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Electronic structure of aperiodic polymers. I. The average-matrix method and the effect of a cluster of impurities on the band structure of a periodic system

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To treat a compositionally disordered one-dimensional polymer with not very different constituent units, a method has been developed in an *ab initio* SCF LCAO (self-consistent-field linear-combination-of-atomic-orbitals) framework. Using the composition and the first neighbor's frequencies of the polymers, the method solves instead of the original problem a periodic problem with average unit cells and average interaction matrices. This procedure is correct in the first order of the deviations of the different units and their interactions from the average unit and the interactions between them. Further, to be able to treat a cluster of impurities and/or defects imbedded in a one-dimensional periodic polymer, a resolvent method has been developed in the Hartree-Fock level using an LCAO basis (*ab initio* SCF LCAO treatment).

I. INTRODUCTION

Polymers play a very important role as plastics; biopolymers, like proteins and nucleic acids (DNA and RNA), have fundamental importance in life processes and recently highly conducting polymers [like the TCNQ-TTF (7, 7, 8, 8-tetracyanoquinodimethane-tetrathiafulvalene system) with pseudo-one-dimensional stacks embedded in a three-dimensional molecular crystal] seem to be possible candidates for the discovery of interesting novel physical phenomena (superconductive-type behavior at higher temperatures, etc.). To understand their different physical and chemical properties (which underlie in the case of biopolymers their biological functions), one has to obtain a fair knowledge of their electronic structure.

If a polymer is periodic, there are well-established methods[1] to calculate its band structure. Most practically important plastics consist of aperiodic polymers and DNA and proteins are also aperiodic. Therefore, it seems to be very important to work out methods to treat, at least in a tolerable approximation, their electronic structure. In this paper, we shall restrict ourselves only to the case when the subunits of an aperiodic polymer are either similar, or to the case when the periodicity of a polymer is perturbed only at one point by (an arbitrarily large) cluster of impurities and/or defects. Both problems will be formulated in the framework of the *ab initio* SCF LCAO CO (self-consistent-field linear-combination-of-atomic-orbitals crystal-orbital) method. The treatment of the general case of aperiodic polymers (being either structurally (geometrically) or/and compositionally disordered) we postpone for later publications in which methods (one-electron Green's function expanded in terms of atomic orbitals) worked out for liquid metals will be applied.[2]

II. AVERAGE-MATRIX METHOD

This method was first developed for the simple tight-binding (Hückel) case by Beleznay and Biczó[3] neglecting overlap. Here we give a generalization of it for the *ab initio* SCF LCAO case taking into account also the nondiagonal elements of the overlap matrix.

Let us assume we have a linear chain with an aperiodic sequence of N subunits, each subunit consisting of m orbitals and let us assume we have r different kinds of subunits.[4] Further, let us assume we know the relative probabilities p_s $(s=1,2,\ldots,r)$ of the different kinds of subunits and their nearest-neighbors frequencies $q_{s,t}$ (these are the probabilities to have after a given kind of subunit another given kind of subunit). It should be mentioned that for a polymer in which the sequence is known (like in certain proteins), these data can be easily obtained, but also for DNA molecules coming from different sources, the nearest-neighbors frequencies have been determined experimentally.[5] Finally, we have to assume that the different kinds of subunits of the chain do not differ too much from each other.

Assuming periodic boundary conditions, we can write down in the first-neighbor's interactions approximation the secular equation which gives the one-electron levels of the chain as

$$\underline{\mathbf{F}}=\begin{vmatrix} \underline{\mathbf{F}}_{1,1}-\underline{\mathbf{S}}_{1,1}\epsilon & \underline{\mathbf{F}}_{1,2}-\underline{\mathbf{S}}_{1,2}\epsilon & \underline{0} & \cdots & \underline{0} & \underline{\mathbf{F}}_{1,N}-\underline{\mathbf{S}}_{1,N}\epsilon \\ \underline{\mathbf{F}}^{\mathrm{tr}}_{1,2}-\underline{\mathbf{S}}^{\mathrm{tr}}_{1,2}\epsilon & \underline{\mathbf{F}}_{2,2}-\underline{\mathbf{S}}_{2,2}\epsilon & \underline{\mathbf{F}}_{2,3}-\underline{\mathbf{S}}_{2,3}\epsilon & \cdots & \underline{0} & \underline{0} \\ \underline{0} & \underline{\mathbf{F}}^{\mathrm{tr}}_{2,3}-\underline{\mathbf{S}}^{\mathrm{tr}}_{2,3}\epsilon & \underline{\mathbf{F}}_{3,3}-\underline{\mathbf{S}}_{3,3}\epsilon & & & \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \underline{0} & \underline{0} & \cdots & & \underline{\mathbf{F}}_{N-1,N-1}-\underline{\mathbf{S}}_{N-1,N-1}\epsilon & \underline{\mathbf{F}}_{N-1,N}-\underline{\mathbf{S}}_{N-1,N}\epsilon \\ \underline{\mathbf{F}}^{\mathrm{tr}}_{1,N}-\underline{\mathbf{S}}^{\mathrm{tr}}_{1,N}\epsilon & \underline{0} & \cdots & & \underline{\mathbf{F}}^{\mathrm{tr}}_{N-1,N}-\underline{\mathbf{S}}^{\mathrm{tr}}_{N-1,N}\epsilon & \underline{\mathbf{F}}_{N,N}-\underline{\mathbf{S}}_{N,N}\epsilon \end{vmatrix}=0 \qquad (2.1)$$

where the kth diagonal submatrix $\underline{\mathbf{F}}_{k,k}$ ($k=1,2,\ldots,N$)

$$\underline{\mathbf{F}}_{k,k}=\begin{bmatrix} F^{(k)}_{1,1} & F^{(k)}_{1,2} & \cdots & F^{(k)}_{1,m} \\ F^{(k)}_{2,1} & F^{(k)}_{2,2} & \cdots & F^{(k)}_{2,m} \\ \cdots & \cdots & \cdots & \cdots \\ F^{(k)}_{m,1} & F^{(k)}_{m,2} & \cdots & F^{(k)}_{m,m} \end{bmatrix} \qquad (2.2)$$

is the Fock matrix of the kth subunit and

$$\underline{\mathbf{F}}_{k,k+1}=\begin{bmatrix} F^{(k,k+1)}_{1,1} & F^{(k,k+1)}_{1,2} & \cdots & F^{(k,k+1)}_{1,m} \\ F^{(k,k+1)}_{2,1} & F^{(k,k+1)}_{2,2} & \cdots & F^{(k,k+1)}_{2,m} \\ \cdots & \cdots & \cdots & \cdots \\ F^{(k,k+1)}_{m,1} & F^{(k,k+1)}_{m,2} & \cdots & F^{(k,k+1)}_{m,m} \end{bmatrix} \qquad (2.3)$$

is the interaction submatrix between the neighboring kth and $(k+1)$th subunits. The submatrices $\underline{\mathbf{S}}_{k,k}$ and $\underline{\mathbf{S}}_{k,k+1}$ are the corresponding overlap matrices (also of dimension $m\times m$) and ϵ is the energy eigenvalue. The elements of the Fock matrices $\underline{\mathbf{F}}_{k,k}$ and $\underline{\mathbf{F}}_{k,k+1}$ are defined in the *ab initio* case in the usual way as[1]

$$\begin{aligned} F^{(k,k+1)}_{f,g} = {} & \Big\langle \chi^k_f \Big| -\tfrac{1}{2}\Delta - \sum_{q_1=k}^{k+1}\sum_{\alpha=1}^{M_{q_1}} \frac{Z^{q_1}_\alpha}{|\vec{\mathrm{r}}-\vec{\mathrm{r}}^{\,q_1}_\alpha|} \Big| \chi^{k+1}_g \Big\rangle \\ & + \sum_{q_1,q_2=k}^{k+1}\sum_{u,v=1}^{m} p(q_1,q_2)_{u,v} \\ & \times\big[\langle \chi^k_f \chi^{q_1}_u | (1/r_{12}) | \chi^{k+1}_g \chi^{q_2}_v\rangle \\ & - \tfrac{1}{2}\langle \chi^k_f \chi^{q_1}_u | (1/r_{12}) | \chi^{q_2}_v \chi^{k+1}_g\rangle\big] , \end{aligned} \qquad (2.4)$$

where in the summations over q_1 and q_2, we have taken into account again only first-neighbors interactions (in the strict sense, I.E., all four-center integrals have been neglected which contain any pair of orbitals centered on second neighbors [for instance, if the orbital χ^{k+1}_g occurs in the integrals of expression (2.4), q_1 and q_2 cannot be $k-1$]. In (2.4) χ^k_f stands for the fth atomic orbtial (AO) in the kth subunit, $\vec{\mathrm{r}}^{\,q_1}_\alpha$ is the position vector of the αth nucleus in the q_1th subunit, $Z^{q_1}_\alpha$ is its nuclear charge, and M_{q_1} is the number of nuclei in the same subunit. In the case of the diagonally placed submatrices $\underline{\mathbf{F}}_{k,k}$ we have to perform the summations over q_1 and q_2 from $k-1$ to $k+1$. Finally, the generalized charge-bond order matrix elements $p(q_1,q_2)_{u,v}$ (bond order between orbital u in subunit q_1 and ortibal v in subunit q_2) are defined in the usual way

$$p(q_1,q_2)=2\sum_{j=1}^{n^*} c^{q_1}_{j,u}c^{q_2}_{j,v} , \qquad (2.5)$$

where n^* is the number of filled molecular orbitals (MOs) in the dimer formed from the subunits q_1 and q_2 (that is, $n^*=n^*_{q_1}+n^*_{q_2}$) and $c^{q_1}_{j,u}$ is the coefficient of the AO $\chi^{q_1}_u$ in the jth MO of the dimer.

Generalizing the derivation of Beleznay and Biczó,[3] let us define the average matrices

$$\underline{\bar{\mathbf{F}}}_{k,k}=\underline{\bar{\mathbf{F}}}_1=\sum_{s=1}^{r} p_s \underline{\mathbf{F}}_{s,s}(0) , \qquad (2.6)$$

$$\underline{\bar{\mathbf{F}}}_{k,k+1}=\underline{\bar{\mathbf{F}}}_2=\sum_{s=1}^{r}\sum_{t=1}^{r} q_{s,t}\underline{\mathbf{F}}_{s,t}(1) , \qquad (2.7)$$

$$\underline{\bar{\mathbf{S}}}_{k,k}=\underline{\bar{\mathbf{S}}}_1=\sum_{s=1}^{r} p_s \underline{\mathbf{S}}_{s,s}(0) , \qquad (2.8)$$

$$\underline{\bar{\mathbf{S}}}_{k,k+1}=\underline{\bar{\mathbf{S}}}_2=\sum_{s=1}^{r}\sum_{t=1}^{r} q_{s,t}\underline{\mathbf{S}}_{s,t}(1) , \qquad (2.9)$$

where $\underline{\mathbf{F}}_{s,s}(0)$ and $\underline{\mathbf{S}}_{s,s}(0)$ are the Fock and overlap matrices, respectively, belonging to the sth kind of subunit, and $\underline{\mathbf{F}}_{s,t}(1)$ and $\underline{\mathbf{S}}_{s,t}(1)$ are the same quantities between the sth kind of unit and its tth kind first neighbor.

Further, we can write the identities

$$\begin{aligned} \underline{\mathbf{F}}_{k,k}-\underline{\mathbf{S}}_{k,k}\epsilon &= \underline{\bar{\mathbf{F}}}_1-\underline{\bar{\mathbf{S}}}_1\epsilon+(\underline{\mathbf{F}}_{k,k}-\underline{\mathbf{S}}_{k,k}\epsilon)-(\underline{\bar{\mathbf{F}}}_1-\underline{\bar{\mathbf{S}}}_1\epsilon) \\ &\equiv \underline{\mathbf{F}}_1-\underline{\mathbf{S}}_1\epsilon+\underline{\tilde{\alpha}}_k , \end{aligned} \qquad (2.10)$$

$$\begin{aligned} \underline{\mathbf{F}}_{k,k+1}-\underline{\mathbf{S}}_{k,k+1}\epsilon & \\ &= \underline{\bar{\mathbf{F}}}_2-\underline{\bar{\mathbf{S}}}_2\epsilon+(\underline{\mathbf{F}}_{k,k+1}-\underline{\mathbf{S}}_{k,k+1}\epsilon)-(\underline{\bar{\mathbf{F}}}_2-\underline{\bar{\mathbf{S}}}_2\epsilon) \\ &\equiv \underline{\bar{\mathbf{F}}}_2-\underline{\bar{\mathbf{S}}}_2\epsilon+\underline{\tilde{\beta}}_{k,k+1} , \end{aligned} \qquad (2.11)$$

$$\underline{\tilde{\alpha}}_k=\underline{\alpha}_k-\underline{\mathbf{S}}_k\epsilon=\underline{\mathbf{F}}_{k,k}-\underline{\bar{\mathbf{F}}}_1-\epsilon(\underline{\mathbf{S}}_{k,k}-\underline{\bar{\mathbf{S}}}_1) , \qquad (2.12)$$

$$\underline{\tilde{\beta}}_{k,k+1}=\underline{\beta}_{k,k+1}-\underline{\mathbf{S}}_{k,k+1}\epsilon=\underline{\mathbf{F}}_{k,k+1}-\underline{\bar{\mathbf{F}}}_2-\epsilon(\underline{\mathbf{S}}_{k,k+1}-\underline{\bar{\mathbf{S}}}_2) . \qquad (2.13)$$

If the r kinds of subunits have similar chemical structures, i.e., the deviations of the corresponding elements in the matrices $\underline{\mathbf{F}}_{s,s}$, $\underline{\mathbf{F}}_{s,t}$, $\underline{\mathbf{S}}_{s,s}$, and $\underline{\mathbf{S}}_{s,t}$ are small, then also the elements of the matrices $\underline{\alpha}_k$ and $\underline{\beta}_{k,k+1}$ will be small as compared to those of $\underline{\overline{\mathbf{F}}}_1$ and $\underline{\overline{\mathbf{F}}}_2$. Taking this into account, we can expand the determinant (2.1) [after substituting into it the identities (2.10) and (2.11)] with respect to the elements of the matrices $\underline{\alpha}_k$ and $\underline{\beta}_{k,k+1}$. Keeping only the first-order terms, one obtains in this way[3]

$$|\underline{\mathbf{F}}| = |\underline{\overline{\mathbf{F}}}| + \sum_{f=1}^{m} \sum_{g=1}^{m} \sum_{k=1}^{N} (-1)^{f+g} [\tilde{\alpha}_{f,g}^{(f)} \,|\tilde{F}_{f,g}^{(f)}| + (-1)^m \tilde{\beta}_{f,g}^{(k,k+1)} |\tilde{F}_{f,g}^{(k,k+1)}| + (-1)^m \tilde{\beta}_{g,f}^{(k,k+1)} |\tilde{F}_{g,f}^{(k,k+1)}|] + \cdots , \tag{2.14}$$

where

$$|\underline{\overline{\mathbf{F}}}| = \begin{bmatrix} \underline{\overline{\mathbf{F}}}_1 - \underline{\overline{\mathbf{S}}}_1 \epsilon & \underline{\overline{\mathbf{F}}}_2 - \underline{\overline{\mathbf{S}}}_2 \epsilon & \underline{0} & \cdots & \underline{0} & \underline{\overline{\mathbf{F}}}_2^{\mathrm{tr}} - \underline{\overline{\mathbf{S}}}_2^{\mathrm{tr}} \epsilon \\ \underline{\overline{\mathbf{F}}}_2^{\mathrm{tr}} - \underline{\overline{\mathbf{S}}}_2^{\mathrm{tr}} \epsilon & \underline{\overline{\mathbf{F}}}_1 - \underline{\overline{\mathbf{S}}}_1 \epsilon & \underline{\overline{\mathbf{F}}}_2 - \underline{\overline{\mathbf{S}}}_2 \epsilon & \cdots & \underline{0} & \underline{0} \\ \underline{0} & \underline{\overline{\mathbf{F}}}_2^{\mathrm{tr}} - \underline{\overline{\mathbf{S}}}_2^{\mathrm{tr}} \epsilon & \underline{\overline{\mathbf{F}}}_1 - \underline{\overline{\mathbf{S}}}_1 \epsilon & \cdots & & \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \underline{0} & \underline{0} & \cdots & & \underline{\overline{\mathbf{F}}}_1 - \underline{\overline{\mathbf{S}}}_1 \epsilon & \underline{\overline{\mathbf{F}}}_2 - \underline{\overline{\mathbf{S}}}_2 \epsilon \\ \underline{\overline{\mathbf{F}}}_2 - \underline{\overline{\mathbf{S}}}_2 \epsilon & \underline{0} & \cdots & & \underline{\overline{\mathbf{F}}}_2^{\mathrm{tr}} - \underline{\overline{\mathbf{S}}}_2^{\mathrm{tr}} \epsilon & \underline{\overline{\mathbf{F}}}_1 - \underline{\overline{\mathbf{S}}}_1 \epsilon \end{bmatrix} = 0, \tag{2.15}$$

and $|\tilde{F}_{f,g}^{(k)}|$ and $|\tilde{F}_{f,g}^{(k,k+1)}|$, respectively, are the minors belonging to the element $(\underline{\overline{\mathbf{F}}}_1)_{f,g} - (\underline{\overline{\mathbf{S}}}_1)_{f,g}\epsilon$ of the kth submatrix in the diagonal of (2.15) and to the element $(\underline{\overline{\mathbf{F}}}_2)_{f,g} - (\underline{\overline{\mathbf{S}}}_2)_{f,g}\epsilon$ of the kth submatrix in the first parallel diagonal above the main diagonal, respectively.

Since in (2.15) always the same matrices $\underline{\mathbf{F}}_1$, $\underline{\mathbf{S}}_1$, $\underline{\mathbf{F}}_2$, and $\underline{\mathbf{S}}_2$ are repeated, $|\tilde{F}_{f,g}^{(k)}| = |\tilde{F}_{f,g}^{(1)}|$ and $|\tilde{F}_{f,g}^{(k,k+1)}| = |\tilde{F}_{f,g}^{(1,2)}|$ independently from the value of k. Consequently on the right-hand side of (2.14), these minors can be factored out from the summations according to k. On the other hand, taking into account the definitions of p_s and $q_{s,t}$, as well Eqs. (2.6)–(2.13), we can write

$$\sum_{k=1}^{N} \tilde{\alpha}_{f,g}^{(k)} = \sum_{k=1}^{N} \{F_{f,g}^{(k)} - (\underline{\overline{\mathbf{F}}}_1)_{f,g} - \epsilon [S_{f,g}^{(k)} - (\underline{\overline{\mathbf{S}}}_1)_{f,g}]\} = \sum_{s=1}^{r} N\{p_s (\underline{\mathbf{F}}_{s,s})_{f,g} - (\underline{\overline{\mathbf{F}}}_1)_{f,g} - \epsilon [p_s (\underline{\mathbf{S}}_{s,s})_{f,g} - (\underline{\overline{\mathbf{S}}}_1)_{f,g}]\} = 0 \tag{2.16}$$

and, similarly,

$$\begin{aligned} \sum_{k=1}^{N} \tilde{\beta}_{f,g}^{(k,k+1)} &= \sum_{k=1}^{N} \tilde{\beta}_{g,f}^{(k,k+1)} = \sum_{k=1}^{N} \{F_{f,g}^{(k,k+1)} - (\underline{\overline{\mathbf{F}}}_2)_{f,g} - \epsilon [S_{f,g}^{(k,k+1)} - (\underline{\overline{\mathbf{S}}}_2)_{f,g}]\} \\ &= \sum_{s=1}^{r} \sum_{t=1}^{r} N\{q_{s,t} (\underline{\mathbf{F}}_{s,t})_{f,g} - (\underline{\overline{\mathbf{F}}}_2)_{f,g} - \epsilon [q_{s,t} (\underline{\mathbf{S}}_{s,t})_{f,g} - (\underline{\overline{\mathbf{S}}}_2)_{f,g}]\} = 0 . \end{aligned} \tag{2.17}$$

As a consequence of the relations (2.16) and (2.17), the triple sum in (2.14) vanishes and therefore, we can write

$$|\underline{\mathbf{F}}| = |\underline{\overline{\mathbf{F}}}| + \cdots , \tag{2.18}$$

where the neglected members are at least of second order in the elements of the $\underline{\alpha}$ and $\underline{\beta}$ matrices. In other words, the one-electron energies of an aperiodic macromolecule with not-strongly differing subunits can be approximated (in the first order) by the energies of a conveniently chosen periodic macromolecule with average unit cells and interactions.

If we want to use the described formalism in an SCF scheme, we have to substitute into the elements of the matrices $\underline{\mathbf{F}}_{s,s}$ and $\underline{\mathbf{F}}_{s,t}$ some starting matrices $\underline{\mathbf{P}}^{(s)}(0)$ and $\underline{\mathbf{P}}^{(s,t)}(1)$. (The first matrix is formed from the charge-bond orders of the single molecule of kind s, the second one from the bond orders between the orbitals of the sth kind of unit and those of a neighboring tth kind of molecule. Both can be obtained from a corresponding calculation of the separated single molecules and molecule pairs.) With the aid of these starting matrices $\underline{\mathbf{P}}^{(s)}(0)$ and $\underline{\mathbf{P}}^{(s,t)}(1)$ we can construct the elements of the average matrices $\underline{\overline{\mathbf{F}}}_1$ and $\underline{\overline{\mathbf{F}}}_2$ as

$$(\overline{\underline{F}}_1)_{f,g}=\sum_{s=1}^{r}p_s[\underline{F}_{s,s}(0)]_{f,g}=\sum_{s=1}^{r}p_s\Bigg(\Big\langle\chi_f^{0(s)}\Big|-\tfrac{1}{2}\Delta-\sum_{t=1}^{r}q'_{s,t}\sum_{\substack{q_1=-1\\ [q_1=0(s)]}}^{1}\sum_{\alpha=1}^{M_{q_1}(t)}\frac{Z_\alpha^{q_1(t)}}{|\vec{r}-\vec{r}_\alpha^{\,q_1(t)}|}\Big|\chi_g^{0(s)}\Big\rangle$$

$$+\sum_{t_1,t_2=1}^{r}q'_{s,t_1}q'_{s,t_2}\sum_{\substack{q_1=-1\\ [q_1,q_2=0(s)]}}^{1}\sum_{q_2=-1}^{1}\sum_{u,v=1}^{m}p[q_1(t_1),q_2(t_2)]_{u,v}$$

$$\times[\langle\chi_f^{0(s)}\chi_u^{q_1(t_1)}|\,1/r_{12}|\quad\chi_g^{0(s)}\chi_v^{q_2(t_2)}\rangle$$

$$-\tfrac{1}{2}\langle\chi_f^{0(s)}\chi_u^{q_1(t_1)}|\,1/r_{12}|\,\chi_v^{q_2(t_2)}\chi_g^{0(s)}\rangle]\Bigg), \quad (2.19)$$

$$q'_{s,t}=\begin{cases}q_{t,s} & \text{if } q_1=-1,\\ 1 & \text{if } q_1=0,\\ q_{s,t} & \text{if } q_1=+1\end{cases}$$

$$(\overline{\underline{F}}_2)_{f,g}=\sum_{s=1}^{r}\sum_{t=1}^{r}q_{s,t}[\underline{F}_{s,t}(1)]_{f,g}=\sum_{s,t=1}^{r}q_{s,t}\Bigg(\Big\langle\chi_f^{0(s)}\Big|-\tfrac{1}{2}\Delta-\sum_{\substack{q_1=0\\ [q_1=0(s),\,q_1=1(t)]}}^{1}\sum_{\alpha=1}^{M_{q_1}(s\text{ or }t)}\frac{Z_\alpha^{q_1(s\text{ or }t)}}{|\vec{r}-\vec{r}_\alpha^{\,q_1(s\text{ or }t)}|}\Big|\chi_g^{1(t)}\Big\rangle$$

$$+\sum_{\substack{q_1,q_2=0\\ [q_1,q_2=0(s)]\\ [q_1,q_2=1(t)]}}^{1}\sum_{u,v=1}^{m}p[q_1(s\text{ or }t),q_2(s\text{ or }t)]_{u,v}$$

$$\times[\langle\chi_f^{0(s)}\chi_u^{q_1(s\text{ or }t)}|\,(1/r_{12})\,|\,\chi_g^{1(t)}\chi_v^{q_2(s\text{ or }t)}\rangle$$

$$-\tfrac{1}{2}\langle\chi_f^{0(s)}\chi_u^{q_1(s\text{ or }t)}|\,(1/r_{12})\,|\,\chi_v^{q_2(s\text{ or }t)}\chi_g^{1(t)}\rangle]\Bigg). \quad (2.20)$$

In (2.19) in the one- and two-electron parts of the Fock operator, we have averaged again over the different kinds of first neighbors t_1 and t_2, respectively (the summations over t_1 or t_1 and t_2), to obtain the average matrix $\overline{\underline{F}}_1$ in a consistent way. So we have used three indices to specify an AO: the subscript refers to the AO of the cell specified by the superscript q_1 or q_2 and in the parenthesis of the superscript t, t_1, or t_2 indicates that the AO belongs to that kind of unit. The letters appearing as arguments or subscripts of the generalized bond orders $p[q_1(t_1),\ q_2(t_2)]_{u,v}$ have the same meaning. $0(s)$ denotes the sth kind of reference cell and $1(t)$ the tth kind of first-neighboring cell (counted in the positive direction, i.e., the first neighbor on the right-hand side of the reference cell). The subscript below the sum $[q_1=0(s)]$ means that if $q_1=0$, then the summation goes over the orbitals of the sth kind of unit only. $q_1=1(t)$ is defined analogously. In both expressions which refer again to a linear chain, the first-neighbors interactions approximation has been used in the strict sense.

Having built up the matrices $\overline{\underline{F}}_1$ and $\overline{\underline{F}}_2$, the cyclic hypermatrix $\overline{\underline{F}}$ corresponding to the determinant (2.15) can be block diagonalized.[1] Thus, finally we obtain for the determination of the *ab initio* approximate band structure of an aperiodic linear chain (consisting of still similar units) in the first-neighbors interactions approximation the familiar matrix equation[1]

$$\underline{F}(k)^{\text{av}}\,\vec{d}(k)_h^{\text{av}}=\epsilon(k)_h^{\text{av}}\,\underline{S}(k)^{\text{av}}\,\vec{d}(k)_h^{\text{av}}, \quad (2.21)$$

with

$$\underline{F}(k)^{\text{av}}=\overline{\underline{F}}_1+\overline{\underline{F}}_2e^{ika}+\overline{\underline{F}}_2^{\text{tr}}e^{-ika}, \quad (2.22)$$

$$\underline{S}(k)^{\text{av}}=\overline{\underline{S}}_1+\overline{\underline{S}}_2e^{ika}+\overline{\underline{S}}_2^{\text{tr}}e^{-ika}. \quad (2.23)$$

The average overlap matrices $\overline{\underline{S}}_1$ and $\overline{\underline{S}}_2$ were defined before [see Eqs. (2.8) and (2.9)] and the individual $\underline{S}_{s,s}(0)$, $\underline{S}_{s,t}(1)$ matrices have the elements

$$[\underline{S}_{s,s}(0)]_{f,g}=\langle\chi_f^{0(s)}|\chi_g^{0(s)}\rangle, \quad (2.24)$$

$$[\underline{S}_{s,t}(1)]_{f,g}=\langle\chi_f^{0(s)}|\chi_g^{1(t)}\rangle. \quad (2.25)$$

We can solve (2.21) in the usual way.[1] Either we can perform only one iteration to obtain the approximate band structure of the aperiodic polymer (which would correspond to a tight-binding approximation with Hückel matrix elements built up from the average Fock matrices of the different subunits and interactions), or we can find an approximate SCF solution for (2.21) in the following way: from the vectors $\vec{d}(k)_h^{\text{av}}$ we can construct the charge-bond order matrices $\underline{P}(0)$, $\underline{P}(1)$, and $\underline{P}(-1)=\underline{P}(1)^{\text{tr}}$ of the average chain using the equation[1]

$$\tilde{p}(q_1, q_2)_{u,v} = \tilde{p}(q_1 - q_2)_{u,v}$$
$$= \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} 2 \sum_{h=1}^{n^*} d^*(k)_{h,u} d(k)_{h,v} \times e^{ik(q_1 - q_2)a}\, dk\,, \qquad (2.26)$$

where a is the elementary translation. Then we can redefine the elements of $\underline{\overline{\mathrm{F}}}_1$ and $\underline{\overline{\mathrm{F}}}_2$ in the nth iteration step as

$$[\underline{\overline{\mathrm{F}}}^{(n)}]_{f,g} = \sum_{s=1}^{r} p_s \Bigg(\langle \chi_f^{0(s)} | -\tfrac{1}{2}\Delta - \sum_{t=1}^{r} q'_{s,t} \sum_{\substack{q_1=-1 \\ [q_1 = 0(s)]}}^{1} \sum_{\alpha=1}^{M_{q_1}(t)} \frac{Z_\alpha^{q_1(t)}}{|\vec{\mathrm{r}} - \vec{\mathrm{r}}_\alpha^{\,q_1(t)}|} | \chi_g^{0(s)} \rangle$$
$$+ \sum_{t_1, t_2 = 1}^{r} q'_{s,t_1} q'_{s,t_2} \sum_{\substack{q_1=-1 \\ [q_1, q_2 = 0(s)]}}^{1} {\sum_{q_2=-1}^{1}}' \sum_{u,v=1}^{m} \tilde{p}(q_1, q_2)_{u,v}^{(n-1)} [\langle \chi_f^{0(s)} \chi_u^{q_1(t_1)} | (1/r_{12}) | \chi_g^{0(s)} \chi_v^{q_2(t_2)} \rangle$$
$$- \tfrac{1}{2} \langle \chi_f^{0(s)} \chi_u^{q_1(t_1)} | (1/r_{12}) | \chi_v^{q_2(t_2)} \chi_g^{0(s)} \rangle] \Bigg)\,, \qquad (2.27)$$

and similarly writing down (2.20) with $\tilde{p}(q_1, q_2)_{u,v}^{(n-1)}$ instead of the matrix elements $p[q_1(s \text{ or } t), q_2(s \text{ or } t)]_{u,v}$. In this way, an iterative procedure can be performed until self-consistency is reached.

No actual calculations have been performed yet with the aid of the described *ab initio* method for aperiodic polymers (with similar subunits), but in the simple tight-binding version it was applied by Beleznay and Biczó[3] to DNA. Using their method they have obtained quite good agreement with the directly computed band structure of

$$\text{poly}\begin{pmatrix} \text{A–T} \\ \\ \text{T–A} \end{pmatrix} = \begin{array}{cccccc} \text{A} & \text{T} & \text{A} & \text{T} & \text{A} & \text{T} \\ | & | & | & | & | & | \\ \text{T} & \text{A} & \text{T} & \text{A} & \text{T} & \text{A} \end{array} \cdots$$

using as different units the base pairs A–T and T–A. (In this simple case $p_{\text{A–T}} = p_{\text{T–A}} = \frac{1}{2}$, $q_{\text{A–T, A–T}} = q_{\text{T–A, T–A}} = 0$, $q_{\text{A–T, T–A}} = q_{\text{T–A, A–T}} = \frac{1}{2}$.) On the other hand, using as subunits A–T and G–C, they have obtained a poor agreement with the band structure of

$$\text{poly}\begin{pmatrix} \text{A–T} \\ \text{G–C} \end{pmatrix},$$

because in this case the subunits are rather different. To treat native DNA, one had to use as subunits the double base pairs

$$\begin{matrix} \text{A–T} \\ \text{G–C} \end{matrix}, \quad \begin{matrix} \text{A–T} \\ \text{C–G} \end{matrix}, \quad \begin{matrix} \text{A–T} \\ \text{T–A} \end{matrix}, \quad \text{and} \quad \begin{matrix} \text{G–C} \\ \text{C–G} \end{matrix}.$$

This would require the knowledge of the sequence of larger DNA segments to obtain the necessary p_s and $q_{s,t}$ values and a very large computer. Perhaps such an *ab initio* calculation could not be performed in the moment (also because the necessary experimental data are missing), but certainly it will be possible to execute such calculations after a couple of years. On the other hand, the described method could be easily applied to aperiodic polymers containing not too large and rather similar subunits. Work along these lines is in progress.

III. TREATMENT OF A CLUSTER OF IMPURITIES IMBEDDED IN A ONE-DIMENSIONAL PERIODIC POLYMER

Kertész and Biczó[6] have developed a method for the treatment of a cluster of impurities and/or defects imbedded in a one-dimensional periodic system in the single tight-binding (Hückel) approximation. Their method is the extension of the resolvent (Green's-function) method proposed first by Koster and Slater[7] to an arbitrary number of impurity orbitals using an AO basis. Here we give the generalization of their derivation for the case $\underline{S} \neq \underline{1}$ and show how the calculations could be performed in an *ab initio* SCF LCAO case.

Let us assume again that we have a periodic polymer of $2N+1$ units with m orbitals in the unit cell. Let us further assume that the μth unit differs from the rest of the polymer units (it can be a different molecule or it can have a different relative position with respect to its neighbors, as in the rest of the polymer). If we denote the cyclic hypermatrix which we obtain if we describe the periodic polymer in terms of the LCAO formalism introducing the Born–von Kármán periodic boundary conditions[1] by $\underline{\mathrm{H}}_0$, we can write for the Hamiltonian matrix of the perturbed polymer

$$\underline{\mathrm{H}} = \underline{\mathrm{H}}_0 + \underline{\mathrm{H}}'\,, \qquad (3.1)$$

where the deviation matrix $\underline{\mathrm{H}}'$, is defined as

$$\underline{H}' = \begin{bmatrix} \underline{0} & & & & & & \underline{0} \\ & \ddots & & & & & \\ & & \underline{0} & \underline{\tilde{F}}_1(1) & \underline{0} & & \\ & & \underline{\tilde{F}}_1(1)^{\mathrm{tr}} & \underline{\tilde{F}}(0) & \underline{\tilde{F}}_2(1) & & \\ & & \underline{0} & \underline{\tilde{F}}_2(1)^{\mathrm{tr}} & \underline{0} & & \\ & & & & & \ddots & \\ \underline{0} & & & & & & \underline{0} \end{bmatrix}, \qquad (3.2)$$

with

$$\underline{\tilde{F}}(0) = \underline{F}_\mu(0) - \underline{F}(0), \qquad (3.3a)$$

$$\underline{\tilde{F}}_1(1) = \underline{F}_1(1) - \underline{F}(1), \qquad (3.3b)$$

$$\underline{\tilde{F}}_2(1) = \underline{F}_2(1) - \underline{F}(1). \qquad (3.3c)$$

Here $\underline{F}(0)$ and $\underline{F}(1)$ are the submatrices building up the cyclic hypermatrix $\underline{H}_0$ in the first-neighbors interactions approximation,[1] $\underline{F}_\mu(0)$ is the submatrix corresponding to the changed μth unit and $\underline{F}_1(1)$ and $\underline{F}_2(1)$, respectively, are the interaction matrices between the μth unit and the neighboring $(\mu-1)$th and $(\mu+1)$th units [in the general case of a combined symmetry operation, like a screw axis, or in the case of structural disorder $\underline{F}_1(1) \neq \underline{F}_2(1)$]. For the overlap matrix of the perturbed periodic polymer, we can write in a similar way

$$\underline{S} = \underline{S}_0 + \underline{S}', \qquad (3.4)$$

where the hypermatrix $\underline{S}'$ is defined in a complete analogy to Eqs. (3.2) and (3.3).

Thus we can formulate our problem as

$$\underline{H}\vec{c} = (\underline{H}_0 + \underline{H}')\vec{c} = \lambda \underline{S}\vec{c} = \lambda(\underline{S}_0 + \underline{S}')\vec{c}. \qquad (3.5)$$

Performing the unitary transformation[8] on the cyclic hypermatrices $\underline{H}_0$ and $\underline{S}_0$ to block diagonalize them[1] and rearranging the resulting equation we obtain

$$\underline{U}^\dagger \underline{H}_0 \underline{U}\,\underline{U}^\dagger \vec{c} - \lambda \underline{U}^\dagger \underline{S}_0 \underline{U}\,\underline{U}^\dagger \vec{c} = -\underline{U}^\dagger \underline{H}' \vec{c} + \lambda \underline{U}^\dagger \underline{S}' \vec{c} \qquad (3.6)$$

or

$$(\underline{\bar{H}}_0 - \lambda \underline{\bar{S}}_0)\underline{U}^\dagger \vec{c} = -\underline{U}^\dagger (\underline{H}' - \lambda \underline{S}')\vec{c},$$

where the matrices

$$\underline{\bar{H}}_0 = \underline{U}^\dagger \underline{H}_0 \underline{U}, \quad \underline{\bar{S}}_0 = \underline{U}^\dagger \underline{S}_0 \underline{U} \qquad (3.7)$$

are block diagonal. Defining the Green's function

$$\underline{Z}' = \underline{U}(\underline{\bar{H}}_0 - \lambda \underline{\bar{S}}_0)^{-1} \underline{U}^\dagger \qquad (3.8)$$

and multiplying Eq. (3.6) from the left-hand side by $\underline{U}(\underline{\bar{H}}_0 - \lambda \underline{\bar{S}}_0)^{-1}$, one obtains the result[9]

$$\vec{c} = -\underline{Z}'(\underline{H}' - \lambda \underline{S}')\vec{c}. \qquad (3.9)$$

Since the deviation matrices $\underline{H}'$ and $\underline{S}'$ contain mostly zero elements [See Eq. (3.2)], this hypermatrix equation reduces to a set of $3m$ homogeneous linear equations, if we write down separately those equations which contain nonzero blocks of $\underline{H}'$ and $\underline{S}'$. In this way, we obtain after a straightforward calculation

$$\underline{\Lambda}'(\lambda)\vec{\omega} = \underline{\Lambda}'(\lambda)\begin{pmatrix} \vec{c}_{\mu-1} \\ \vec{c}_\mu \\ \vec{c}_{\mu+1} \end{pmatrix} = \begin{pmatrix} \underline{\alpha}'_{\mu-1,\mu} + \underline{1} & \underline{\beta}'_{\mu-1,\mu} & \underline{\gamma}'_{\mu-1,\mu} \\ \underline{\alpha}'_{\mu,\mu} & \underline{\beta}'_{\mu,\mu} + \underline{1} & \underline{\gamma}'_{\mu,\mu} \\ \underline{\alpha}'_{\mu+1,\mu} & \underline{\beta}'_{\mu+1,\mu} & \underline{\gamma}'_{\mu+1,\mu} + \underline{1} \end{pmatrix} \begin{pmatrix} \vec{c}_{\mu-1} \\ \vec{c}_\mu \\ \vec{c}_{\mu+1} \end{pmatrix} = \underline{0}, \qquad (3.10)$$

with

$$\underline{\alpha}'_{q,\mu} = \underline{Z}'_{q,\mu}[\underline{\tilde{F}}_1(1) - \lambda \underline{\tilde{S}}_1(1)]^{\mathrm{tr}}, \qquad (3.11a)$$

$$\underline{\beta}'_{q,\mu} = \underline{Z}'_{q,\mu-1}[\underline{\tilde{F}}_1(1) - \lambda \underline{\tilde{S}}_1(1)] + \underline{Z}'_{q,\mu}[\underline{\tilde{F}}(0) - \lambda \underline{\tilde{S}}(0)] + \underline{Z}'_{q,\mu+1}[\underline{\tilde{F}}_2(1) - \lambda \underline{\tilde{S}}_2(1)]^{\mathrm{tr}}, \qquad (3.11b)$$

$$\underline{\gamma}'_{q,\mu} = \underline{Z}'_{q,\mu}[\underline{\tilde{F}}_2(1) - \lambda \underline{\tilde{S}}_2(1)] \quad (q = \mu - 1, \mu, \mu + 1). \qquad (3.11c)$$

Equation (3.10) leads to

$$\det[\underline{\Lambda}'(\lambda)] = 0 \qquad (3.12)$$

for λ. In Eqs. (3.11) the blocks $\underline{Z}'_{q,\mu}$ of the matrix $\underline{Z}'$ can be obtained from its definition (3.8) and the form of $\underline{U}$ given in Ref. 8 as[10]

$$\underline{Z}'_{q,\mu} = \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} \exp[ia(q-\mu)k] \times [\underline{h}_0(k) - \lambda \underline{s}_0(k)]^{-1} dk. \qquad (3.13)$$

Here

$$\underline{h}_0(k) = \underline{h}(0) + \underline{h}(1)e^{ika} + \underline{h}(1)^{\mathrm{tr}} e^{-ika}, \qquad (3.14a)$$

$$\underline{s}_0(k) = \underline{s}(0) + \underline{s}(1)e^{ika} + \underline{s}(1)^{\mathrm{tr}} e^{-ika} \qquad (3.14b)$$

are the matrices which determine the band structure of the periodic polymer in the first-neighbors interactions approximation through the equation[1]

$$\underline{h}_0(k)\vec{d}(k)_j = \epsilon(k)_j \underline{s}_0(k)\vec{d}(k)_j \qquad (3.15)$$

(a is the elementary translation and k is the crystal momentum).

Instead of stopping at the block diagonalization of $\underline{H}_0$ with the aid of the unitary transformation $\underline{U}^\dagger\underline{H}_0\underline{U}$, one can solve also the generalized eigenvalue equation (3.15) and in this way determine the eigenvalues $\epsilon(k)_j$ belonging to the matrix $\tilde{\underline{h}}_0(k) = \underline{s}_0(k)^{-1/2}\underline{h}_0(k)\underline{s}_0(k)^{-1/2}$ applying Löwdin's symmetric orthogonalization procedure. After this, the whole procedure leading from (3.5) to Eqs. (3.10)–(3.12) can be repeated (as Kertész and Biczó[6] already did in the Hückel case). In this way, the same expressions can be obtained as before only the definition of $\underline{Z}'$ will become different

$$\underline{Z}^1 = \underline{S}_0^{-1/2}\underline{U}\underline{B}(\tilde{\underline{H}}_0^{\text{diag}} - \lambda\underline{E})^{-1}\underline{B}^\dagger\underline{U}^\dagger\underline{S}_0^{-1/2}, \tag{3.16}$$

where the fully diagonal matrix

$$\tilde{\underline{H}}_0^{\text{diag}} = \underline{B}^\dagger\underline{U}^\dagger\tilde{\underline{H}}_0\underline{U}\underline{B}; \quad \tilde{\underline{H}}_0 = \underline{S}_0^{-1/2}\underline{H}_0\underline{S}_0^{-1/2} \tag{3.17}$$

and $\underline{E}$ is the unit matrix. Further

$$\underline{B} = \underline{S}_0^{1/2}\underline{D} \tag{3.18}$$

with the $m\times m$ blocks $\underline{D}_{p,s}$ of the matrix $\underline{D}$ defined[11] as

$$\underline{D}_{p,s} = \delta_{p,s}\underline{d}(p) \quad (p = -N, -N+1, \ldots, 0, 1, \ldots, N). \tag{3.19}$$

Here finally the $m\times m$ matrix $\underline{d}(p)$ is constructed from the vectors $\vec{d}(p)_j$ satisfying the equivalent of Eq. (3.15) with the discrete variable p instead of the continuous k. We can substitute into (3.16) for[1] $\underline{S}^{-1/2}$

$$\underline{S}_0^{-1/2} = \underline{V}\tilde{\underline{s}}_0^{-1/2}\underline{V}^\dagger, \tag{3.20}$$

where the $m\times m$ blocks of the unitary matrix $\underline{V}$ are

$$\underline{V}_{p,s} = \delta_{p,s}\underline{v}(p),$$

and the matrix $\underline{v}(p)$ is constructed from the eigenvectors $\vec{v}(p)_j$ of the equation

$$\overline{\underline{s}}_0(p)\vec{v}(p)_j = s(p)_j\vec{v}(p)_j \quad (p = -N, \ldots, N) \tag{3.21}$$

[$\overline{\underline{s}}_0(p)$ is the pth block of the block-diagonal matrix $\underline{S}_0$ defined in (3.7)], and the diagonal hypermatrix $\tilde{\underline{s}}_0$ is defined as

$$\tilde{\underline{s}}_0 = \begin{bmatrix} s(-N)_1 & & & & & & & & & & & \underline{0} \\ & s(-N)_2 & & & & & & & & & & \\ & & \ddots & & & & & & & & & \\ & & & s(-N)_m & & & & & & & & \\ & & & & \ddots & & & & & & & \\ & & & & & s(p)_1 & & & & & & \\ & & & & & & \ddots & & & & & \\ & & & & & & & s(p)_m & & & & \\ & & & & & & & & \ddots & & & \\ & & & & & & & & & s(N)_1 & & \\ & & & & & & & & & & \ddots & \\ \underline{0} & & & & & & & & & & & s(N)_m \end{bmatrix} \tag{3.22}$$

Further, taking into account the definition of the matrix $\underline{U}$ given in Ref. 8 and Eqs. (3.17)–(3.19), we obtain after a somewhat lengthy but straightforward calculation for the f,gth element of the p,sth block of $\underline{Z}'$

$$\begin{aligned}[(\underline{Z}')_{p,s}]_{f,g} = \sum_{i,l,q,r=1}^{m} & v_{i,f}(p)v_{i,q}^*(p)[s(p)_i]^{-1/2}v_{l,r}(p)\times v_{l,g}^*(p)[s(p)_l]^{-1/2} \\ & \times\frac{a}{2\pi}\int_{-\pi/a}^{\pi/a} e^{ika(p-s)}\sum_{j=1}^{m} b_{j,q}^*(k)b_{j,r}(k)[\epsilon(k)_j - \lambda]^{-1}\,dk. \end{aligned} \tag{3.23}$$

Here $v_{i,f}(p)$ is the fth component of the vector $\vec{v}(p)_i$ defined by (3.21) and the vector components $b_{j,r}(k)$ belong to the vectors $\vec{b}(k)_j$ which are the eigenvectors of the transformed matrix

$$\tilde{\underline{h}}_0(k)\vec{b}(k)_j = \overline{\underline{s}}_0(k)^{-1/2}\underline{h}_0(k)\overline{\underline{s}}_0(k)^{-1/2}\vec{b}(k)_j = \epsilon(k)_j\vec{b}(k)_j. \tag{3.24}$$

Equation (3.23), despite its more complicated nature, is much more advantageous than (3.13) because here we could express single elements of the matrix $\underline{Z}'$ and so we have not to perform matrix inversions as in the case of (3.13).

It should be mentioned further that we can write down for the elements of the submatrices $\underline{F}_\mu(0)$, $\underline{F}(0)$, $\underline{F}(1)$, $\underline{F}_1(1)$, and $\underline{F}_2(1)$ occurring in Eqs. (3.3) the corresponding *ab initio* SCF LCAO expressions. The elements of the matrices $\underline{F}(q)(q=0,1)$ belonging to the periodic problem[1] are (again in the first-neighbors interactions approximation in the strict sense)

$$[\underline{F}(q)]_{f,g} = \langle \chi_f^0 | \hat{H}^N | \chi_g^q \rangle + \sum_{q_1,q_2=-1}^{1}{}' \sum_{u,v=1}^{m} p(q_1,q_2)_{u,v} [\langle \chi_f^0 \chi_u^{q_1} | (1/r_{12}) | \chi_g^q \chi_r^{q_2} \rangle - \tfrac{1}{2} \langle \chi_f^0 \chi_u^{q_1} | (1/r_{12}) | \chi_v^{q_2} \chi_g^q \rangle], \tag{3.25}$$

where the one-electron operator $\hat{H}^N$ was defined in (2.4) and the $p(q_1,q_2)_{u,v}$ matrix elements in (2.26), if we substitute in it instead of the $d(k)_{h,u}^{\text{av}}$ components of the average vectors satisfying Eq. (2.21) the components of the vectors $d(k)_{h,u}$ defined through Eq. (3.15). We can write in a similar way for the elements of the matrix $\underline{F}_\mu(0)$

$$\begin{aligned}[\underline{F}_\mu(0)]_{f,g} = {} & \langle \chi_f^\mu | -\tfrac{1}{2}\Delta - \sum_{\alpha=1}^{M_\mu} \frac{Z_\alpha^\mu}{|\vec{r}-\vec{r}_\alpha^{\,\mu}|} - \sum_{\substack{q_1=\mu-1 \\ (q_1\neq\mu)}}^{\mu+1} \sum_{\alpha=1}^{M} \frac{Z_\alpha}{|\vec{r}-\vec{r}_\alpha^{\,q_1}|} | \chi_g^\mu \rangle \\ & + \sum_{q_1,q_2=\mu-1}^{\mu+1} \sum_{u,v=1}^{m} p^\mu(q_1,q_2)_{u,v} [\langle \chi_f^\mu \chi_u^{q_1} | (1/r_{12}) | \chi_g^\mu \chi_v^{q_2} \rangle - \tfrac{1}{2} \langle \chi_f^\mu \chi_u^{q_1} | (1/r_{12}) | \chi_v^{q_2} \chi_g^\mu \rangle],\end{aligned} \tag{3.26}$$

where the elements of the matrices $\underline{p}^\mu(q_1,q_2)$ are depending instead of the vectors $\vec{d}(k)_j$ on the vectors $\vec{c}_{j,\mu-1}$, $\vec{c}_{j,\mu}$, and $\vec{c}_{j,\mu+1}$,

$$p^\mu(q_1,q_2)_{u,v} = 2 \sum_{j=1}^{\tilde{n}^*} c_{j,q_1;u} c_{j,q_2;v} \quad (q_1,q_2 = \mu-1, \mu, \mu+1) \tag{3.27}$$

and $\tilde{n}^* = \tfrac{1}{2}[n^*(q_1) + n^*(q_2)]$ to allow different numbers of filled MOs in the μth unit and in its neighbors.[12]

Further, we can write for the interaction matrices between the μ unit and its $(\mu-1)$th and $(\mu+1)$th neighbors, respectively,

$$\begin{aligned}[\underline{F}_1(1)]_{f,g} = {} & \langle \chi_f^\mu | -\tfrac{1}{2}\Delta - \sum_{\alpha=1}^{M} \frac{Z_\alpha}{|\vec{r}-\vec{r}_\alpha^{\,\mu-1}|} - \sum_{\alpha=1}^{M_\mu} \frac{Z_\alpha^\mu}{|\vec{r}-\vec{r}_\alpha^{\,\mu}|} | \chi_g^{\mu-1} \rangle \\ & + \sum_{q_1,q_2=\mu-1}^{\mu} \sum_{u,v=1}^{m} p^\mu(q_1,q_2)_{u,v} [\langle \chi_f^\mu \chi_u^{q_1} | (1/r_{12}) | \chi_g^{\mu-1} \chi_v^{q_2} \rangle - \tfrac{1}{2} \langle \chi_f^\mu \chi_u^{q_1} | (1/r_{12}) | \chi_v^{q_2} \chi_g^{\mu-1} \rangle],\end{aligned} \tag{3.28}$$

$$\begin{aligned}[\underline{F}_2(1)]_{f,g} = {} & \langle \chi_f^\mu | -\tfrac{1}{2}\Delta - \sum_{\alpha=1}^{M_\mu} \frac{Z_\alpha^\mu}{|\vec{r}-\vec{r}_\alpha^{\,\mu}|} - \sum_{\alpha=1}^{M} \frac{Z_\alpha}{|\vec{r}-\vec{r}_\alpha^{\,\mu+1}|} | \chi_g^{\mu+1} \rangle \\ & + \sum_{q_1,q_2=\mu}^{\mu+1} \sum_{u,v=1}^{m} p^\mu(q_1,q_2)_{u,v} [\langle \chi_f^\mu \chi_u^{q_1} | (1/r_{12}) | \chi_g^{\mu+1} \chi_v^{q_2} \rangle - \tfrac{1}{2} \langle \chi_f^\mu \chi_u^{q_1} | (1/r_{12}) | \chi_v^{q_2} \chi_g^{\mu+1} \rangle].\end{aligned} \tag{3.29}$$

It should be emphasized again that these matrices depend through the quantities $p^\mu(q_1,q_2)_{u,v}$ [see (3.27)] again on the vectors $\vec{c}_{j,q_1}$ $(q_1 = \mu-1, \mu, \mu+1)$ and *not* on the vectors $\vec{d}(k)_j$ of the periodic problem.

Thus, the solution of the problem of a cluster of impurities and/or defects imbedded into a periodic polymer consists of the following steps: (i) the solution of the periodic problem; (ii) solving Eq. (3.12) [preferably using the expression (3.23) of the fully diagonalized case for the elements of $\underline{Z}'$] for different λ's using starting charge-bond order matrices in $\underline{F}_\mu(0)$, $\underline{F}_1(1)$, and $\underline{F}_2(1)$, respectively; (iii) the solution of the system of linear homogeneous equations (3.10) for which, for instance, the method worked out by Marquardt[13] using a very well converging iterative procedure to minimalize the least squares

$$\sum_{k=1}^{3m+1} | y_k - \langle y_k \rangle |^2 \tag{3.30}$$

could be used. Here for $k=1, \ldots, 3m$, $y_k = 0$, if we have the correct solution for the components of the vectors $\vec{c}_{\mu-1}$, $\vec{c}_\mu$, and $\vec{c}_{\mu+1}$, respectively, in (3.10) and $\langle y_k \rangle$ are the corresponding quantities calculated with starting guess vectors $\vec{c}_{\mu-1}^{(0)}$, etc. Finally, if $k=3m+1$, we have the normalization condition

$$y_{3m+1}=(\vec{c}_{\mu-1}^{\dagger}\vec{c}_{\mu}^{\dagger}\vec{c}_{\mu+1}^{\dagger})\begin{pmatrix}\vec{c}_{\mu-1}\\ \vec{c}_{\mu}\\ \vec{c}_{\mu+1}\end{pmatrix}=\vec{\omega}^{\dagger}\vec{\omega}=1\,. \tag{3.31}$$

(iv) From the vectors $\vec{c}_{\mu-1}$, $\vec{c}_{\mu}$, and $\vec{c}_{\mu+1}$ the formation of new charge-bond order matrices and the repetition of the procedure until self consistency is reached.

In the most difficult step of the outlined procedure, in step (ii), one can write instead of $\underline{\Lambda}'(\lambda)\vec{\omega}=0$ [see Eq. (3.10)] $\underline{\Lambda}^{H}(\lambda)\vec{\omega}=0$, where $\underline{\Lambda}^{H}(\lambda)=(\underline{H}'-\lambda\underline{S}')\underline{\Lambda}'(\lambda)$. It is easy to show that $\underline{\Lambda}^{H}(\lambda)$ is then a Hermitian matrix. To find the λ's satisfying the equation $\det[\underline{\Lambda}^{H}(\lambda)]=0$, one can use probably the method due to van der Avoird *et al.*[14,15] which determines the roots λ_i's by finding the zero eigenvalues $[E_j(\lambda)=0]$ of the equation

$$\underline{\Lambda}^{H}(\lambda)\vec{\alpha}_j(\lambda)=E_j(\lambda)\vec{\alpha}_j(\lambda)\,. \tag{3.32}$$

The outlined method may seem a somewhat too complicated (especially in its *ab initio* form), but its application could contribute to the solution of important biological problems.[16] Further, it contains as special case the open-ended linear chain with surface states corresponding to the chain ends.[6] For that case in the simple tight-binding approximation (Hückel) Kertész and Biczo have already obtained solutions for different linear chains treating in this way only the π electrons.[6] One hopes that in a few years also this more accurate and complicated version of the method can be coded and tried out.

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[4] Of course we could assume also that each kind of subunit contains a different m_s $(s=1, 2, \ldots, r)$ number of orbitals. In this case, the submatrices occurring in the determinate Eq. (1) have to be enlarged with the aid of rows and columns containing only zero elements to the order of $m_{s_{\max}}$, the subunit consisting of the maximal number of orbitals.

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[7] G. F. Koster and J. C. Slater, Phys. Rev. 96, 1208 (1954). For further references about the resolvent method, see Ref. 6.

[8] The p, qth submatrix of the unitary matrix $\underline{U}$ which block diagonalizes the cyclic hypermatrices $\underline{H}_0$ and $\underline{S}_0$ is defined as $\underline{U}_{p,q}=(2N+1)^{-1/2}e^{i2pq/(2N+1)}\underline{1}$ (Ref. 1).

[9] If we investigate only those energy levels λ which lie outside of the energy bands belonging to the periodic problem, the inverse $(\underline{\bar{H}}_0-\lambda\underline{\bar{S}}_0)^{-1}$ exists.

[10] In the derivation leading to (3.13), we have assumed that $N\rightarrow\infty$ and therefore we could substitute the summation over the blocks of the block-diagonal matrices $\underline{H}_0$ and $\underline{S}_0$, respectively, by the integration over k.

[11] For the definition of the matrix $\underline{D}$, we cannot use the continuous variable $k=2\pi p/(2N+1)a$, but we have to return to the original discrete variable p (Ref. 1).

[12] We could allow also that m_μ, the number of basis orbitals in the impurity cluster μ is different from m. For the sake of simplicity writing down (3.26) we have assumed $m_\mu=m$.

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[14] It should be mentioned that in the paper of van der Avoird *et al.* [see Ref. (15)] which deals with a similar problem to our one (with the problem of surface states and adsorption) our Eq. (3.9) has been already derived [Eq. (19) in this paper] in a different way using projection operators.

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