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Original Investigations

Periodic Perturbations of a Polymer

David A. Morton-Blake

Department of Chemistry, Trinity College, Dublin 2, Ireland

The reduction of the short range translational symmetry of a polymer chain (caused by, for example, the loss of an isoconformational structure) is accommodated as a periodic perturbation in a semi-empirical tight-binding LCAO calculation. Using the results of a calculation on an unperturbed chain in a perturbational mixing procedure an energy matrix can be calculated whose order is equal to (or even less than) that of the unperturbed structure. The method is applied to the generation of various chain conformations from all-trans polyacetylene and is shown to work successfully.

Key words: Crystal orbitals – Periodic perturbations – conformations of polyacetylene – *cis*- and *trans*-chain segments.

1. Introduction

The effect of a reduction in the translational symmetry of a polymer may be investigated by a number of quantum mechanical methods, including the introduction of chain disorder via random function generators [1] or Green's function averaging procedures [2], and single-site perturbation of a periodic chain [3]. A different approach [4] to the problem is to reduce the short range order of the chain while retaining the long range order as a true periodicity; in this way the problem can still be treated by (for example) tight-binding LCAO methods [5] based on the cyclic lattice condition, but an appropriately larger unit cell is thereby defined. In such a case the degree to which the chain symmetry could be reduced is obviously limited by the eventual size of the unit cell and the prohibitively large number of basis functions for construction of the energy matrix.

Recently a procedure based on the latter approach was proposed [6] which obviated the need for an enlarged unit cell. This was done by perturbing the band

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orbital functions calculated for a high-order chain by means of interaction changes between the atomic orbitals of adjacent segments, arising from the adoption of a slightly less ordered chain conformation. The theory was specifically presented for, and applied to, the perturbation of all-*trans* polyacetylene (ATPA) to the *trans-cis* conformer (TCPA). The lowest σ band and the π band of TCPA calculated in this way from ATPA data was found to be in quite good agreement with the results of the direct (unit cell enlarged) calculation on TCPA. There were, however, some unsatisfactory features of this method: (i) the second σ band showed poor agreement with the results of the direct calculation, (ii) a scaling factor of $\frac{1}{2}$ was rather arbitrarily applied to the perturbation energies, and (iii) TCPA was the only conformer whose band structure could be thus calculated.

In the present work the theory underlying the perturbation of a high-order polymer chain whose tight-binding LCAO functions are known will be presented for application to a polymer with quite a general periodic configuration, and perturbative interactions will not be limited to adjacent segments. The band structures thus calculated will be required to agree exactly with those from the direct method without the use of any scaling factor.

2. Theory

2.1. *Perturbation Matrix*

We write the wave function of the unperturbed chain as a linear combination of the ν atomic orbitals (AOs) $\chi_r^{j_1}$ in each repeat segment j_1, the resulting segment functions being themselves combined in accordance with the Bloch theorem [7]:

$$\Psi_\alpha(k) = N^{-1/2} \sum_{j_1=0}^{\pm\frac{1}{2}(N-1)} e^{ij_1k} \sum_{r=1}^{\nu} c_{r\alpha}(k)\chi_r^{j_1}. \tag{1}$$

N is the (practically infinite) number of segments comprising the chain and k the wave vector defined as a continuous variable within the range $0 \leqslant k < 2\pi$. This k range defines a continuum of functions $\Psi_\alpha(k)$ and of energies $E_\alpha(k)$ which we take to satisfy the equation

$$H_0\Psi_\alpha(k) = E_\alpha^0(k)\Psi_\alpha(k)$$

where H^0 is the Hamiltonian of the unperturbed chain. The energy continuum $E_\alpha^0(k)$ constitutes the αth *energy band*, of which Eq. (1) leads us to expect a total number ν.

Let us now think of the continua $\Psi_\alpha(k)$ and $E_\alpha^0(k)$ as a set of quasi-discrete "microstates" of the αth band. Then any perturbation of the chain that can be described by the addition of a term V to the Hamiltonian H^0 may be treated by forming linear combinations of the microstate functions $\Psi_\alpha(k)$. These new functions

$$\Psi_q^1 = \sum_i \sum_\alpha^\nu g_{q\alpha}(k_i)\Psi_\alpha(k_i)$$

will be eigenfunctions of the Hamiltonian $H^1 = H^0 + V$ of the perturbed chain with energies E_q^1 defining *altered* bands:

$$H^1\Psi_q^1 = E_q^1\Psi_q^1.$$

The energy matrix $\mathbb{H}^1$ whose diagonalization provides the desired energies E_q^1 is defined by its elements:

$$H_{\alpha\beta}^1(k_1, k_2) = E_\alpha^0(k_1)\delta_{\alpha\beta}\delta(k_1, k_2) + V_{\alpha\beta}(k_1, k_2)$$

where, using Eq. (1), the general element $V_{\alpha\beta}(k_1, k_2) \equiv \int \Psi_\alpha^*(k_1) V \Psi_\beta(k_2)\, \mathrm{d}\tau$ of the perturbation matrix is given by

$$V_{\alpha\beta}(k_1, k_2) = N^{-1} \sum_{j_1, j_2 = 0}^{\pm\frac{1}{2}(N-1)} \mathrm{e}^{i(j_2k_2 - j_1k_1)} \sum_{r_1, r_2}^{\nu} c_{r_{1\alpha}}^*(k_1) c_{r_2\beta}(k_2) V_{r_1r_2}^{j_1j_2}. \tag{2}$$

The quantity $V_{r_1r_2}^{j_1j_2} \equiv \int \chi_{r_1}^{j_1} V \chi_{r_2}^{j_2}\, d\tau$ measures the *change* in the interaction between $\chi_{r_1}^{j_1}$ in segment j_1 and $\chi_{r_2}^{j_2}$ in segment j_2 as a result of the perturbation of the chain. In terms of the Hamiltonian operators of the chain in the unperturbed condition (H^0) and in the perturbed condition (H_1), $V_{r_1r_2}^{j_1j_2}$ is defined by

$$\begin{aligned} V_{r_1r_2}^{j_1j_2} &= \int \chi_{r_1}^{j_1} H^1 \chi_{r_2}^{j_2}\, d\tau - \int \chi_{r_2}^{j_2} H^0 \chi_{r_2}^{j_2}\, d\tau \\ &= (H_{r_1r_2}^{j_1j_2})^1 - (H_{r_1r_2}^{j_1j_2})^0. \end{aligned} \tag{3}$$

The perturbation V which we shall consider will be one which lowers, but does not destroy, the translational symmetry of the chain. The new periodicity of the chain must now be described using a larger repeat cell[1] (Fig. 1) so as to include n segments rather than a single segment as was the case for the unperturbed chain. This n-segment periodicity must now be introduced into $V(k_1, k_2)$ in (2) so as to remove the infinite quantity N in this expression. Since the new translational symmetry of the chain is reflected in the AO perturbation element $V_{r_1r_2}^{j_1j_2}$, whose value depends on the segment j_1 of the first AO and the separation $j = j_2 - j_1$ of the second AO, and we shall rewrite this as $V_{r_1r_2}^{j_1}(j)$. The j_1-periodicity of $V_{r_1r_2}^{j_1}(j)$ is also exhibited by the parameter

$$U_{j_1}(j) \equiv \sum_{r_1, r_2}^{\nu} c_{r_1\alpha}^*(k_1) c_{r_2\beta}(k_2) V_{r_1r_2}^{j_1}(j) \tag{4}$$

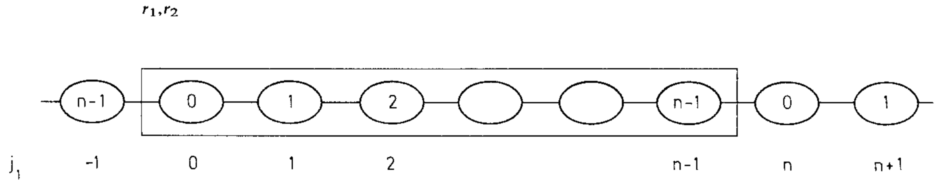

Fig. 1. Segments of the isoconformational chain and the n-segment reference cell (boxed) of the perturbed chain

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[1] The n-segment cell defined here is a "unit cell" only with respect to the periodicity of the *perturbation*. The true unit cell of the new conformer chain, defining its translational symmetry, may contain $2n$ segments (see Fig. 3).

whose dependence on k_1, k_2, α and β is omitted in order to avoid a cumbersome string of labels. The perturbation element (2) now becomes

$$V_{\alpha\beta}(k_1, k_2) = N^{-1} \sum_{j_1=0}^{\pm\frac{1}{2}(N-1)} \mathrm{e}^{ij_1(k_2-k_1)} \sum_{j=\pm 1}^{\pm} \mathrm{e}^{ijk_2} U_{j_1}(j) \tag{5}$$

where the $j = 0$ condition is omitted on the second summation sign since AOs in the same segment ($j_1 = j_2$) do not perturb each other in the type of perturbation envisaged here. The limits of the j summation are not specified since the $U_{j_1}(j)$ terms decay to insignificance beyond a few segments in either direction from j_1. In order to see how we may eliminate the infinite quantities from (5) let us write out some of the terms involved in the two summations:

$$\begin{aligned} V_{\alpha\beta}(k_1, k_2) = N^{-1}[&\mathrm{e}^{-i(k_2-k_1)}\{\mathrm{e}^{-ik_2}U_{-1}(-1) + \mathrm{e}^{ik_2}U_{-1}(1) + \mathrm{e}^{2ik_2}U_{-1}(2) + \cdots\} \\ &+ \mathrm{e}^0\{\mathrm{e}^{-ik_2}U_0(-1) + \mathrm{e}^{ik_2}U_0(1) + \mathrm{e}^{2ik_2}U_0(2) + \cdots\} \\ &+ \mathrm{e}^{i(k_2-k_1)}\{\mathrm{e}^{-ik_2}U_1(-1) + \mathrm{e}^{ik_2}U_1(1) + \mathrm{e}^{2ik_2}U_1(2) + \cdots\} \\ &+ \mathrm{e}^{2i(k_2-k_1)}\{\mathrm{e}^{-ik_2}U_2(-1) + \mathrm{e}^{ik_2}U_2(1) + \mathrm{e}^{2ik_2}U_2(2) + \cdots\} \\ &\vdots \\ &+ \mathrm{e}^{i(n-1)(k_2-k_1)}\{\mathrm{e}^{-ik_2}U_{n-1}(-1) \\ &+ \mathrm{e}^{ik_2}U_{n-1}(1) + \mathrm{e}^{2ik_2}U_{n-1}(2) + \cdots\} \\ &+ \mathrm{e}^{in(k_2-k_1)}\{\mathrm{e}^{-ik_2}U_n(-1) + \mathrm{e}^{ik_2}U_n(1) + \mathrm{e}^{2ik_2}U_n(2) + \cdots\} \\ &+ \cdots]. \end{aligned} \tag{6}$$

The periodicity of $U_{j_1}(j)$ in j_1 means that $U_{j_1}(j) = U_{j_1+n}(j)$. Therefore the terms in curly brackets in (6) repeat after n lines; those in the first line ($j_1 = -1$) for example, are equal in value to those in lines 5 and 6 ($j_1 = n - 1$), and the terms multiplying e^0 in line 2 are equal in value to those multiplying $\mathrm{e}^{in(k_2-k_1)}$ in line 7. There are therefore only n distinct sets of terms, each of which occurs N/n times in (6), which becomes

$$\begin{aligned} V_{\alpha\beta}(k_1, k_2) = N^{-1}\Big[&\{\cdots + \mathrm{e}^0 + \mathrm{e}^{in(k_2-k_1)} + \mathrm{e}^{2in(k_2-k_1)} + \cdots\} \sum_j^{\pm} \mathrm{e}^{ijk_2} U_0(j) \\ &\{\cdots + \mathrm{e}^{i(k_2-k_1)} + \mathrm{e}^{i(n+1)(k_2-k_1)} + \mathrm{e}^{i(2n+1)(k_2-k_1)} + \cdots\} \sum_j \mathrm{e}^{ijk_2} U_1(j) \\ &\{\cdots + \mathrm{e}^{2i(k_2-k_1)} + \mathrm{e}^{i(n+2)(k_2-k_1)} + \mathrm{e}^{i(2n+2)(k_2-k_1)} \\ &+ \cdots\} \sum_j \mathrm{e}^{ijk_2} U_2(j) \\ &\vdots \\ &\{\cdots + \mathrm{e}^{i(n-1)(k_2-k_1)} + \mathrm{e}^{i(2n-1)(k_2-k_1)} + \mathrm{e}^{i(3n-1)(k_2-k_1)} \\ &+ \cdots\} \sum_j^{\pm} \mathrm{e}^{ijk_2 U_{n-1}(j)}\Big] \end{aligned}$$

$$
\begin{aligned}
&=N^{-1}\Big[\{\cdots+1+\mathrm{e}^{in(k_2-k_1)}+\mathrm{e}^{2in(k_2-k_1)}+\cdots\}\sum_j^{\pm}\mathrm{e}^{ijk_2}U_0(j)\\
&\{\cdots+1+\mathrm{e}^{in(k_2-k_1)}+\mathrm{e}^{2in(k_2-k_1)}+\cdots\}\sum_j^{\pm}\mathrm{e}^{ijk_2}U_1(j)\\
&+\mathrm{e}^{2i(k_2-k_1)}\{\cdots+1+\mathrm{e}^{in(k_2-k_1)}+\mathrm{e}^{2in(k_2-k_1)}+\cdots\}\sum_j^{\pm}\mathrm{e}^{ijk_2}U_2(j)\\
&\vdots\\
&+\mathrm{e}^{i(n-1)(k_2-k_1)}\{\cdots+1+\mathrm{e}^{in(k_2-k_1)}+\mathrm{e}^{2in(k_2-k_1)}\\
&+\cdots\}\sum_j^{\pm}\mathrm{e}^{ijk_2}U_{n-1}(j)\Big].
\end{aligned}
$$

The common terms in each line,

$$J(k_1, k_2)\equiv N^{-1}\sum_l \mathrm{e}^{inl(k_2-k_1)}$$

sum to zero unless we have the condition that k_2-k_1 is zero or an even multiple of π. If this condition is obeyed all N/n terms in the summation are unity, leaving $J(k_1, k_2)$ with the value n^{-1}. The perturbation element is now given by

$$V_{\alpha\beta}(k_1, k_2)=J(k_1, k_2)\sum_{j_1=0}^{n-1}\sum_{j=\pm1}\mathrm{e}^{ijk_2}U_{j_1}(j). \tag{7}$$

Although we have achieved our objective of eliminating the infinite quantities N from (5) the result (7) is not in the most convenient form for programming since it involves a j-summation in both positive and negative directions. A more economic expression would avoid the computation of the $j\leq-1$ terms $U_{j_1}(j)$ for each j_1 since the same quantities would in any case be evaluated for some (other) j_1 and a positive j. In other words we shall seek to replace the second summation in (7) with one over positive j.

Segregation of the positive and negative j terms in (7) yields

$$V_{\alpha\beta}(k_1, k_2)=J(k_1, k_2)\sum_{j_1=0}^{n-1}\sum_{j\geq1}[\mathrm{e}^{ijk_2}U_{j_1}(j)+\mathrm{e}^{-ijk_2}U_{j_1}(-j)]. \tag{8}$$

Let us concentrate on the second (summed) term in (8). Expansion according to (4) gives the result:

$$\sum_{j_1=0}^{n-1}\sum_{j_2(<j_1)}^{-}\mathrm{e}^{(j_2-j_1)ik_2}\sum_{r_1, r_2}^{\nu}c_{r_{1\alpha}}^{*}(k_1)c_{r_{2\beta}}(k_2)V_{r_1r_2}^{j_1j_2}$$

where we have reverted to the (j_1, j_2) notation. Since j_1 is still in the range $0\leq j_1\leq n-1$ the AO $\chi_{r_1}^{j_1}$ is in the reference cell depicted in Fig. 1. Since $j_2<j_1$ the other interacting AO $\chi_{r_2}^{j_2}$ implied by the term must lie either within the same cell or in one to its left, in the sense of the figure. In the latter case we should like to replace this pair of AOs by one in which one AO is in the reference cell and the other in a cell to its right.

To do this note that the n-segment periodicity of the chain renders the quantity $V_{r_1r_2}^{j_1j_2}$ invariant to an addition of the same multiple λ of n to j_1 and j_2. The result, $V_{r_1r_2}^{j_1+\lambda n,\, j_2+\lambda n}$, can equally well be written $V_{r_2r_1}^{j_2+\lambda n,\, j_1+\lambda n}$ since the same AO interactions are implied. Now the sense of the labels is that the *first* subscript and superscript refer to an AO within the reference cell and the *second* to an AO in the same cell or in one to its right; we therefore decide to define the value of λ as that number which brings the first AO, $\chi_{r_2}^{j_2+\lambda n}$ into the reference cell. The addition of λn to the labels displaces the pair of AOs to the right; the second AO $\chi_{r_1}^{j_1+\lambda n}$ is shifted to a position to the right of the former—just as is required for the algorithm.

The second summation term in (8) is now

$$\sum_{j_1=0}^{n-1} \sum_{j_2(<j_1)}^{-} \mathrm{e}^{(j_2-j_1)ik_2} \sum_{r_1,\, r_2}^{\nu} c_{r_1\alpha}^{*}(k_1)c_{r_2\beta}(k_2)V_{r_2r_1}^{j_2+\lambda n,\, j_1+\lambda n}$$

$$= \sum_{J_1(>J_2)}^{+} \sum_{J_2=0}^{n-1} \mathrm{e}^{(J_2-J_1)ik_2} \sum_{r_1,\, r_2}^{\nu} c_{r_1\alpha}^{*}(k_1)c_{r_2\beta}(k_2)V_{r_2r_1}^{J_2J_1} \quad \text{where} \begin{cases} J_1 = j_1+\lambda n \\ J_2 = j_2+\lambda n \end{cases}$$

$$= \sum_{j_1=0}^{n-1} \sum_{j_2(>j_1)}^{+} \mathrm{e}^{-(j_2-j_1)ik_2} \sum_{r_1,\, r_2}^{\nu} c_{r_2\alpha}^{*}(k_1)c_{r_1\beta}(k_2)V_{r_1r_2}^{j_1j_2}.$$

Between the last two lines the non-significance of the summation labels outside the summations has been used to replace J_1 and J_2 by j_2 and j_1 respectively and to interchange r_1 and r_2. The expression for the general element of the perturbation matrix therefore follows from (8), together with the above development of the second term, as

$$V_{\alpha\beta}(k_1, k_2) = J(k_1, k_2) \sum_{j_1=0}^{n-1} \sum_{j\geqslant 1} \sum_{r_1,\, r_2} [\mathrm{e}^{ijk_2}c_{r_1\alpha}^{*}(k_1)c_{r_2\beta}(k_2)$$
$$+\mathrm{e}^{-ijk_2}c_{r_2\alpha}^{*}(k_1)c_{r_1\beta}(k_2)]V_{r_1r_2}^{j_1j_2}. \tag{9}$$

2.2. *Internal Segment Symmetry*

While Eq. (1) appears to predict a total of ν energy bands arising from the interaction of ν AOs in the repeat segment of the undistorted polymer it must be remembered that the presence of certain symmetry elements in the unit segment may render some of the bands equivalent. For example the glide plane or screw axis in the all-*trans* conformations of polyethylene or polyacetylene determines the relative coefficients of the symmetrically equivalent AOs in the two halves of the segment and hence defines the segment symmetry orbitals

$$\Psi_{\alpha}^{\pm}(k) = N^{-1/2} \sum_{j} \mathrm{e}^{ijk} \sum_{r=1}^{\frac{1}{2}\nu} c_{r\alpha}(k)[\chi_{ra}^{j} \pm \mathrm{e}^{\frac{1}{2}ik}\chi_{rb}^{j}]. \tag{10}$$

according to the application [8] of the line group symmetry of the chain. This pair of functions, related by a relative displacement of $k = 2\pi$, gives rise to the two *equivalent* dispersion energy curves $E_{\alpha}^{\pm}(k)$ shown in Fig. 2. These, like each of the functions in (10) require a k range 0 to 4π for their complete description.

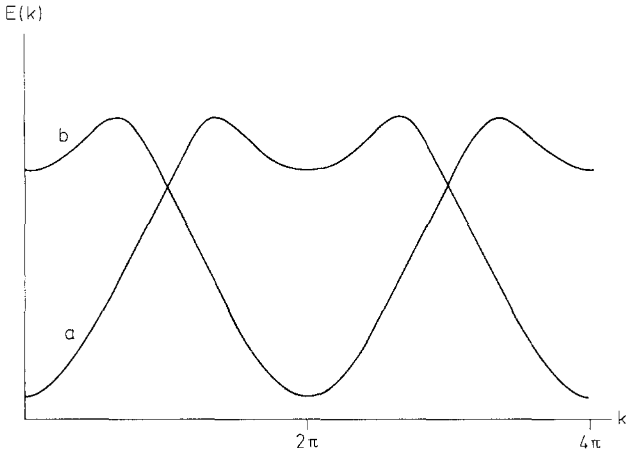

Fig. 2. Two equivalent energy bands that may result from the presence of certain symmetry elements within the polymer repeat segment

Thus the effect of the internal symmetry of the segment is to define either (i) the *complementary* pair of symmetry orbital functions $\Psi_\alpha^\pm(k)$ and their associated energy bands $E_\alpha^\pm(k)$ in the range $0 \leqslant k < 2\pi$ or (ii) *one* of these functions and its energy band in the extended Brillouin zone range $0 \leqslant k < 4\pi$.

This discussion is relevant to the selection of k values for the construction of the perturbation matrix $\mathbb{V}$ whose elements were defined in (9). Because of the discriminating character of the function $J(k_1, k_2)$ the only k_1, k_2 combinations leading to non-zero $V_{\alpha\beta}$ elements are those in which $k_1 = k_2$ or $k_1 = k_2 + \text{integer} \times 2\pi$. The latter relation could be used only in case (ii) of the last paragraph when the internal symmetry allows the selection $k_1 = k_2 + 2\pi$. However calculations and programming are clearly simpler for case (i), when the two parts of the energy band may be treated as if they were separate bands and the calculation of the perturbation matrix involves a single k value, e.g. we would calculate the "vertical" element $V_{\alpha,\alpha+1}(k, k)$ rather than $V_{\alpha\alpha}(k, k+2\pi)$. This is the alternative which we shall adopt.

As a result the energy matrix $\mathbb{H}^1$ to be diagonalized is given by

$$\mathbb{H}^1(k) = \mathbb{E}^0(k) + \mathbb{V}(k) \tag{11}$$

where the rows and columns refer to different bands with the same k value, $\mathbb{E}^0(k)$ is a diagonal matrix of zeroth order energies $[E_\alpha^0(k)$ for $\alpha = 1$ to $\nu]$ and the elements of $\mathbb{V}$ may be derived from (9) using the arguments of the present section:

$$V_{\alpha\beta}(k) = n^{-1} \sum_{j_1=0}^{n-1} \sum_{j \geqslant 1} \sum_{r_1, r_2}^{\nu} [\mathrm{e}^{ijk} c_{r_1\alpha}^*(k) c_{r_2\beta}(k) + \mathrm{e}^{-ijk} c_{r_2\alpha}^*(k) c_{r_1\beta}(k)] V_{r_1 r_2}^{j_1 j_2}. \tag{12}$$

The Hamiltonian matrix $\mathbb{H}^1$ defined by (11), (12) and (3) may now be constructed and diagonalized for any selected values of k in order to yield the new band structure.

3. Application

3.1. MO Method

Before applying the procedure in a numerical calculation a small complication must be pointed out.

Let us recall the objective of this work which was stated in the last paragraph of Sect. 1. The method was to offer a band structure computational procedure for polymer chains which were structurally identical but in different conformations. This has been done through a perturbational mixing of orthogonal functions Ψ_α for a chain of isoconformational segments followed by the calculation of the energy eigenvalues defined by the equation det $|E_\alpha^0\delta_{\alpha\beta} + V_{\alpha\beta} - E^1| = 0$. Now this should produce identical numerical results as would be obtained (with greater computational labour) from a direct calculation on a chain embodying the anisoconformational segments in a larger unit cell by evaluating the energy eigenvalues in the usual way from the equation det $|H_{rs} - ES_{rs}| = 0$. But in order to judge the success of our procedure we must firstly ensure that the two methods whose results are to be compared are entirely compatible. A simple examination shows that the perturbational mixing method does not completely correct for that part of the normalization of Ψ^1 arising from the change in overlap integrals S_{rs} upon adoption of the new conformation. Consequently, since our primary objective at this stage must be a demonstration of the success or failure of the general method proposed we decide to adopt the zero-overlap condition ($S_{rs} = \delta_{rs}$) in the calculation of the isoconformational (zeroth order) functions (1).

As a simple MO method on which to try the procedure the extended Hückel theory [9] (EHT) was chosen, but because of the neglect of the overlap integrals in the diagonalization of the energy matrix the factor K in the Wolfsberg–Helmholtz [10] expression for H_{rs} was changed from the commonly used value of 1.75. The best fit with the results of the "full" EHT method (in which the overlaps were included) when applied to the calculation of the band structure of all-*trans* polyacetylene was obtained [11] with $K \sim 0.8$. Although the use of this value showed a tendency to compress some of the (unoccupied) high-energy bands the structures of the valence and conduction bands were well reproduced; consequently in the calculations described below, where attention in the discussion section will be largely on the latter band types, the value $K = 0.8$ was used.

3.2. Conformational Perturbation and Codes

In this work we select all-*trans* polyacetylene (ATPA), +CH=CH+_n, as our unperturbed chain. We consider periodic perturbations which allow 180° internal rotations around certain bonds thus producing another planar conformer of ATPA, but which has a lower translational symmetry. Although all CC and CH bond lengths are assumed invariant (1.40 and 1.10 Å respectively) we decide to limit the *cis* and *trans* conformations to those in a chain in which only *alternate* CC bonds are capable of internal rotation. In other words the conformers to be produced are those that would be obtained from an alternating polyene chain in which the CC bonds of higher order would preclude internal rotation. This selection of conformers eliminates the sterically strained chains containing adjacent *cis* linkages. How close such a model is to real polyene chain is uncertain but a rather sparse set of experimental data and good quality calculations (see Karpfen and Petkov [12] for a recent *ab initio* work and a discussion of some experimental implications) would appear to point to an alternating chain.

The AO perturbation elements $V^{i_1i_2}_{r_1r_2}$ defined in (3) were calculated from the Wolfsberg–Helmholtz interaction terms between the AOs of the origin cell and those to their right (Fig. 1) for the polyacetylene (PA) chain in the all-*trans* and in the selected conformation. The latter was specified by an n-digit code $J_1J_2J_3 \cdots J_n$ where n is the number of segments in the repeat unit and where J_i is 0 if the ith "permitted" chain link is *trans* and 1 if it is *cis*. For example a chain in which each 3rd and 5th link is *cis* while the rest are *trans* would have the code 0 0101, though the cyclic order is immaterial, so that 01010 etc. would be equally good. Fig. 3 shows some examples of PA conformers defined by their codes. Although we refer to the conformers below in this way $(\mathrm{PA}-J_1J_2 \cdots J_n)$ it will be convenient to retain the label ATPA for the all-*trans* conformer (otherwise PA-0).

An algorithmic subroutine was written to calculate the atomic coordinates of the perturbed chain from those of the ATPA chain and the configuration code. Then from the difference between the $H^{i_1i_2}_{r_1r_2}$ values for the two conformations the elements of the perturbation matrix were calculated using (3) and (12). (The j-terms in the second summation of (12) showed a rapid decay—in consequence very few segments required to be taken for convergence.)

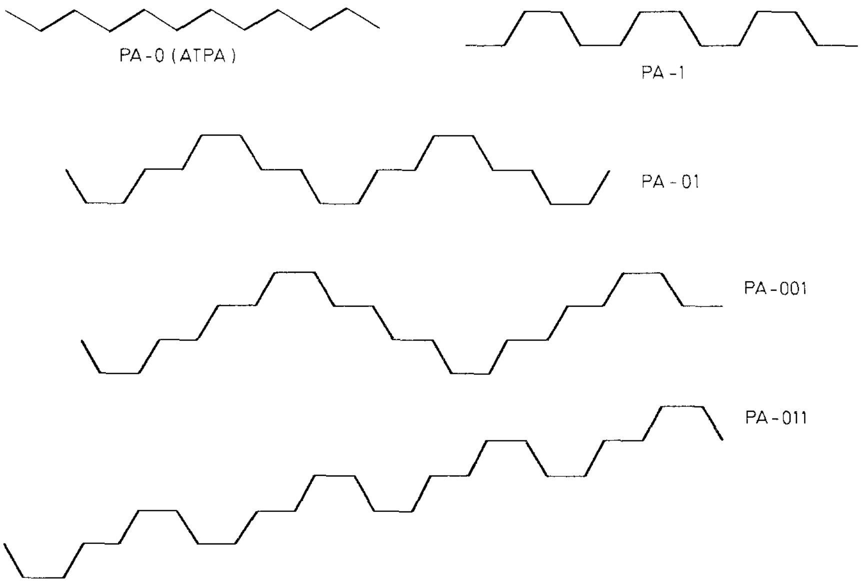

Fig. 3. Conformations of polyacetylene and their codes. Internal rotation is "permissible" only around alternate bonds (thin lines)

4. Results

4.1. *ATPA → PA-01*

When the procedure described in Sects. 2 and 3 was applied to the calculation of the band structure of an arbitrarily chosen PA conformer, the results were found to be identical to those obtained from a "direct" EHT calculation on the same conformer. The validity of the method is therefore confirmed.

Before discussing the general features of the conversion from all-*trans* to other conformations let us look at some of the details of the calculation involved in the perturbation of ATPA to PA-1 (the latter is the conformer called TCPA in Ref. 6 and refered to in Sect. 1). This conversion, corresponding to a 180° rotation about each permissible chain link, constitutes the greatest degree of perturbation of the type defined here, and we discuss it as a model system.

The band structure of the valence and conduction bands in PA-1 is shown in Fig. 4 together with that of the corresponding bands in ATPA which were used as basis microstate wave functions in the calculation. (Note that although the unoccupied bands are not shown in the figure, for the reason discussed at the end

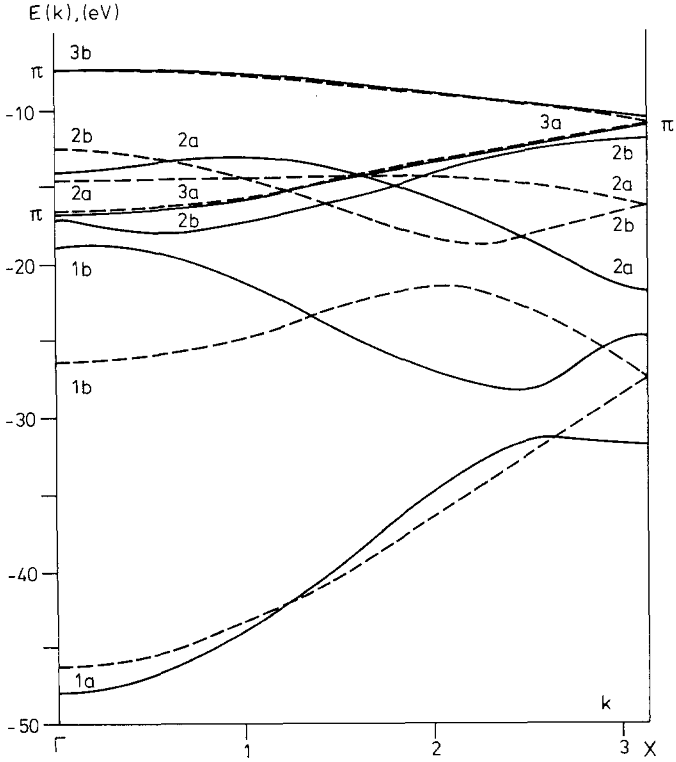

Fig. 4. Energy band structure of PA-1 (———) calculated from that of ATPA (– – – – –). (Bands are labelled so as to "correspond" between ATPA and PA-1, with the moiety labels *a* and *b* as used in Fig. 2.)

Table 1. Energies $-E(k)$ (in eV) at selected k points for the occupied and conduction bands in ATPA and PA-1

k		$1a(\sigma)$	$1b(\sigma)$	$2a(\sigma)$	$2b(\sigma)$	$3a(\pi)$	$3b(\pi)$
0	ATPA	46.06	26.44	14.68	12.49	16.51	7.53
	PA-1	47.78	18.85	14.02	17.15	16.64	7.42
$\pi/4$	ATPA	44.29	25.34	14.52	13.68	15.97	7.71
	PA-1	45.21	20.07	13.21	17.72	16.01	7.66
$\pi/2$	ATPA	39.70	22.71	14.34	16.70	14.52	8.27
	PA-1	38.91	24.75	14.12	15.54	14.43	8.35
$3\pi/4$	ATPA	33.69	22.23	14.78	18.56	12.64	9.29
	PA-1	32.08	28.43	17.60	13.18	12.53	9.40
π	ATPA	27.50	27.50	16.31	16.31	10.78	10.78
	PA-1	31.79	24.81	21.86	12.10	10.91	10.67

of Sect. 3.1, they were of course used to calculate the perturbation matrix elements according to Eq. (12).) Table 1 compares selected microstates for both conformers. Unlike the practice in Ref. 6 a comparison of $E(k)$ values with those from the direct EHT calculation will not be recorded since the two are identical. However it should be noted that the bands obtained by the latter method, in which the true unit cell contains twice the number of basis functions as in ATPA, would have to be "folded out" in order to obtain a meaningfully comparable band structure. By this is meant that in the $0 \leqslant k \leqslant \pi$ portion of the Brillouin zone generally used to display the band structure the part $E_+(k)$ of a band such as that shown in Fig. 2 must be re-labelled $E(\frac{1}{2}k)$ and the other half of the band $E_-(k)$ must show its continuity with the latter dispersion energy function by being re-labelled $E(\pi - \frac{1}{2})k$.

The results (Fig. 4 and Table 1) show the removal of the "pseudo-degeneracy" of the ATPA bands at the X point ($k = \pi$) as expected from symmetry arguments [8], leading to the creation of band gaps (within the context of the EHT approximations[2]) for the lower σ valence band and, to a smaller extent, in the π conduction band. The directions of the band displacements in the ATPA → PA-1 conversion can be discussed in terms of first order perturbation theory [6].

Let us again recall our stated objective of seeking a method of performing a band structure calculation on a conformationally perturbed polymer without the need to consider an excessively enlarged unit cell. We have shown that this is possible, for by combining unperturbed chain functions under the action of a conformation perturbation the energy matrix for diagonalization is of order 10 rather than 20 as it would be for PA-1 or 40 for PA-01 etc. using the direct MO method. Leaving aside the possibility of applying point symmetry considerations to the unit cell we now ask whether the size of the energy matrix may be still further reduced by applying approximations which do not incur unacceptable inaccuracy.

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[2] Of course it may not be necessary to destroy the point group symmetry of the ATPA repeat segment in order to produce a band gap. A "perturbation" caused by the inclusion of some degree of configuration interaction into the calculation may also reveal such a gap [13].

One possibility would be to combine fewer bands than the total number of 5. We might expect that the bands substantially different in energy from the one considered would have negligible effect on the energy shift of the latter. The lowest band was selected for this investigation. Fig. 5 shows the result of (a) mixing just the two parts of this band, (b) including in addition the second (σ) band, and (c) adding the other two (unoccupied) bands. Note that

(i) case (a) was also followed in Ref. 6,
(ii) for symmetry reasons the π bands are not involved in the mixing, and
(iii) case (c) corresponds to the "exact" calculation whose results are displayed in Fig. 4 and Table 1.

The results show that the ATPA band investigated requires interaction with at least the next band in order to obtain a good approximation of the corresponding PA-1 band. In this case, therefore, the first band calculation could indeed be reduced to a set of energy matrices of order 4 rather than 10 (if the perturbation is applied without the present approximation) or 20 (the "direct" method).

4.2. *The Behaviour of the π Bands Towards the Loss of All-trans Conformation; an Approximation Procedure*

Having subjected the ATPA chain to perturbations which converted it to a series of *cis/trans* conformers we select for discussion the π bands out of the total band structures. This is because of the important role of the energy gap between occupied and conduction bands in the properties of conducting polymer chains [14]. For this purpose we shall evaluate $E_- - E_+$ at the X point of the Brillouin zone. Substituting $k = \pi$ in (12) we get

$$V_{\pm\pm} = 2n^{-1}|c_\pm|^2 \sum_{j_1=0}^{n-1} \sum_{j=1}^{+} [V_{aa}^{j_1}(j) + V_{bb}^{j_1}(j)] \cos j\pi$$

and (13)

$$V_{-+} = 2in^{-1} c_-^* c_+ \sum_{j_1=0}^{n-1} \sum_{j=1}^{+} [V_{ab}^{j_1}(j) \sin (j+\tfrac{1}{2})\pi - V_{ba}^{j_1}(j) \sin (j-\tfrac{1}{2})\pi]$$

where the labels + and − refer to the "pseudo-degenerate" microstates at the X point where the $E_\pm(k)$ curves cross, and subscripts a and b denote the two $C(2p_\pi)$ AOs in the ATPA unit segment which are related by the screw axis symmetry of the segment. Finally this point symmetry has been used [8] to write

$$c_{\pm,b}(k) = \pm e^{\frac{1}{2}ik} c_{\pm,a}(k)$$

which permits the dropping of the a and b labels in the coefficients, and these, $c_\pm(\pi)$ at the X point, will be written simply as $c_\pm$.

It was previously shown [6] that the most important $V_{r_1 r_2}^{j_1}(j)$ term in (13) for the perturbations to the π MOs was $V_{ab}^{j_1}(1)$ when segments j_1 and j_1+1 are in the *cis* configuration (otherwise $V_{ab}^{j_1}(1)$ is of course zero); the next largest term, $V_{aa}^{j_1}(2)$ (with j_1 and j_1+1 still *cis*), is only 3% of the former. If we could neglect all but this term in (13); there would survive only the second order term, which

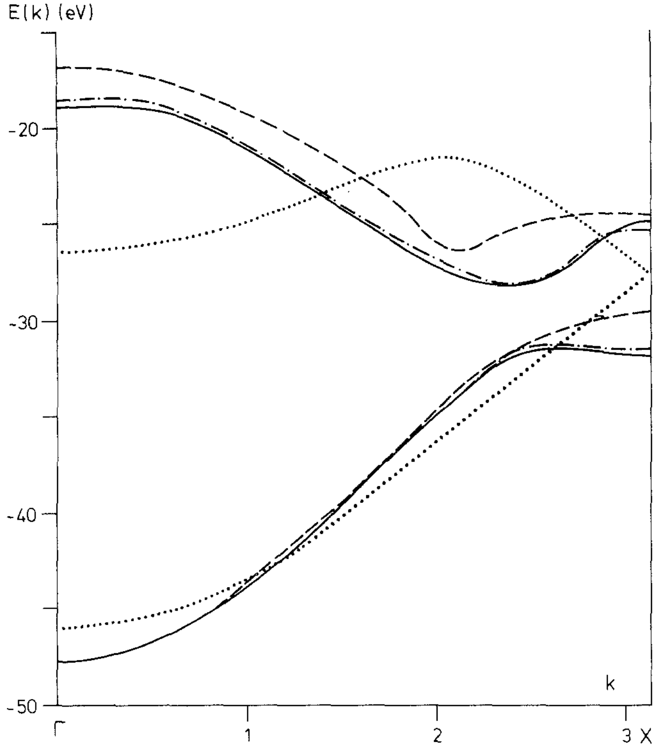

Fig. 5. Band 1 of ATPA (· · ·) and its perturbation to that of PA-1 by mixing in (a) just band 1 (– – –), (b) bands 1+2 (– · – ·) and (c) all the bands (———)

becomes

$$V_{-+} = -2in^{-1}c_-^*c_+ \sum_{j_1=0}^{n-1} V_{ab}^{j_1}(1).$$

Substituting $V_{ab}(1) = -0.1372$ eV from (3) and the Wolfsberg–Helmholtz relation, and $c_-^*c_+ = 0.5000$ from the results of the EHT application to ATPA (or just the normalization condition), the energies E_X of the perturbed chain at the X point, are given by

$$\begin{vmatrix} E_X^0 - E_X & V_{-+}^* \\ V_{-+} & E_X^0 - E_X \end{vmatrix} = 0$$

where $E_X^0 (= -10.783 \text{ eV})$ is the energy of the ATPA π band at $k = \pi$. The band energies at the position of the gap are therefore

$$E_X^{\pm} \simeq E_X^0 \pm \left| n^{-1} \sum_{j_1=0}^{n-1} V_{ab}^{j_1}(1) \right|. \tag{14}$$

The application of (14) to a PA conformation specified by the n-digit coding system introduced in Sect. 3.2 uses the value $V_{ab}^{j_1}(1) = -0.1372$ eV if $J_{j_1} = 1$ and $V_{ab}^{j_1}(1) = 0$ if $J_{j_1} = 0$. For PA-0011, for example, the energies would be calculated

Table 2. Energies (in eV) of π valence $E_X(1)$ and conduction $E_X(2)$ bands, and the energy gap $|\Delta E_X|$ at the X point for some PA conformers, using (a) full perturbational mixing theory and (b) the approximation of Eqn. (14)

	Eqn. (12)			Eqn. (14)		
	$-E_X(1)$	$-E_X(2)$	$\lvert\Delta E_X\rvert$	$-E_X(1)$	$-E_X(2)$	$\lvert\Delta E_X\rvert(2)$
PA-1	10.91	10.67	0.24	10.92	10.65	0.27
PA-01	10.84	10.72	0.12	10.85	10.71	0.14
PA-001	10.82	10.74	0.08	10.83	10.74	0.09
PA-0001	10.81	10.75	0.06	10.82	10.75	0.07
PA-011	10.87	10.71	0.16	10.87	10.69	0.18
PA-0011	10.84	10.72	0.12	10.85	10.71	0.14
PA-0	10.78	10.78	0.00	10.78	10.78	0.00

as

$$E_X^{\pm} = -10.783 \pm \tfrac{1}{4} \times 0.1372(0+0+1+1) = -10.85 \text{ or } -10.71 \text{ eV},$$

indicating a band gap of 0.14 eV. The corresponding energies calculated by the procedure of the earlier sections, which does not involve the approximations made here, are respectively −10.84 and −10.72, giving a band gap of 0.12 eV. Some band gaps calculated by both methods for a number of PA conformers are given in Table 2. The deficiency of the nearest-segment approximation may be seen in the slightly worse results for those conformers containing $J_{j_1} = J_{j_1+1} = 1$ linkages. It is clear that in such cases of neighbouring *cis* linkages the inclusion of $V^{j_1}_{r_1 r_2}(j)$ terms other than just the one in (14) would improve the accuracy.

5. Discussion

The economy of the method lies in the considerable reduction in the order of the energy matrix that can be achieved prior to diagonalization. This reduction can occur, not only through the application of the main theory which shows that the size of the matrix need not exceed that associated with the unperturbed chain but also through a judicious *selection* of bands for interaction. The reduction in the size of $\mathbb{H}$ rendered possible is important if (1) matrix diagonalization constitutes the rate-determining step of the computation, as might be the case in a semi-empirical method where the perturbation terms can be rapidly evaluated, or (2) the array storage capacity is limited. The release of the additional space might be profitably utilized to accommodate a polymer with a large unit cell in the unperturbed conformation, and the perturbation features to be applied could be made quite complex.

Such a procedure could provide means of following certain properties of a polymer chain as it relaxes from a high-order structure, undergoes a phase change or becomes subject to the pseudo-random perturbations that might be incorporated in a model of a liquid or solution.

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