Theoret. Chim. Acta (Berl.) 61, 193–202 (1982)

THEORETICA CHIMICA ACTA

Changes in the Band Structure of a Simple Polymer on Lowering the Translational Symmetry

D. A. Morton-Blake

Department of Chemistry, Trinity College, Dublin 2, Ireland

By combining the one-dimensional "crystal orbitals" of a simple polymer under the action of a perturbation which extends the repeating segment from one site to *n* sites a perturbation method allows the band structure of the new chain to be calculated. As well as estimating the band gaps to a fairly good agreement with the results of the "direct" method the present technique shows how specific gaps created by the symmetry-lowering will respond to the characteristics of the perturbations imposed.

Key words: Polymer orbitals – Periodic perturbations – Band structure.

1. Introduction

Since the development of quantum chemical methods to treat regular, infinite lattices [1, 2] a number of methods have recently been proposed [3] to try to incorporate disorder in these lattices and thereby investigate the removal or reduction of the translational symmetry. Among these has been one involving the reduction of short-range order of a one-dimensional regular polymer chain by increasing the size of the unit segment [4, 5]. This work showed that if the perturbations of the original chain were small, as would for instance obtain from certain (periodic) internal rotations, the new conformation could be treated by combining certain energy-band states (k-states or microstates) by adding terms describing the perturbation to the zeroth order hamiltonian.

In the present paper we shall study the effect of reducing the short-term symmetry of a periodic chain $-X-X-X-$, where X depicts an atom or group of atoms and will be referred to as a "site", by enlarging the unit segment through a periodic perturbation of the sites. In Ref. [5] the perturbations enlarging the unit segment were applied to the interactions *between* the sites – since conformational changes were being investigated the sites themselves retained their regular-chain characteristics: our task now is to try to answer questions such as "What is the result on the band structure of the simple regular polymer $\cdots -X-X-X- \cdots$ when the sites X experience periodic perturbations which result in the chain $\cdots -X_1-X_2-X_3-X_1-X_2-X_3-X_1- \cdots$?". We shall suppose that the environmental changes which transform X to X_j are sufficiently small to permit the use of perturbation theory, and we shall work with a general size n of the asymmetric segment $-(X_1-X_2- \cdots -X_n)-$ which will allow us to infer the result of decreasing the regularity of the chain by letting n become progressively larger.

Physically, such a model might describe the imposition of a set of different structural changes in the sites as might obtain in a polypeptide chain or protein when some periodic sequence of amino-acid residues —NHR—CO— differing in side group R confers a set of periodic electronegativity changes $\delta\alpha_j$ on the main chain atoms. Alternatively the model might represent a simple polymer chain adsorbed on, or trapped in, a crystal lattice, and thus subjected to a periodicity derived from the lattice. We might also consider the system as an extension of that in an earlier work [6] in which a perturbation was applied at a unique site in the chain (simulating chemical attack) to one in which simultaneous attack occurs at specific periodic sites along the chain. Also important is its relevance to the possibility of creating "made to measure" band gaps in semiconducting polymers [7] by controlled substitutions by impurity atoms.

In all these examples a method such as the one envisaged would eventually permit an approximate quantum chemical treatment of periodic chains whose unit segments would entail such a large number of sites and basis functions as to forbid treatment by existing methods. For certain biopolymers, particularly proteins, for which the possibility of electrical conductivity [8] is of biological interest, and for which partial electron delocalization on the chain precludes model calculations on constituent fragments, such a method might prove useful.

2. Theory

2.1. The Unperturbed System

Consider a one-dimensional chain of N identical sites where N is an (odd) infinite number. Then applying the Born–Kármán boundary conditions for a cyclic lattice the electronic "crystal orbital" of the chain is expressed by the usual Bloch function [1]

$$\Psi(k) = N^{-1/2} \sum_{j=0}^{\pm\frac{1}{2}(N-1)} e^{ijk} \chi_j \tag{1}$$

where χ_j is the electronic wave function associated with the jth site and the one-dimensional wave vector k used here is a continuous variable in the range $0 \leq k < 2\pi$. If the Hamiltonian of the chain is H^0 and if the orbitals involved in χ_j are such that the interaction $\beta^{(J)} \equiv \int \chi_{j_1}^* H^0 \chi_{j_2}\, d\tau$ depends only on the separation

$J \equiv |j_1 - j_2|$ of the centres χ_{j_1} and χ_{j_2} (and not on their relative orientation), then the energies $E^0(k)$ satisfying the equation

$$H^0\Psi(k) = E^0(k)\Psi(k) \tag{2}$$

in an independent-electron model are given by

$$E^0(k) = \int \Psi^*(k) H^0 \Psi(k)\, d\tau = \alpha + 2 \sum_{J=1}^{+\frac{1}{2}(N-1)} \beta^{(J)} \cos jk.$$

The continuum of energy values $E^0(k)$ for the defined range constitutes an energy band, and there will be as many such bands as there are functions like χ_j on the jth site. However since we are restricting our present attention to only one set of functions the Bloch orbital functions $\Psi(k)$ and energies $E^0(k)$ need not carry a band label. Purely for the convenience of keeping the later numerical applications of the theory to a maximum simplicity the Hückel nearest-neighbour restrictions will be imposed. We therefore omit the terms with $J > 1$ from the dispersion energy expression, leaving

$$E^0(k) = \alpha + 2\beta \cos k \tag{3}$$

but it must be remembered that the theory does not depend on this restriction.

2.2. The Perturbation

If V describes a periodic perturbation of the chain as described in Sect. 1 so that the hamiltonian of the resulting system is $H \equiv H^0 + V$ the functions $\Psi(k)$ satisfying Eq. (2) become zeroth order functions which may be mixed by V.

The orthonormality of the $\Psi(k)$ follows from their form Eq. (1) and requires that the general matrix element of the new hamiltonian H be

$$\begin{aligned} H(k_1, k_2) &= E^0(k_1)\delta(k_1, k_2) + V(k_1, k_2) \\ V(k_1, k_2) &= N^{-1} \sum_{j_1, j_2} e^{i(j_2 k_2 - j_1 k_1)} \int \chi_{j_1}^* V \chi_{j_2}\, d\tau. \end{aligned}$$

But since, in this work, we are perturbing the sites alone, and not the interactions between them, the power of V will be restricted to producing non-zero integrals of the kind appearing on the right hand side of the last equation only when $j_1 = j_2$. Writing the resulting integral as v_j this quantity may be identified as the increment in the Hückel α term of the j-th site as a result of the perturbation. The perturbation matrix element thus becomes

$$\begin{aligned} V(k_1, k_2) = N^{-1}[&v_1\{e^{i\Delta k} + e^{i\Delta k(n+1)} + e^{i\Delta k(2n+1)} + \cdots\} \\ &+ v_2\{e^{2i\Delta k} + e^{i\Delta k(n+2)} + e^{i\Delta k(2n+2)} + \cdots\} \\ &\vdots \\ &+ \\ &\vdots \\ &+ v_n\{e^{in\Delta k} + e^{2in\Delta k} + e^{3in\Delta k} + \cdots\}] \\ = N^{-1}[1 + e^{in\Delta k} &+ e^{2in\Delta k} + \cdots][v_1 e^{i\Delta k} + v_2 e^{2i\Delta k} + \cdots + v_n e^{in\Delta k}]. \end{aligned} \tag{4}$$

The presence of the initial factor N^{-1} requires that if the expression is not to vanish the first bracketed factor, consisting of N/n terms, must sum to a value which is at least an appreciable fraction of N. But because of the cyclic nature of these terms a *general* value of Δk results in a vanishing sum. The only way in which mutual annihilation would not occur would be if the k interval obeyed the conditions $\Delta k = 0, 2\pi/n, 4\pi/n$, etc. However the states available for combination are just those in the first Brillouin zone, so the k interval is subject to the further restriction $|\Delta k| \leq 2\pi$. Respect for both these conditions yields

$$\left.\begin{aligned} &\Delta k = 2\pi l/n \\ &\text{where} \\ &l = 0, 1, 2, \ldots, n-1. \end{aligned}\right\} \tag{5}$$

Application of Eq. (5) to Eq. (4) causes the infinitesimal and infinite factors to be replaced by the finite quantity n^{-1}, thus giving the final expression of the perturbation matrix element which, depending on the interval between the k values rather than on the values themselves, can be completely characterized by the label l:

$$\left.\begin{aligned} &V_l \equiv V(k, k+2\pi l/n) = n^{-1} \sum_{j=1}^{n} v_j\, e^{2\pi i j l/n} \\ &\text{where} \\ &l = 0, 1, 2, \ldots, n-1. \end{aligned}\right\} \tag{6}$$

Substitution of Eq. (6) into the expression for the general element of the energy matrix,

$$H(k, k+2\pi l/n) = E^0(k)\delta(l) + V_l$$

generates the energy matrix $\mathbb{H}$ whose eigenvalues are identical to those of the standard $n \times n$ complex Hückel tight-binding energy matrix that would be obtained by considering a unit segment of n sites. We shall refer to the latter procedure as the direct calculation and that involving the calculation of V_l as a perturbation method.

2.3. *Perturbation Energy*

The energy E_k^2 of the perturbed chain, to second-order is given by

$$E_k^2 = E_k^0 + V_0 + \sum_{l=1}^{n-1} \frac{|V_l|^2}{\Delta_l(k)} \tag{7}$$

where the zeroth-order energy E_k^0 is given by Eq. (3), while the first order correction term V_0 is the diagonal perturbation matrix element given by Eq. (6) when $l = 0$. The quantity $\Delta_l(k)$ is the energy interval between state k and one of the states allowed to couple with it as explained in the previous section. This interval, defined as $\Delta_l(k) = E_k^0 - E_{k+2\pi l/n}^0$ is given by

$$\left.\begin{aligned} &\Delta_l(k) = 2\beta[\cos k - \cos(k + 2\pi l/n)] \\ &\text{where} \\ &l = 1, 2, \ldots, n-1 \end{aligned}\right\} \qquad (8)$$

and where we have used Eq. (3).

Unlike the other quantities in the first- and second-order contributions to the energy expressed in Eq. (7) $\Delta_l(k)$ is k-dependent and for each permitted value of l becomes zero twice in the complete range $0 \leq k < 2\pi$ of the Brillouin zone, or once in the half range used in Fig. 1 (with $n = 5$) to display the non-redundant energy features. Each zero value of $\Delta_l(k)$ confers an isolated singularity on E_k^2 at the k points for which the direct calculation predicts discontinuities corresponding to *band gaps*, i.e. at $k = \pi/n, 2\pi/n, \ldots, \pi(n-1)/n$ in the half-zone. As finiteness is restored to E_k^2 from $\pm\infty$ (depending on the direction from the singularity) band gaps will also be described by Eq. (7), but it is not yet obvious how adequate second order perturbation theory is in the region of the turning points to predict the magnitudes of the band gaps.

Since each $\Delta_l(k) = 0$ condition in Fig. 1 corresponds to a unique value of l the latter can be used to label the band gaps. It is easy to see that in the half-range $0 \leq k \leq \pi$ band gaps occurring at k values defined by $k = (n-l)/n$ correspond to the zeros of the expression in Eq. (8).

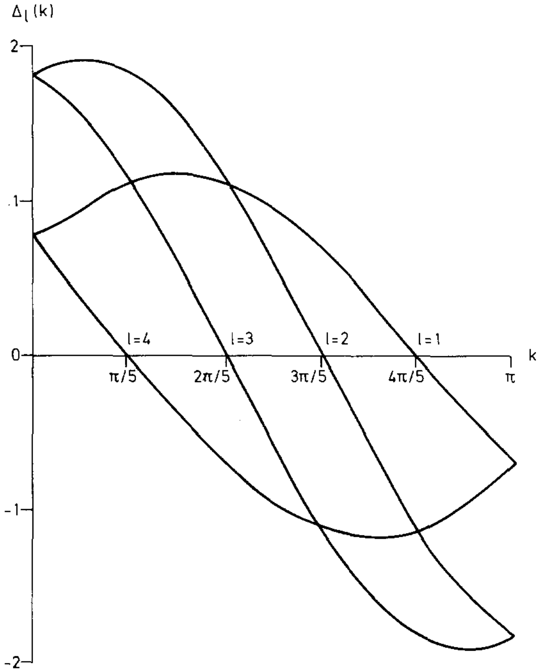

Fig. 1. Energy interval $\Delta_l(k)$ in β units between states k and $k + 2\pi l/n$ for a single-site polymer chain with $n = 5$ and dispersion energy given by Eq. (3)

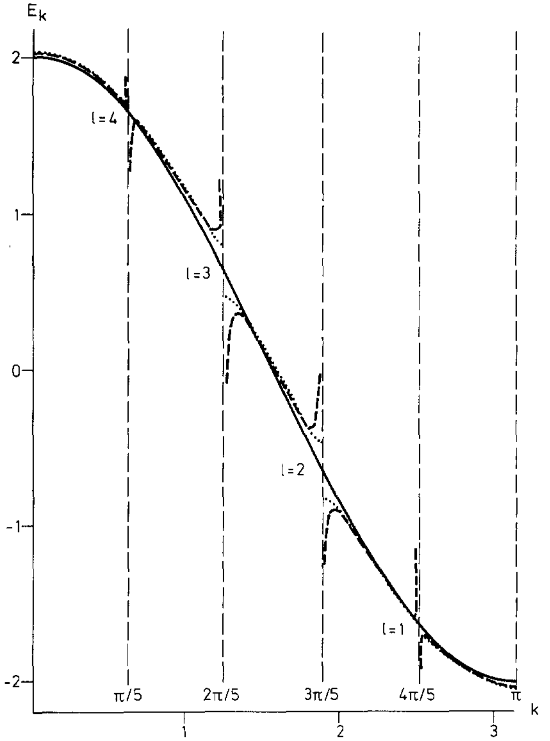

Fig. 2. Dispersion energy E_k^0 for a single-site chain (———) and the result E_k of periodic perturbations (0.1 −0.2 0.3 −0.4 0.2) by (a) the direct method (· · · ·) and (b) Eq. (7) (– – – –). All energies are multiples of β

3. Application

3.1. The Dispersion Energy

A polymer chain was subjected to the arbitrary set of periodic perturbations $v_1 = 0.1\beta$, $v_2 = -0.2\beta$, $v_3 = 0.3\beta$, $v_4 = -0.4\beta$, $v_5 = 0.2\beta$, whose average is zero, thus defining a new translational symmetry based on an enlarged, 5-site, unit segment. In Fig. 2 the dispersion curve (a) is the result of the "direct" calculation[1] in which the 5×5 complex energy matrix has diagonal elements $\alpha + v_j$ ($j = 1$ to 5) and curve (b) was calculated with the same set v_j producing the V_l terms defined by Eqs. (6) and (7), together with the energy intervals $\Delta_l(k)$ given by Eq. (8). (The dispersion curve E_k^0 of the unperturbed chain is also shown for comparison.) Except for the singularity regions at $k = (n-l)\pi/n$ Eq. (7) accounts quite well for the effect of the perturbation, including the *creation* of band gaps. Although these are a little exaggerated it is satisfying that the general appearance of the energy band structure of an n-site chain can be calculated in terms of the perturbations imposed on the corresponding 1-site chain.

---

[1] The dispersion energy calculated by the latter method consisted of 5 energy bands. In order to draw curve (b) in Fig. 2 (and also those of Fig. 3) these bands have been extended into successive Brillouin zones and the k values re-scaled so that the resulting E_k curve refers to the same Brillouin zone as that (E_k^0) of the unperturbed chain, and is therefore also directly comparable with curve (a).

3.2. The Band Gap and the Unit Segment

Note that the four band gaps in Fig. 2 as calculated by either method are generally unequal, and as they probably depend on the nature of the perturbation it seems desirable to investigate this important effect.

Eqs. (6) and (7) show that in regions $k \sim (n-l)\pi/n$ where $\Delta_l(k)$ tends to zero the E_k curves on either side of the singularity repel each other the more, the greater the value of $|V_l|^2$. We must therefore see how this description of the formation of the gaps depends on the perturbations and their distribution.

If the whole chain were placed in a uniform environment so that all the αs were changed equally we would have $v_1 = v_2 = \cdots = v_n = \text{const.}\ (v)$ for any size of segment we chose. Then the only non-zero V_l possible is the diagonal element $l = 0$ because Eq. (6) shows that all other contributions consist of mutually-annihilating terms. The result is then, as expected, a shift of the energy by the first-order term

$$V_0 = \frac{1}{n}\sum_{j=1}^{n} v_j = v, \qquad \text{with no band gaps created.}$$

A similar result obtains in the opposite extreme for a truly aperiodic chain. For, allowing the aperiodicity to be attained by letting the size n of the asymmetric unit segment go to infinity, the random nature of the perturbations v_j in Eq. (6) will also lead to zero sum in all cases except $l = 0$. The theory therefore predicts an E_k curve which is simply shifted from E_k^0 by the average perturbation

$$\frac{1}{n}\sum_{j=1}^{n} v_j, \qquad \text{and so again there are no band gaps.}$$

Now consider an intermediate case, in which a finite size n of the asymmetric unit segment confers a true translational symmetry of the chain. The sums

$$\frac{1}{n}\sum_{j=1}^{n} v_j\, e^{2\pi i j/n}$$

now no longer vanish generally for $l \neq 0$, and thus second order perturbation elements V_l are generated which, by Eqs. (6) and (7), determine the band gap through the quantity

$$|V_l|^2 \equiv \left[\sum_{j=1}^{n} v_j \cos(2\pi j l/n)\right]^2 + \left[\sum_{j=1}^{n} v_j \sin(2\pi j l/n)\right]^2. \tag{9}$$

Eq. (9) shows that the set of perturbations v_j ($j = 1$ to n) contributing most importantly to $|V_l|^2$ would be one for which the sequence of v_j along the unit segment displays a (stationary) wave-like variation in relative amplitude and nodal behaviour. Thus the larger energy gaps at $k = 2\pi/5$ and $3\pi/5$ ($l = 3$ and $l = 2$) in the above example, shown in Fig. 2, are explained by the closer correspondence between the relative amplitudes and nodal behaviour of the perturbation sequence ($1\ -2\ 3\ -4\ 2$) and that of $\sin\phi_l$ for $l = 2$ and $l = 3$ than those of $\sin\phi_l$ or $\cos\phi_l$ for $l = 1$ and $l = 4$ (Table 1).

Table 1. Cosines and sines of $\phi_j(l) \equiv 2\pi jl/5$ for comparison with the perturbation sets producing the results shown in Fig. 3

j	1	2	3	4	5
$\cos\phi_0(j)$	1	1	1	1	1
$\sin\phi_0(j)$	0	0	0	0	0
$\cos\phi_1(j)$	0.309	−0.809	−0.809	0.309	1
$\sin\phi_1(j)$	0.751	0.588	−0.588	−0.951	0
$\cos\phi_2(j)$	−0.809	0.309	0.309	−0.809	1
$\sin\phi_2(j)$	0.588	−0.951	0.951	−0.588	0
$\cos\phi_3(j)$	−0.809	0.309	0.309	−0.809	1
$\sin\phi_3(j)$	−0.588	0.951	−0.951	0.588	0
$\cos\phi_4(j)$	0.309	−0.809	−0.809	0.309	1
$\sin\phi_4(j)$	−0.951	−0.588	0.588	0.951	0

This conclusion is confirmed in Fig. 3 which compares E_k curves calculated by the direct method for the perturbation distributions A (0.15 −0.40 −0.40 0.15 0.50) and B (−0.20 0.40 −0.40 0.20 0.00), both sets in units of β. As can be seen by reference to Table 1, A follows the cos ϕ_l sequence for $l = 1$ and $l = 4$ and therefore gives rise to larger gaps at these points than at

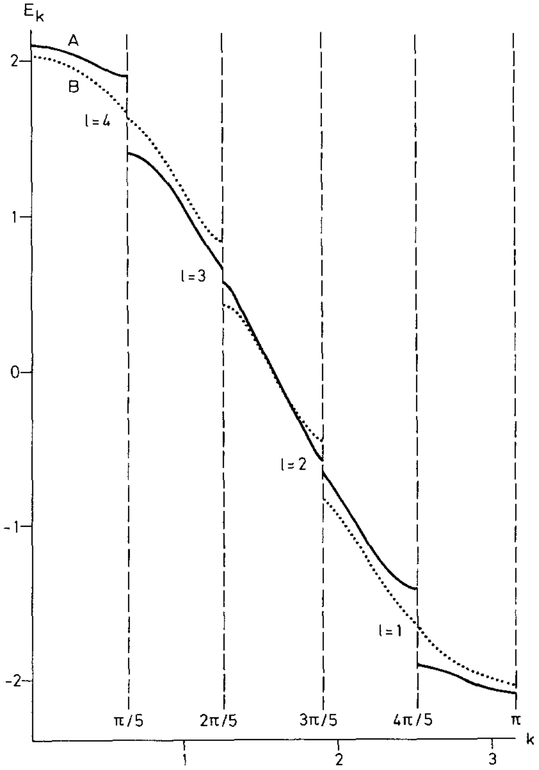

Fig. 3. A comparison of the band structures resulting from two sets of 5-site perturbations of the simple chain. Case A (———) has the set (0.15 −0.4 −0.4 0.15 0.5) and case B (· · · ·) the set (−0.2 0.4 −0.4 0.4 0). Energies are in β units

$l=2$ and $l=3$, while the opposite is true for the B distribution, which follows $\sin\phi_2$ and $\sin\phi_3$.

3.3. A More Accurate Estimation of the Band Gaps?

As was observed in Sect. 3.1 the magnitudes of the band gaps were somewhat overestimated in the perturbation method because of the diminishing accuracy of the second order expression (7) as we approach the singularities where the coupling states k and $k-2\pi l/n$ have vanishingly close E_k^0 values, which we denote ε_l^0.

But since this pair of k states is thereby selected for strong coupling we might reasonably wonder whether the interaction is so strong in this region that its contribution could be dominant in the creation of the band gap. Since the zeroth order energies of the coupling states are equal (ε_l^0) the assumption would lead to the expression of the interaction as

$$\begin{vmatrix} \varepsilon_l^0+V_0-\varepsilon_l & V_l \\ V_l^* & \varepsilon_l^0+V_0-\varepsilon_l \end{vmatrix}=0.$$

The band gap would then be the difference between the roots of this equation, i.e.

$$\Delta\varepsilon_l \simeq |V_l|. \tag{10}$$

Applied to the example taken in Sect. 3.1 whose results were shown in Fig. 2 the calculated band gaps are compared in Table 2. Although Eq. (10) still somewhat overestimates the values it affords a better estimation than the second order expression (7).

4. Summary and Discussion

When applied to the n-site segments defining the chain considered in Sect. 3 dispersion curves were obtained showing the same general features as those calculated by diagonalizing the $n\times n$ energy matrix. Although the band gaps thus calculated are a little exaggerated, as a labour-saving device to estimate the band structure of a polymer possessing the kind of short-term disorder referred to in Sect. 1 the method appears promising.

The model polymer was chosen to be a simple hydrocarbon chain in order that effects arising from the charge distributions could be minimized. In a polymer

Table 2. Band gaps created by the perturbations (0.1 −0.2 0.3 −0.4 0.2) to the simple chain (cf. band structure in Fig. 2). Multiples of β

band gap label l:	1	2	3	4
direct method	0.09	0.37	0.35	0.05
second order perturbation				
Eq. (7)	0.10	0.51	0.51	0.10
Eq. (10)	0.08	0.40	0.40	0.08

where such effects are important the crystal orbitals corresponding to the same degree of perturbation as the energy Eq. (7) would have to be calculated, and the inferred atomic charges used to modify the α terms through additional terms in Eq. (6).

Although some of the limitations of the procedure are of course imposed by those of the particular one-electron tight-binding method which it seeks to reproduce, it demonstrates how the latter would respond to increasing "disorder" of the chain as the size n of the asymmetric segment increases until the band gaps are eliminated. Moreover the analytic expression of the dispersion energy E_k of the perturbed chain in terms of the deviation of the sites from uniformity allows the width of a specific gap to be related to these deviations. This suggests a practical method of "tuning" a selected gap l by modifying the structure of the unit segment (e.g. through the substitution of atoms on the main chain or in side groups) so as to mimic sin ϕ_l or cos ϕ_l. Moreover, knowing how the band structure and its physical corollaries e.g. electrical conductivity and mobility – quantities of interest in the question of semi- and super-conducting chains [9] and in biopolymers [10] – respond to a set of site fluctuations, experimental measurements might be correlated with regular or random effects which reduce the translational symmetry of the polymer chain.

References

1. Quinn, C. M.: Quantum theory of solids. Oxford: Clarendon 1973; Levin, A. A.: Solid state quantum chemistry. New York: McGraw Hill 1977
2. André, J.-M., Delhalle, J., Ladik, J., eds.: The quantum theory of polymers. Dordrecht: D. Reidel 1978; André, J.-M., Brédas, J.-L., Delhalle, J., Ladik, J., Leroy, G., Moser, C.: Recent advances in the quantum theory of polymers (Proceedings, Namur 1979). Berlin: Springer 1980
3. Martino, F.: The quantum theory of polymers (v. Ref. [2]) p. 169; McCubbin, W. L.: *ibid*, p. 185; Martino, F.: Recent advances in the quantum theory of polymers (v. Ref. [2]) p. 264; Seel, M.: *ibid*, p. 271
4. Morton-Blake, D. A.: Intern. J. Quantum Chem. **19**, 937 (1980)
5. Morton-Blake, D. A.: Theoret. Chim. Acta (Berl.) **59**, 213 (1981)
6. Morton-Blake, D. A.: Theoret. Chim. Acta (Berl.) **56**, 93 (1980)
7. Katon, J. E., ed.: Organic semiconducting polymers. London: Arnold 1968; Meier, H.: Dark- and photoconductivity of organic solids. Weinheim: Verlag Chemie 1974; Baughman, R. H.: Pearse, E. M., Schaefgen, J. R., eds.: Contemporary topics in polymer science, vol. 2, p. 205. New York: Plenum 1977; Keller, H. J., ed.: Chemistry and physics of one-dimensional metals. New York: Plenum 1977; André, J. J.: Recent advances in the quantum theory of polymers (Ref. [2]) p. 35 and refs therein
8. Evans, M. G., Gergely, J.: Biochim. Biophys. Acta **3**, 188 (1949); Suard, M., Berthier, G., Pullman, B.: *ibid* **52**, 254 (1961); Ladik, J., Suhai, S., Seel, M.: Intern. J. Quantum Chem.: Quantum Biology Symposium **5**, 35 (1978); Lewis, T. J.: *ibid*, p. 149; Pethig, R.: *ibid*, p. 159
9. Bloor, D.: Recent advances in the quantum theory of polymers (v. Ref. [2]) p. 14; André, J.-M.: *ibid* p. 35; Suhai, S.: *ibid* p. 213; Ladik, J.: Quantum Theory of Polymers (v. Ref. [2]) p. 279; Csavinsky, P.: *ibid* pp. 289
10. Kertesz, M., Koller, J., Ažman, A.: Intern. J. Quantum Chem. Quantum Biology Symposium **7**, 177 (1980) and references therein; Ladik, J., Suhai, S.: *ibid* 181; Ladik, J.: Quantum theory of polymers (v. Ref. [2]) p. 257

Received October 8/December 3, 1981