum_{s}' a_{ms} \, a_{k\,s-2} \left(\pi_{11}^{ij} - \gamma_i \, a_{1}^{ij} \right) + \sum_{s}' a_{ms} \, a_{k\,s+2} \left(\pi_{22}^{ij} - \gamma_i \, a_{2}^{ij} \right) \right\} \, .$$

With the method outlined in a) the first member of (24) is as follows :

$$\frac{1}{\varepsilon_i - \varepsilon_j} \left\{ \pi_{12}^{ij} \sum_{s} a_{m\,s-1} \, a_{k\,s-1} + \pi_{21}^{ij} \sum_{s} a_{m\,s+1} \, a_{k\,s+1} + \right.$$
$$\left. + \pi_{11}^{ij} \sum_{s} a_{m\,s+1} \, a_{k\,s-1} + \pi_{22}^{ij} \sum_{s} a_{m\,s-1} \, a_{k\,s+1} \right\} \, .$$

The second member :

$$- \frac{2 \gamma_i \cos k\alpha}{(\varepsilon_i - \varepsilon_j)^2} \left\{ \vartheta_{1}^{ij} \sum_{t} a_{mt} \, a_{kt-1} + \vartheta_{2}^{ij} \sum_{t} a_{mt} \, a_{kt+1} \right\} \, .$$

Using the following relation :

$$2 \cos k\alpha \cdot a_{kf} = a_{kf+1} + a_{kf-1}$$

and (33) the above result is obtained

$$\sum_{j\neq i}^{e} \left(\sum_{m=1}^{n} (jm/ik\,;2)\ a_{mf} \right) a_j = a_{kf}\,\breve{\vartheta}_i + a_{kf-2}\,\breve{n}_i + a_{kf+2}\,\breve{f}_i\,, \tag{41}$$

where:

$$\breve{\vartheta}_i = \sum_{j\neq i}^{e} \frac{\varphi^{ij}}{\varepsilon_i - \varepsilon_j}\,a_j\,, \qquad \breve{n}_i = \sum_{j\neq i}^{e} \frac{\psi^{ij}}{\varepsilon_i - \varepsilon_j}\,a_j\,, \qquad \breve{f}_i = \sum_{j\neq i}^{e} \frac{\chi^{ij}}{\varepsilon_i - \varepsilon_j}\,a_j\,. \tag{42}$$

$$\varphi^{ij} = \begin{cases} \pi_{12}^{ij} + \pi_{21}^{ij} - \gamma_i\left(a_1^{ij} + a_2^{ij}\right)\,, & \text{if} \quad f\neq 1\,, f\neq n\,. \\[2mm] \pi_{12}^{ij} - \gamma_i\,a_2^{ij}\,, & \text{if} \quad f = 1\,, \\[2mm] \pi_{21}^{ij} - \gamma_i\,a_1^{ij}\,, & \text{if} \quad f = n\,. \end{cases} \tag{43}$$

ψ^{ij}, χ^{ij} can be given in an analogous manner, however, their explicit form is not needed in the following.

e)

$$\sum_{m\neq k}^{n} (im/ik\,;2)\ a_{mf} = \frac{1}{2\gamma_i}\left\{ (\lambda_i - \mu_i)\sum_1^{12f} + (\lambda_i - \nu_i)\sum_1^{nn-1f} + \right.$$

$$+ \left(\gamma_i\varrho_{11}^{i} - \nu_i\right)\sum_1^{n-1nf} + \left(\gamma_i\varrho_{22}^{i} - \mu_i\right)\sum_1^{21f} + (\lambda_i - \gamma_i\varrho_{12}^{i})\left(\sum_1^{21f} + \sum_1^{n-1\,nf}\right)\right\} -$$

$$- \frac{1}{(2\gamma_i)^2}\left\{ (1 - a_{k1}^2)(\zeta_{11}^{i} + \zeta_{22}^{i}) + 2\,(1 - na_{k1}^2)\,\zeta_{12}^{i}\right\}\,. \tag{44}$$

$$\left\{ -\zeta_{11}^{i}\sum_2^{nnf} - \zeta_{22}^{i}\sum_2^{11f} + \zeta_{12}^{i}\left(\sum_2^{11f} + \sum_2^{nnf}\right)\right\}.$$

In deducing formula e) the chief steps are the following: For the calculation of the first member of (23) formula (40) is used and in a manner analogous to that described above the following is obtained:

$$\sum_j \sum_v (\mathfrak{p}_{im}^0\,P\mathfrak{p}_{jv}^0)(jv/ik\,;2) = [\nu_i + \varkappa_i - \gamma_i(\varrho_{11}^{i} + \varrho_{21}^{i})]\sum_t a_{kt-1}\,a_{kt} +$$

$$+ [\mu_i + \varkappa_i - \gamma_i(\varrho_{12}^{i} + \varrho_{22}^{i})]\sum_t a_{nt+1}\,a_{kt} + (\lambda_i - \mu_i)\,a_{k1}\,a_{m2} + (\lambda_i - \nu_i)\,a_{kn}\,a_{mn-1} +$$

$$+ \left(\nu_i - \gamma_i\varrho_{11}^{i}\right)\left(\sum_t a_{mt}\,a_{kt-1} - a_{mn}\,a_{kn-1}\right) + \left(\mu_i - \gamma_i\varrho_{22}^{i}\right)\left(\sum_t a_{mt}\,a_{kt+1} - a_{m1}\,a_{k2}\right) +$$

$$+ \left(\lambda_i - \gamma_i\varrho_{12}^{i}\right)\sum_t (a_{mt+1}\,a_{kt-2} + a_{mt-1}\,a_{kt+2}) =$$

$$= \left(\varkappa_i - \gamma_i\varrho_{12}^{i}\right)\sum \underbrace{(a_{mt-1} + a_{mt+1})}_{2\,a_{mt}\cos m\,\alpha}\,a_{kt} + (\nu_i + \mu_i - \gamma_i\,[\varrho_{11}^{i} + \varrho_{22}^{i}])\sum_{t=1}^{n}\underbrace{(a_{kt+1} + a_{kt-1})}_{2\,a_{kt}\cos k\,\alpha}\,a_{mt} +$$

$$+ (\lambda_i - \mu_i)\,a_{k1}\,a_{m2} + (\lambda_i - \nu_i)\,a_{kn}\,a_{mn-1} -$$

$$- \left(\nu_i - \gamma_i\varrho_{11}^{i}\right)a_{mn}\,a_{kn-1} - \left(\mu_i - \gamma_i\varrho_{22}^{i}\right)a_{m1}\,a_{k2} +$$

$$+ \left(\lambda_i - \gamma_i\varrho_{12}^{i}\right)(a_{m1}a_{k2} + a_{mn}\,a_{kn-1})$$

in the case of $m\neq k$ the values of the first two sums are zero. Summing, the first part of e) is obtained. For the computation of the second part of the formula the same line must be followed as in the evaluation of a) and c) resp.

Using the formulae $a)$—$e)$ and the values of $\sum_i^{\varkappa\lambda f}$ the perturbed eigen-vectors take up the following forms :

$$(\mathfrak{p}_{ik}^0)_f = a_{kf}\,\mathfrak{a}_i\,,$$

$$(\mathfrak{p}_{ik}^1)_f = a_{kf+1}\,(D_i\,\mathfrak{a}_i + \breve{b}_i) - a_{kf-1}\,(E_i\,\mathfrak{a}_i - \breve{c}_i)\,,$$

$$(\mathfrak{p}_{ik}^2)_f = a_{kf}\,(F_i\,\mathfrak{a}_i + \breve{g}_i) + \frac{a_{kf}}{\sin^2 ka}\,G_i\,\mathfrak{a}_i + \qquad (45)$$

$$+ a_{kf+2}\,(H_i\,\mathfrak{a}_i + \breve{n}_i) + a_{kf-2}\,(I_i\,\mathfrak{a}_i + \breve{f}_i)\,.$$

D_i — ... — I_i are independent of k, each can be separated into sums of products, the first factor of which contains quantities referring only to the basic unit, and the second to the data of the series (n, f). The separations for the quantities needed in the further steps are given in the following.

$$D_i = \frac{n - 2f}{n + 1}\,A_i - \bar{A}_i\,, \qquad E_i = D_i + \frac{2}{n + 1}\,A_i\,.$$

$$F_i = -\frac{1}{2}\,(\varrho_{11}^i + \varrho_{22}^i) + \frac{A_i}{2\,\gamma_i^2\,(n + 1)}\,[e\,(B_i + C_i) + 2\,C_i] + \qquad (46)$$

$$+ \frac{\bar{A}_i}{2\gamma_i^2}\,(B_i + C_i)\,(n + 1 - 2f), \qquad \begin{matrix} f \neq 1\,, \\ f \neq n\,, \end{matrix}$$

$$\overset{(1)}{F_i} = \overset{(n)}{F_i} = F_i - \frac{1}{4}\,\varrho_{1-}^i + \frac{3}{4}\,\varrho_{22}^i\,, \qquad \begin{matrix} f = 1\,, \\ f = n\,, \end{matrix}$$

where

$$A_i = \zeta_{12}^i - \frac{1}{2}\,(\zeta_{11}^i + \zeta_{12}^i)\,, \qquad \bar{A}_i = \frac{1}{2}\,(\zeta_{11}^i - \zeta_{22}^i)\,,$$

$$B_i = \zeta_{12}^i + \frac{1}{2}\,(\zeta_{11}^i + \zeta_{22}^i)\,, \qquad C_i = \frac{1}{n + 1}\,\left[n\,\zeta_{12}^i - \frac{1}{2}\,[\zeta_{11}^i + \zeta_{22}^i]\right], \quad (47)$$

$$e = \frac{1}{3}\,\{3\,(n + 1 - f)^2 - 2\,(n + 1)^2 + 3f^2 - 1\}\,.$$

5. Calculation of bond order

Formulae (45) allow the investigation of the bond order by means of the perturbation method. The partial bond order belonging to the (ik)-th level and referring to two neighbouring atoms a and b, will be defined as follows :

$$p_{ab}^{ik} = c_a^{ik}\,c_b^{ik}\,. \qquad (48)$$

Taking components a and b, of the vector equations (45) the coefficients belonging to atom a and b occurring in the f-th unit are obtained. The bond order is obtained by summing the partial bond orders over the occupied levels and multiplying them with the number of electrons in the individual levels. In the following only the case in which the basic unit contains an even number of atoms will be investigated in detail. In it the summation over i runs from 1 to $e/2$ and over k from 1 to n. Summing over k the following two relations are used :

$$\sum_{K=1}^{n} a_{kl}\, a_{km} = \delta_{lm}, \qquad \sum_{k=1}^{n} \frac{a_{kf}^2}{\sin^2 ka} = \frac{2}{n+1} f(n+1-f) . \qquad (49)$$

The bond order is computed including the second-order members.

a) Both atoms are in the same unit

Because of (45) the first-order correction vanishes and thus within the individual units only the second-order correction is added to the original bond order. Likewise the third-order correction vanishes too. All this shows that the bonds within the single units are affected only to a small extent.

b) The two atoms are in different, neighbouring units

In this case the value of the second-order correction is zero.

In the case of $a)$ and $b)$, resp. the correction of the bond order is the following :

a) $\quad \Delta p_{ab} = 2 \sum_{i=1}^{e/2} \left\{ (D_i^2 + E_i^2)\, c_a^i c_b^i + D_i \, (c_a^i \, \check{b}_b^i + c_b^i \, \check{b}_a^i) + E_i \, (c_a^i \, \check{c}_b^i + c_b^i \, \check{c}_a^i) + \right.$

$$\left. + \check{b}_a^i \check{b}_b^i + \check{c}_a^i \check{c}_b^i + (c_a^i \check{d}_b^i + c_b^i \check{d}_a^i) + \right. \qquad (50)$$

$$\left. + 2\, c_a^i c_b^i \left[F_i + \frac{2}{n+1}\, f(n+1-f)\, G_i \right] \right\} .$$

b) $\quad \Delta p_{ab} = 2 \sum_{i=1}^{e/2} \left\{ (D_i - E_i)\, c_a^i c_b^i + c_a^i \check{b}_b^i + c_b^i \check{b}_a^i \right\}, \qquad \begin{array}{l} a \to f, \\ b \to f+1 . \end{array} \qquad (51)$

With this result the purpose outlined in the introduction is achieved also in the case of the bond orders, as the use of formulae (50) and (51) allow the uniform treatment of the members of the series. After determining the quantities relating to the basic unit the bond order for any member of the series can be easily computed with the help of formulae (50), (51) and (46).

II

The investigation of the polyrylene series with the perturbation method

1. *Justification of the use of the method*

The members of the polyrylene series can be obtained by the successive condensation of naphtalene. A few members were investigated with the molecular orbital method with respect to their physical and chemical properties by PAUNCZ and WILHEIM [3]. According to their results the method renders the main features of the spectra qualitatively correctly, however, from the quantitative point of view strong deviations occur. As for the first transition a too small excitation energy is obtained and this result is essentially less good than was to be expected from the usual power of the molecular orbital method.

The second interesting conclusion is that the bond lengths corresponding to the bonds connecting the single units are the longest among all the bond lengths occurring in the molecule ; this shows that the connection between the individual units is essentially weaker than the connection within the units. Thus, the condition for the applicability of the perturbation method given in paragraph I.2 is fulfilled and this allows a uniform examination of the series.

In the treatment of the condensed aromatic compounds using the molecular orbital method the following assumptions are made :

The most important physical and chemical properties of the molecule are determined by the so called π-electron distributions. Their number equals the number of the carbon atoms. The molecular orbital given in I.1 is a linear combination of these π-electron atomic orbitals. Regarding the H_{ik} matrix elements the following assumptions are used :

$$\text{a) } H_{ii} = \alpha ; \qquad \text{b) } H_{ik} = \beta ;$$

i and k are indices of neighbouring atoms.

Let us divide each equation in the systems of equations (2) by β and introduce the following notation :

$$\frac{\alpha - \varepsilon}{\beta} = - x . \tag{52}$$

In the investigation of PAUNCZ and WILHEIM the value of all integrals $\int u_i^* H u_k \, d\tau$ corresponding to neighbouring atoms was assumed to be equal.

The perturbation method renders possible the investigation of the problem of how the eigenvalues and bond orders are affected if allowance is made for the fact that the values of the integrals $\int u_i^* H u_k \, d\tau$ are different in the molecule,

as a consequence of the differences in the bond lengths. In the following it will only be taken into account that the bond lengths corresponding to the bonds connecting the individual units are greater than the length of the average bond within the individual units. Consequently, the value of β belonging to the former is smaller than that of the average β_{av}. In the further steps allowance should be made for the fact that even within the units the bond lengths are not the same and consequently the β-values are different. This problem will not be investigated in this paper.

It follows from the above that our aim is not the full exploration of the problem, but only the examination of the extent to which the method elaborated in I contributes to the explanation of the physical and chemical behaviour of the series.

Let us denote the quotient of β and β_{av} by λ. Allowing for the dependence of β on the bond length, the value 0,8 will be used for λ.

2. Symmetry considerations

Each member of the series has the common property of being symmetrical with respect to the vertical axis of the molecule, the molecular orbitals are therefore either symmetrical or antisymmetrical with respect to that axis. This fact allows a simplification in the computations, as the value of ϑ_1^{ij} and ϑ_2^{ij} occurring in each quantity and referring to the basic unit is zero, if i and j refer to two states belonging to different symmetry species. Therefore, the summations can be carried out separately for the symmetrical and antisymmetrical levels. In the case of the eigenvalues this means that for a symmetrical eigenvalue the corrections are calculated only from the symmetrical ϑ_1^{ij} and ϑ_2^{ij}, respectively and the situation is analogous in the case of the antisymmetrical eigenvalues.

A further simplification arises from the fact that the basic unit (the naphtalene molecule) is symmetrical with respect to the horizontal axis. As the atoms occurring in the bonds connecting the single units are arranged symmetrically about the horizontal axis, their coefficients are either identical or have opposite sign. With an appropriate numbering of the levels

$$\vartheta_1^{ij} = (-1)^{\,i+j}\,\vartheta_2^{ij}\,.$$

From this follows :

$$\varrho_{11}^i = \varrho_{22}^i\,, \qquad \zeta_{11}^i = \zeta_{22}^i\,.$$

It is worth while to mention the fact that in the levels $\pm\beta$ of the basic unit both the values of ϑ_1^{ij} and ϑ_2^{ij} are zero for all j-s. As a consequence all expressions

occurring in the perturbation formulae vanish as all of them are derived from the $\vartheta_\varkappa^{ij}$-s. This consideration remains valid even for the higher approximations, hence the levels $\pm\beta$ are not at all affected by the perturbation, the only difference being that they occur with the corresponding multiplicity : in the molecule containing n units the levels $+\beta$ and $-\beta$ occur n times. This result is in complete agreement with the conclusions of BRADBURN, COULSON and RUSHBROKE [4], who investigated the eigenvalues of the same compounds using RUTHERFORD's method [5]. From the above it follows that these levels do not contribute to the correction of the bond orders.

3. Results of calculation

Our results obtained by means of formulae (13) and (16) referring to the perturbation calculation of the eigenvalues are shown in Table I below. The bond lengths calculated with the use of bond orders (COULSON's semi-empirical method [6]) are illustrated in the Figure.

Both in the case of the eigenvalues and the bond lengths the calculations were performed for the following cases: a) The strength of the bond connecting the units is taken to be equal to the strength of other bonds ($\lambda = 1$). b) The results of the preceding calculation can be compared with those obtained by the straightforward application of the molecular orbital method (direct calculation), where the same assumptions were used. c) In the further calculation allowance was made for the fact that the strength of the bonds between the units is weaker than the strength of the other bonds. Accordingly, λ is taken to be 0,8. In the case of the eigenvalues the levels corresponding to states which are symmetrical and antisymmetrical, resp. with respect to the vertical axis are shown separately.

In Table I only the positive levels are shown. The absolute values of the negative levels are identical with those of the positive levels. The perturbation preserves the property of the levels characteristic for alternant hydrocarbons. The levels corresponding to $x = 1$ possessing the given multiplicity are not shown in Table I as their value does not change under the influence of the perturbation.

4. The discussion of the results

The results will be discussed from two points of view. On hand of the given example it will be examined to what extent the method elaborated in I is useful for the investigation of series, and further the dependence of the quantities occurring in the investigation of the polyrylene series on the parameter λ will be investigated. To judge the applicability of the method we have to compare the first and second columns of the Figure and Table I, resp.
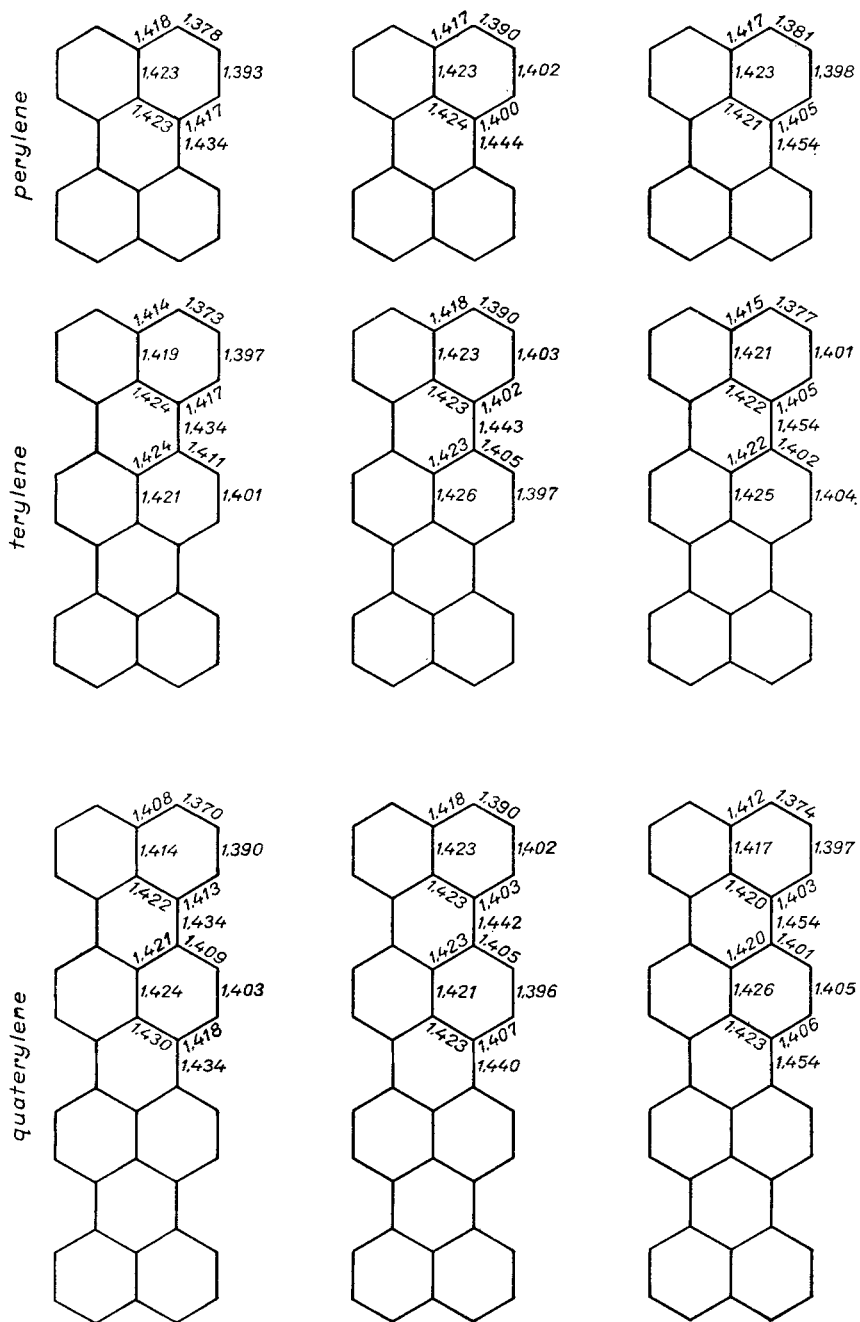
Fig. 1

　　　　　　　　　　　　　　　R. PAUNCZ

Surveying the data of the Table it can be concluded that the eigenvalues calculated by means of the perturbation method show an acceptable agreement with the values calculated by the direct method using the same assumptions. In view of the fact that the calculation of the eigenvalues by means of the perturbation

Table I

Symmetrical levels			x_i	Antisymmetrical levels		
pert. ($\lambda = 1$)	($\lambda = 1$) direct	pert. ($\lambda = 0,8$)		pert. ($\lambda = 1$)	($\lambda = 1$) direct	pert. ($\lambda = 0,8$)
$n = 2$ perylene						
2,5642	2,5863	2,4990		1,8345	1,8794	1,7786
2,2030	2,1819	2,2100		1,5581	1,5321	1,5576
1,6195	1,5936	1,5566		1,0581	1	0,9575
0,9809	1	1,0458		0,3345	0,3474	0,3787
$n = 3$ terylene						
2,6650	2,6614	2,5690		1,8973	1,9419	1,8280
2,4324	2,4550	2,3857		1,7633	1,7709	1,7110
2,1442	2,1299	2,1604		1,5065	1,4970	1,5154
1,7677	1,7171	1,6726		1,2135	1,1361	1,0810
1,2656	1,2703	1,2790		0,7633	0,7092	0,7110
0,8647	0,8895	0,9502		0,1903	0,2410	0,2624
$n = 4$ quaterylene						
2,6907	2,6902	2,5978		1,9166	1,9659	1,8449
2,5613	2,5666	2,4861		1,8633	1,8649	1,7889
2,3379	2,3669	2,3073		1,6925	1,7044	1,6517
2,1061	2,1010	2,1302		1,4694	1,4780	1,4871
1,8458	1,7837	1,7330		1,2783	1,2053	1,1342
1,4659	1,4377	1,4387		1,0015	0,8914	0,8992
1,0713	1,1004	1,1231		0,5543	0,5473	0,5414
0,8130	0,8359	0,9064		0,1077	0,1845	0,1978

Table II
The wavelength corresponding to the first allowed transition ($m\mu$)

	direct ($\lambda = 1$)	pert. ($\lambda = 0,8$)	experiment
perylene	621	564	438
terylene	893	818	516
quaterylene ...	1168	1087	

method is very simple, it is worth while to use this treatment for a rapid approximative determination of the level-system of series.

The agreement in the case of the bond length is somewhat weaker but acceptable. The difference between the two results calculated by the two methods is not greater than the error occurring in the present experimental determination of bond lengths. The method is especially suitable for the investigation of the bond length of bonds connecting units as the calculation is relatively simple.

In making a comparison one must take into account the fact that the case $\lambda = 1$ is disadvantageous for the convergence of the perturbation treatment, in the case $\lambda < 1$ a better agreement can be expected. The other advantage of the use of the perturbation method consists in the fact that it renders easily possible the examination of the dependence on λ of the quantities characterising the molecule, i. e. the dependence on the strength of the bonds connecting the single units.

From this point of view the behaviour of the polyrylene series can be examined by comparing the second and third columns of Table I and the Figure, resp. For the eigenvalues it is found that for $\lambda = 0,8$ the distance of the highest and lowest occupied levels decreases as compared to the case $\lambda = 1$. The levels get closer to each other and simultaneously the distance corresponding to the first allowed transition increases. In Table II the wavelengths corresponding to the first allowed transition are summarized.

From the data it can be seen that parallel to the increasing of the bond length of the bonds connecting the units the wavelength corresponding to the first allowed transition decreases, that means a better result is obtained than in the calculation of PAUNCZ and WILHEIM. The magnitude of the decrease is, however, not yet big enough, because even in this case the wavelength of the first transition turns out to be too great. This shows that other factors besides that mentioned above have to be taken into account, in order to get an acceptable agreement with the experiment (configurational interaction, etc.)

The calculations relating to the bond lengths show that the bond lengths, mainly those within a unit, are not much affected by the perturbation.

Acknowledgement

APPENDIX

In the investigation of the eigenvectors using the perturbation method the following sums occur :

$$\sum_{i}^{\lambda \mu f} = \sum_{m \neq k}^{n} \frac{a_{k\lambda}\, a_{m\mu}\, a_{mf}}{(\cos k a - \cos m a)^{i}} \quad , \qquad a = \frac{\pi}{n+1} \; .$$

Their computation can be reduced to the evaluation of the followings sums :

$$^{(i)}A_k^f = \sum_{m \neq k}^{n} \frac{\cos mf\, a}{(\cos ka - \cos ma)^i} \quad . \tag{A.1}$$

In view of the fact that, beside the completion of the above-mentioned task, their use makes possible the evaluation of some quantities occurring in the perturbation treatment of the polyenes, their investigation seems useful.

From their definition the following properties follow :

a) $\quad ^{(i)}A_k^{-f} = {}^{(i)}A_k^f \quad .$ $\qquad$ *b)* $\quad ^{(i)}A_k^{n+1-f} = \sum_{m \neq k}^{n} \frac{(-1)^m \cos mf\, a}{(\cos ka - \cos ma)^i} \quad \cdot$

c) $\quad ^{(i)}A_k^{f-1} - 2 \cos ka\, {}^{(i)}A_k^f + {}^{(i)}A_k^{f+1} = -2^{(i-1)}A_k^f \quad .$

In the latter case the following identity was used :

$$\cos m(f-1)\,a - 2\cos ka\, \cos mf a + \cos m(f+1)\,a = -2(\cos ka - \cos ma)\cos mf a \quad .$$

With *a)* and *c)* is obtained for $f = 0$

$$^{(i)}A_k^1 = \cos ka \quad {}^{(i)}A_k^0 - {}^{(i-1)}A_k^0 \quad . \tag{A.2}$$

It is sufficient to evaluate $^{(i)}A_k^0$ as on this basis (knowing the value of $^{(i-1)}A_k^0$ from equation(2)) $^{(i)}A_k^1$, further using *c)* all others can be successively evaluated.

1. $\qquad\qquad\qquad {}^{(0)}A_k^0 = \sum_{m \neq k}^{n} \cos m0 \cdot a = n - 1 \quad , \tag{A.3}$

$$^{(0)}A_k^f = \sum_{m=1}^{n} \cos mf a - \cos Kf a = \begin{cases} -1 - \cos kf a \,, & \text{if} \quad f \text{ is even,} \\ -\cos kf a \,, & \text{if} \quad f \text{ is odd.} \end{cases} \tag{A.4}$$

2. For the evaluation of $^{(1)}A_k^0$ the fact is used that $\cos k\, a$ is the k-th root of the Tschebyheff polynomial of n-th degree, of second kind.

$$U_n(\cos \vartheta) = \frac{\sin(n+1)\vartheta}{\sin \vartheta} \quad . \tag{A.5}$$

With the use of the factored form of the polynomial

$$U_n(\cos \vartheta = \prod_{m=1}^{n} (\cos \vartheta - \cos ma) \tag{A.6}$$

$$\sum_{m=1}^{n} \frac{1}{\cos \vartheta - \cos ma} = \frac{U'_n}{U_n} = g(\cos \vartheta) \tag{A.7}$$

is obtained, where

$$g(\cos \vartheta) = \frac{1}{\sin^2 \vartheta} \left\{ \cos \vartheta - (n+1) \cos(n+1)\vartheta \cdot \frac{1}{U_n} \right\} \quad . \tag{A.8}$$

(The derivation occurs with respect to $x = \cos \vartheta$.)

On the basis of (7) $^{(i)}\Lambda_k^0$ can be obtained as follows :

$$^{(1)}\Lambda_k^0 = \lim_{\vartheta \to ka} \left(g \left(\cos \vartheta \right) - \frac{1}{\cos \vartheta - \cos ka} \right) \ . \tag{A. 9}$$

The prescribed passage to limit can be performed with the repeated application of l'Hospital's rule, the result being :

$$^{(1)}\Lambda_k^0 = \frac{3}{2} \frac{\cos ka}{\sin^2 ka} \ . \tag{A. 10}$$

On the basis of equations (2), (3) and (10) :

$$^{(1)}\Lambda_k^1 = -n + \frac{\cos^2 ka + 2}{2 \sin^2 ka} \ . \tag{A. 11}$$

In the following we shall verify that for $^{(1)}\Lambda_k^f$ the formula is valid :

$$^{(1)}\Lambda_k^f = [f - (n+1) \, sgf] \, \frac{\sin kfa}{\sin ka} + \frac{\cos kfa \cos ka + h}{2 \sin^2 ka} \ , \tag{A. 12}$$

where

$$h = \begin{cases} 2 \cos ka \ , & \text{if } f \text{ even} \, , \\ 2 \ , & \text{if } f \text{ odd} \, ; \end{cases} \qquad sgf = \begin{cases} 1 \, , & > 0, \\ 0 \, , & \text{if} \quad f = 0, \\ -1 \, , & < 0. \end{cases}$$

For $f = 0$ and $f = 1$ formula (12) is the same as (10) and (11). To prove it one must only show that formula (12) satisfies equation c). Let f be even, then the following relation must be fulfilled :

$$^{(1)}\Lambda_k^{f-1} - 2 \cos ka \ ^{(1)}\Lambda_k^f + {}^{(1)}\Lambda_k^{f+1} = 2 + 2 \cos kfa \ .$$

Substituting (12)

$$[f - (n+1) \, sgf] \, \frac{1}{\sin ka} \left\{ \underbrace{\sin k \, (f-1) \, a - 2 \cos ka \sin kfa + \sin k \, (f+1) \, a}_{= \, 0} \right\} - $$

$$- \frac{\sin k \, (f-1) \, a - \sin k \, (f+1) \, a}{\sin ka} + \frac{\cos k \, a}{2 \sin^2 ka} \left\{ \underbrace{\cos k \, (f-1)a - 2 \cos ka \cos kfa + \cos k(f+1)a}_{= \, 0} \right\} + $$

$$+ \frac{4 - 4 \cos^2 ka}{2 \sin^2 ka} = 2 + 2 \cos kfa$$

is obtained.

Thus the correctness of the formula is proved. In a completely analogous manner the proof can also be performed in the case of odd f.

3. The calculation of $^{(2)}\Lambda_k$ occurs in a manner analogous to the procedure given in detail above. By means of equation (7) :

$$\sum_{m=1}^{n} \frac{1}{(\cos \vartheta - \cos ma)^2} = - g' \left(\cos \vartheta \right) \, ,$$

$$^{(2)}\Lambda_k^0 = \lim_{\vartheta \to ka} \left\{ - g' \left(\cos \vartheta \right) - \frac{1}{(\cos \vartheta - \cos ka)^2} \right\} \ . \tag{A. 13}$$

The limit operation gives the following result :

$$^{(2)}\Lambda_k^0 = \frac{4(n+1)^2 + 17}{12 \sin^2 ka} - \frac{11}{4 \sin^4 ka} \ . \tag{A.14}$$

Using equations (2), (10) and (16) the following is obtained :

$$^{(2)}\Lambda_k^1 = \frac{4(n+1)^2 - 1}{12 \sin^2 ka} \cos ka - \frac{11 \cos ka}{4 \sin^4 ka} \ . \tag{A.15}$$

The formula for $^{(2)}\Lambda_k^f$ for arbitrary f is as follows :

$$^{(2)}\Lambda_k^{ff} = \frac{4(n+1)^2 - 12f(n+1)\,sgf + 6f^2 + 53}{12 \sin^2 ka} \cos kfa + \frac{(n-3)sgf - f}{\sin^3 ka} \cdot \cos ka \, \sin kfa -$$

$$- \frac{11 \cos kfa}{4 \sin^4 ka} + \frac{2 \cos(|f| - 2)ka}{\sin^4 ka} + h^{(2)} \ ,$$

$$h^{(2)} = \begin{cases} - \dfrac{3 + \cos 2ka}{2 \sin^4 ka} \ , & \text{if } f \text{ is even} , \\[3mm] - \dfrac{2 \cos ka}{\sin^4 ka} \ , & \text{if } f \text{ is odd.} \end{cases} \tag{A.16}$$

The demonstration of formula (16) occurs in the same manner as that of (12) above. Substituting $f = 0$ and $f = 1$, equations (14) and (15) are obtained. In the further steps using simple trigonometrical relations it can be proved that (16) satisfies the following equation :

$$^{(2)}\Lambda_k^{f-1} - 2 \cos ka \ ^{(2)}\Lambda_k^f + {}^{(2)}\Lambda_k^{f+1} = - 2 \ ^{(1)}\Lambda_k^f \ .$$

On the basis of (12) and (16) all $\Sigma_2^{\times \, \lambda f}$ occurring in the second-order perturbation calculation can be calculated. The results are given below.

$$(n+1)\,sgf - 2f \equiv g$$

$$\sum_1^{11f} + \sum_1^{nnf} = \frac{1}{n+1}\left\{(g-1)\,a_{kf+1} - (g+1)\,a_{kf-1}\right\} \ , \qquad \Bigg\}$$
$$\sum_1^{11f} - \sum_1^{nnf} = sgf\left\{a_{kf+1} - a_{kf-1}\right\} \ . \qquad\qquad\qquad \tag{A.17}$$

$$\sum_1^{12f} + \sum_1^{nn-1f} = \frac{1}{n+1}\left\{(g-3)\,a_{kf+2} + 2\,a_{kf} - (g+3)\,a_{kf-2}\right\} \ , \qquad \Bigg\}$$
$$\sum_1^{12f} - \sum_1^{nn-1f} = sgf\left\{a_{kf+2} - a_{kf-2}\right\} \ . \qquad\qquad\qquad \tag{A.18}$$

$$\sum_1^{21f} + \sum_1^{n-1nf} = \frac{1}{n+1}\left\{(g-1)\,a_{kf+2} - 2\,a_{kf} - (g+1)\,a_{kf-2}\right\} \ , \qquad \Bigg\}$$
$$\sum_1^{21f} - \sum_1^{n-1nf} = sgf\left\{a_{kf+2} - a_{kf-2}\right\} \ . \qquad\qquad\qquad \tag{A.19}$$

$$\sum_2^{11f} + \sum_2^{nnf} = \frac{1}{n+1}\left\{\frac{3(n+1-f)^2 - 2(n+1)^2 + 3f^2 - 1}{3} + \frac{1}{\sin^2 ka}\right\}a_{kf} \ , \qquad \Bigg\}$$
$$\sum_2^{11f} - \sum_2^{nnf} = (n+1-2f)\,a_{kf} \ . \qquad\qquad\qquad\qquad\qquad\qquad \tag{A.20}$$

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ПРИМЕНЕНИЕ МЕТОДОВ МАЛЫХ ВОЗМУЩЕНИЙ ПРИ КВАНТОВО-ХИМИЧЕСКОМ ИССЛЕДОВАНИИ СИСТЕМ, СОСТОЯЩИХ ИЗ ТОЖДЕСТВЕННЫХ ЧАСТЕЙ

Р. ПАУНЦ

Р е з ю м е

В работе даётся исследование молекулы, состоящей из тождественных элементарных единиц, методом малых возмущений. С помощью рассуждений, опирающихся на простой вариант метода молекулярной траектории, удаётся разделить результат на сумму произведений, как в случае значения энергии, так и порядка связи. Один из сомножителей содержит только такие данные, которые относятся к основному элементу, а другой сомножитель зависит от данных ряда.

Во второй части показана применимость этого метода на примере полириленового ряда. Результат расчета показывает, что метод применим с успехом и с его помощью можно исследовать, каким образом зависят характеристики ряда от прочности связи между отдельными элементами.