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Self-Consistent-Field Tight-Binding Treatment of Polymers.
I. Infinite Three-Dimensional Case

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A general self-consistent-field tight-binding linear-combination-of-atomic-orbitals (LCAO) formalism is given for three-dimensional polymers containing many atoms in the elementary cell with all neighbors interacting, taking overlap explicitly into account. This formalism, which corresponds essentially to the formulation given by Roothaan for closed-shell molecules, has been developed with the aid of Hermitian complex matrices. The special cases of nearest-neighbor approximation and of a linear chain are then derived from the general expression obtained. Finally, formulas are given, again in complex-matrix formulation, for the dependence of the energy levels and wave functions of the polymer on the wave number k.

I. INTRODUCTION

The tight-binding approximation for a crystal has been well known for a long time.[1] It is usually formulated for cases where there is only one, or only a few, atoms within the elementary cell. The method has been used mostly for metals,[2] and only rarely for organic and inorganic polymers. Some work has been done on the calculation of the energy-band structure of a linear organic polymer by Koutecký and Zahradnik.[3] The extension of their method to the case of many atoms in the elementary cell and of many interactions between them has been developed by two of us and by Appel for the calculation of the energy-band structure of periodic deoxyribonucleic acid models[4,5] and of some other polymers of biological interest.[6]

In the present paper we develop a general self-consistent-field (SCF) tight-binding linear-combination-of-atomic-orbitals (LCAO) formalism (corresponding essentially to Roothaan's formalism[7] for molecules) for infinite three-dimensional polymers, taking into account all neighbor interactions and not neglecting overlap integrals. To be able to apply it to cases with many atoms within the elementary cell and many types of interactions between them, we have formulated our problem with the aid of complex matrices.

The general scheme presented here includes as simplified cases the previously published[8,9] semi-empirical π-electron treatments in the Hückel and Pariser-Parr-Pople approximation of one- and three-dimensional polymers.

To fulfill our task we first show how an infinite cyclic matrix can be brought to a block-diagonal form. This result is then applied to solve the eigenvalue equation (referred in general to a nonorthogonal orbital basis) of the polymer. Finally, we reformulate the matrices of the eigenvalue equation so as to find the form they take in the self-consistent scheme.

The results presented, of course, do not eliminate possible reservations as regards the applicability of the current theory to *a priori* calculations.

II. GENERAL FORMULATION OF THE PROBLEM

A. Block Diagonalization of the Hypermatrix of the Polymer

1. Let us suppose that we have a three-dimensional polymer containing together n orbitals in the elementary cell of one or more atoms. For the sake of simplicity, let the number of elementary cells in the direction of each crystal axis be equal to an odd number: $N_1=N_2=N_3=2N+1$. Further, we suppose that $N\rightarrow\infty$ and the Born–von Kármán periodic boundary condition holds.

Let us suppose then that there is an interaction between orbitals belonging to different elementary cells. We can then describe, in the one-electron approximation, the delocalized crystal orbitals of the polymer, with the aid of the LCAO approximation, in the form

$$\varphi^{\mathbf{p}f}=\sum_{\mathbf{q}}\sum_{g=1}^{n} C_{\mathbf{q}g}{}^{\mathbf{p}f}\chi^{\mathbf{q}g}, \qquad (1a)$$

where $\mathbf{p}=(p_1,p_2,p_3)$; $\mathbf{q}=(q_1,q_2,q_3)$; p_j and $q_j=-N,\cdots,0,\cdots,N$; $f=1,\cdots,n$, and $\sum_{\mathbf{q}}$ is a shorthand notation for

$$\sum_{q_1=-N}^{N}\sum_{q_2=-N}^{N}\sum_{q_3=-N}^{N}.$$

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[1] See, for instance, R. Reitz, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1955), Vol. 1, p. 1.

[2] See, for instance, J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

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[6] J. Ladik, Nature **202**, 1208 (1964).

[7] C. C. J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951).

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[9] J. Ladik, Acta Phys. Acad. Sci. Hung. **18**, 185 (1965).

Here the letter g in the indices of the constants $C_{\mathbf{q}g}{}^{\mathbf{p}f}$ refers to the orbital within an elementary cell and the boldface letter $\mathbf{q}$ to the different elementary cells. The indices $\mathbf{p}$ and f indicate within the fth band the level characterized by the vector $\mathbf{p}$. The notation $\chi^{\mathbf{q}g}$ means the gth atomic orbital of the cell characterized by the lattice vector

$$\mathbf{R}_{\mathbf{q}}=q_1\mathbf{a}_1+q_2\mathbf{a}_2+q_3\mathbf{a}_3\,,\quad q_j=-N,\cdots,0,\cdots,N\,, \tag{2}$$

where $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are the three basis vectors of the crystal.

Let us denote by

$$\boldsymbol{\chi}^{\mathbf{q}}=\boldsymbol{\chi}^{q_1q_2q_3}=(\chi^{\mathbf{q}1},\cdots,\chi^{\mathbf{q}g},\cdots,\chi^{\mathbf{q}n}) \tag{3a}$$

the row vector of the n atomic orbitals of the cell characterized by the vector $\mathbf{q}$. From the row vectors $\boldsymbol{\chi}^{\mathbf{q}}$ one can build up the hyper-row-vector containing the atomic orbitals of the chain of the cells characterized by the two components q_1 and q_2:

$$\boldsymbol{\chi}^{q_1q_2}=(\boldsymbol{\chi}^{q_1q_2(-N)},\cdots,\boldsymbol{\chi}^{q_1q_2q_3},\cdots,\boldsymbol{\chi}^{q_1q_2N})\,, \tag{3b}$$

which have $n(2N+1)$ components. From the hyper-row-vectors $\boldsymbol{\chi}^{q_1q_2}$ one can also build up hyper-row-vectors containing the atomic orbitals of the cells arranged in the plane characterized by the vector component q_1:

$$\boldsymbol{\chi}^{q_1}=(\boldsymbol{\chi}^{q_1(-N)},\cdots,\boldsymbol{\chi}^{q_1q_2},\cdots,\boldsymbol{\chi}^{q_1N})\,, \tag{3c}$$

which have $n(2N+1)^2$ components. In the last step, from the hyper-row-vectors $\boldsymbol{\chi}^{q_1}$ one can build up a hyper-row-vector containing all atomic orbitals of the whole crystal:

$$\boldsymbol{\chi}=(\boldsymbol{\chi}^{(-N)},\cdots,\boldsymbol{\chi}^{q_1},\cdots,\boldsymbol{\chi}^{N})\,, \tag{3d}$$

which have $n(2N+1)^3$ components. Using this notation, we can express the set of crystal orbitals in matrix form as

$$\begin{aligned}\boldsymbol{\varphi}=\boldsymbol{\chi}\mathbf{C}&=\sum_{q_1=-N}^{N}\boldsymbol{\chi}^{q_1}\mathbf{C}_{q_1}=\sum_{q_1=-N}^{N}\sum_{q_2=-N}^{N}\boldsymbol{\chi}^{q_1q_2}\mathbf{C}_{q_1q_2}\\&=\sum_{\mathbf{q}}\boldsymbol{\chi}^{\mathbf{q}}\mathbf{C}_{\mathbf{q}}=\sum_{\mathbf{q}}\sum_{g=1}^{n}\chi^{\mathbf{q}g}\mathbf{C}_{\mathbf{q}g}\end{aligned} \tag{1b}$$

or

$$\varphi^{\mathbf{p}f}=\boldsymbol{\chi}\mathbf{C}^{\mathbf{p}f}. \tag{1c}$$

Here $\mathbf{C}$ is a square matrix of order $n(2N+1)^3$ formed from the coefficients $C_{\mathbf{q}g}{}^{\mathbf{p}f}$, and one can build up the column vectors $\mathbf{C}^{\mathbf{p}f}$ and row vectors $\mathbf{C}_{\mathbf{q}g}$ of $\mathbf{C}$ by the same method as in the case of the row vector $\boldsymbol{\chi}$. Here and hereafter the subscripts denote the row indices and the superscripts denote the column indices of a matrix, written with Latin letters. In this manner $\mathbf{C}_{\mathbf{q}g}$ or $\mathbf{F}_{\mathbf{p}f}$ are always row vectors, and $\mathbf{C}^{\mathbf{p}f}$, for example, is a column vector. $\mathbf{C}_{q_1}$, $\mathbf{C}_{q_1q_2}$, and $\mathbf{C}_{\mathbf{q}}$ are rectangular submatrices of $\mathbf{C}$ with $n(2N+1)^2$, $n(2N+1)$, and n rows, respectively, and with $n(2N+1)^3$ columns.

2. If we form the expectation value

$$\langle\varphi^{\mathbf{p}f}|H_{\mathrm{eff}}|\varphi^{\mathbf{p}f}\rangle$$

of the one-electron effective Hamiltonian H_{eff} and perform a Ritz variational procedure for the coefficients in Eq. (1a), we obtain finally for the whole polymer the matrix equation

$$\mathbf{F}\mathbf{C}^{\mathbf{p}f}=\epsilon(\mathbf{p},f)\mathbf{S}\mathbf{C}^{\mathbf{p}f}. \tag{4a}$$

The hypermatrix $\mathbf{F}$ of dimension $n(2N+1)^3$ has the submatrices $\mathbf{F}_{\mathbf{p}}{}^{\mathbf{q}}$ of dimension n consisting of interactions between the orbitals belonging to the elementary cells characterized by the lattice vectors $\mathbf{R}_{\mathbf{p}}$ and $\mathbf{R}_{\mathbf{q}}$, respectively. The f,gth element $F_{\mathbf{p}f}{}^{\mathbf{q}g}$ of the matrix $\mathbf{F}_{\mathbf{p}}{}^{\mathbf{q}}$ is then given by

$$F_{\mathbf{p}f}{}^{\mathbf{q}g}=\langle\chi^{\mathbf{p}f}|H_{\mathrm{eff}}|\chi^{\mathbf{q}g}\rangle. \tag{5}$$

The overlap matrix $\mathbf{S}$ can be written in a block form similar to the matrix $\mathbf{F}$, and

$$S_{\mathbf{p}f}{}^{\mathbf{q}g}=\langle\chi^{\mathbf{p}f}|\chi^{\mathbf{q}g}\rangle. \tag{6}$$

3. In consequence of the Born–von Kármán boundary condition and the three-dimensional translational symmetry of the polymer, the matrices $\mathbf{F}$ and $\mathbf{S}$ are cyclic hypermatrices. Therefore it can be shown[10] that with the aid of a unitary hypermatrix $\mathbf{U}$, both $\mathbf{F}$ and $\mathbf{S}$ can be transformed to a block-diagonal form. To do this, let us define the submatrices $\mathbf{U}_{\mathbf{p}}{}^{\mathbf{q}}$ of the hypermatrix $\mathbf{U}$ as

$$\mathbf{U}_{\mathbf{p}}{}^{\mathbf{q}}=(2N+1)^{-3/2}\exp[2\pi i\mathbf{p}\cdot\mathbf{q}/(2N+1)]\mathbf{I}, \tag{7}$$

where $\mathbf{I}$ is a unit matrix of order n, and $\mathbf{pq}$ is a scalar product of the vectors $\mathbf{p}$ and $\mathbf{q}$ having three integer components. Then it can be proved that $\mathbf{U}$ is unitary [$\mathbf{U}\mathbf{U}^{\dagger}=\mathbf{I}$; $\mathbf{I}$ is a unit matrix of order $n(2N+1)^3$] and the hypermatrices $\mathbf{F}'=\mathbf{U}^{\dagger}\mathbf{F}\mathbf{U}$ and $\mathbf{S}'=\mathbf{U}^{\dagger}\mathbf{S}\mathbf{U}$ have a block-diagonal form. The diagonal blocks are matrices of order n only. Therefore, if instead of (4a), we write

$$\mathbf{U}^{\dagger}\mathbf{F}\mathbf{U}\mathbf{U}^{\dagger}\mathbf{C}^{\mathbf{p}f}=\epsilon(\mathbf{p},f)\,\mathbf{U}^{\dagger}\mathbf{S}\mathbf{U}\mathbf{U}^{\dagger}\mathbf{C}^{\mathbf{p}f}, \tag{4b}$$

or with the notation

$$\mathbf{D}^{\mathbf{p}f}=\mathbf{U}^{\dagger}\mathbf{C}^{\mathbf{p}f}, \tag{8}$$

$$\mathbf{F}'\mathbf{D}^{\mathbf{p}f}=\epsilon(\mathbf{p},f)\mathbf{S}'\mathbf{D}^{\mathbf{p}f} \tag{9}$$

and take into account the block-diagonal form of $\mathbf{F}'$ and $\mathbf{S}'$, respectively, we arrive at the much simpler matrix equation

$$\mathbf{F}'(\mathbf{p})\mathbf{d}^{f}(\mathbf{p})=\epsilon(\mathbf{p},f)\mathbf{S}'(\mathbf{p})\mathbf{d}^{f}(\mathbf{p}). \tag{10a}$$

Here the matrices

$$\mathbf{F}'(\mathbf{p})=\sum_{\mathbf{q}}\exp[2\pi i\mathbf{p}\cdot\mathbf{q}/(2N+1)]\mathbf{F}(\mathbf{q}) \tag{11a}$$

and

$$\mathbf{S}'(\mathbf{p})=\sum_{\mathbf{q}}\exp[2\pi i\mathbf{p}\cdot\mathbf{q}/(2N+1)]\mathbf{S}(\mathbf{q}), \tag{12a}$$

which form the diagonal blocks of $\mathbf{F}'$ and $\mathbf{S}'$, respectively, are only $n\times n$ matrices, and the vectors $\mathbf{d}^{f}(\mathbf{p})$ have only n components. The elements of $\mathbf{F}(\mathbf{q})$ and

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[10] See, for instance, P.-O. Löwdin, J. Appl. Phys. 33, 251 (1962).

$\mathbf{S}(\mathbf{q})$ are defined by

$$F_f{}^g(\mathbf{q}) = \langle \chi^{0f} | H_{\mathrm{eff}} | \chi^{\mathbf{q}g} \rangle \tag{13}$$

and

$$S_f{}^g(\mathbf{q}) = \langle \chi^{0f} | \chi^{\mathbf{q}g} \rangle , \tag{14}$$

respectively, where χ^{0f} stands for the fth atomic orbital (AO) of that elementary cell where we put the origin of the coordinate system, and $\chi^{\mathbf{q}g}$ for the gth AO of the elementary cell which can be characterized by $\mathbf{R}_\mathbf{q}$ in the same coordinate system.

According to the detailed calculations, if we take into account that $N \rightarrow \infty$, and introduce the wave vector $\mathbf{k}$, we can write the matrices $\mathbf{F}'(\mathbf{p})$ and $\mathbf{S}'(\mathbf{p})$ in the following form:

$$\mathbf{F}'(\mathbf{k}) = \sum_{\mathbf{q}}^{\pm\infty} e^{i\mathbf{k}\cdot\mathbf{R}_\mathbf{q}} \mathbf{F}(\mathbf{q}) , \tag{11b}$$

$$\mathbf{S}'(\mathbf{k}) = \sum_{\mathbf{q}}^{\pm\infty} e^{i\mathbf{k}\cdot\mathbf{R}_\mathbf{q}} \mathbf{S}(\mathbf{q}) , \tag{12b}$$

and we can rewrite (10a) as

$$\mathbf{F}'(\mathbf{k})\mathbf{d}^f(\mathbf{k}) = \epsilon(\mathbf{k},f)\mathbf{S}'(\mathbf{k})\mathbf{d}^f(\mathbf{k}) . \tag{10b}$$

In Eqs. (11b) and (12b), $\sum_{\mathbf{q}}{}^{\pm\infty}$ is a shorthand notation for

$$\sum_{q_1=-\infty}^{\infty} \sum_{q_2=-\infty}^{\infty} \sum_{q_3=-\infty}^{\infty}$$

and the wave vector $\mathbf{k}$ is

$$\mathbf{k} = k_1\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3 , \tag{15}$$

where $\mathbf{b}_1$ etc. are the basis vectors of the reciprocal space (by definition $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$). The components k_j of $\mathbf{k}$ can be expressed by

$$k_j = (2\pi)^{-1}(a_{jx}k_x + a_{jy}k_y + a_{jz}k_z) , \quad j = 1, 2, 3 \tag{16}$$

where k_x, k_y, and k_z are the rectangular coordinates of $\mathbf{k}$,[11] and a_{jx}, a_{jy}, and a_{jz} are the rectangular coordinates of the basis vector $\mathbf{a}_j$.

3. As is well known,[12] we can eliminate from Eq. (10b) the overlap matrix $\mathbf{S}'(\mathbf{k})$. To do this, we first diagonalize it. Taking into account that $\mathbf{S}'(\mathbf{k})$ is a complex Hermitian matrix, we can rewrite its eigenvalue equation

$$\mathbf{S}'(\mathbf{k})\mathbf{V}(\mathbf{k}) = \mathbf{V}(\mathbf{k})\mathbf{S}_0(\mathbf{k}) \tag{17a}$$

[where $\mathbf{V}(\mathbf{k})$ is a unitary matrix containing in its columns the normalized eigenvectors of $\mathbf{S}'(\mathbf{k})$, and $\mathbf{S}_0(\mathbf{k})$ is a real diagonal matrix containing the eigenvalues of $\mathbf{S}'(\mathbf{k})$], or

$$\{\mathrm{Re}[\mathbf{S}'(\mathbf{k})] + i\,\mathrm{Im}[\mathbf{S}'(\mathbf{k})]\}\{\mathrm{Re}[\mathbf{V}(\mathbf{k})] + i\,\mathrm{Im}[\mathbf{V}(\mathbf{k})]\} = \{\mathrm{Re}[\mathbf{V}(\mathbf{k})] + i\,\mathrm{Im}[\mathbf{V}(\mathbf{k})]\}\mathbf{S}_0(\mathbf{k}) \tag{17b}$$

in a real form[4]:

$$\begin{pmatrix} \mathrm{Re}[\mathbf{S}'(\mathbf{k})] & -\mathrm{Im}[\mathbf{S}'(\mathbf{k})] \\ \mathrm{Im}[\mathbf{S}'(\mathbf{k})] & \mathrm{Re}[\mathbf{S}'(\mathbf{k})] \end{pmatrix} \begin{pmatrix} \mathrm{Re}[\mathbf{V}(\mathbf{k})] & -\mathrm{Im}[\mathbf{V}(\mathbf{k})] \\ \mathrm{Im}[\mathbf{V}(\mathbf{k})] & \mathrm{Re}[\mathbf{V}(\mathbf{k})] \end{pmatrix} = \begin{pmatrix} \mathrm{Re}[\mathbf{V}(\mathbf{k})] & -\mathrm{Im}[\mathbf{V}(\mathbf{k})] \\ \mathrm{Im}[\mathbf{V}(\mathbf{k})] & \mathrm{Re}[\mathbf{V}(\mathbf{k})] \end{pmatrix} \begin{pmatrix} \mathbf{S}_0(\mathbf{k}) & \mathbf{0} \\ \mathbf{0} & \mathbf{S}_0(\mathbf{k}) \end{pmatrix} , \tag{17c}$$

where the elements of the last matrix on the right-hand side are the doubly degenerate real eigenvalues. To calculate the matrices $\mathrm{Re}[\mathbf{S}'(\mathbf{k})]$ and $\mathrm{Im}[\mathbf{S}'(\mathbf{k})]$ we have only to take into account Eq. (12b). Then we can write down immediately

$$\mathrm{Re}[\mathbf{S}'(\mathbf{k})] = \sum_{\mathbf{q}}^{\pm\infty} \cos(\mathbf{k}\mathbf{R}_\mathbf{q})\mathbf{S}(\mathbf{q}) \tag{12c}$$

and

$$\mathrm{Im}[\mathbf{S}'(\mathbf{k})] = \sum_{\mathbf{q}}^{\pm\infty} \sin(\mathbf{k}\mathbf{R}_\mathbf{q})\mathbf{S}(\mathbf{q}) . \tag{12d}$$

After the diagonalization of $\mathbf{S}'(\mathbf{k})$ we can rewrite (10b) as

$$\mathbf{V}^\dagger(\mathbf{k})\mathbf{F}'(\mathbf{k})\mathbf{V}(\mathbf{k})\mathbf{V}^\dagger(\mathbf{k})\mathbf{d}^f(\mathbf{k}) = \epsilon(\mathbf{k},f)\mathbf{S}_0(\mathbf{k})\mathbf{V}^\dagger(\mathbf{k})\mathbf{d}^f(\mathbf{k}) . \tag{10c}$$

The second step is to write (10c) in the form[13]

$$\mathbf{S}_0(\mathbf{k})^{-1/2}\mathbf{V}^\dagger(\mathbf{k})\mathbf{F}'(\mathbf{k})\mathbf{V}(\mathbf{k})\mathbf{S}_0(\mathbf{k})^{-1/2}\mathbf{S}_0(\mathbf{k})^{1/2} \times \mathbf{V}^\dagger(\mathbf{k})\mathbf{d}^f(\mathbf{k}) = \epsilon(\mathbf{k},f)\mathbf{S}_0(\mathbf{k})^{1/2}\mathbf{V}^\dagger(\mathbf{k})\mathbf{d}^f(\mathbf{k})$$

and introduce the notation

$$\mathbf{F}_0(\mathbf{k}) = \mathbf{S}_0(\mathbf{k})^{-1/2}\mathbf{V}^\dagger(\mathbf{k})\mathbf{F}'(\mathbf{k})\mathbf{V}(\mathbf{k})\mathbf{S}_0(\mathbf{k})^{-1/2} ; \tag{18a}$$

$$\mathbf{b}^f(\mathbf{k}) = \mathbf{S}_0(\mathbf{k})^{1/2}\mathbf{V}^\dagger(\mathbf{k})\mathbf{d}^f(\mathbf{k}) . \tag{19}$$

Thus we obtain the simple matrix eigenvalue problem for the determination of the energy bands of the three-dimensional polymer:

$$\mathbf{F}_0(\mathbf{k})\mathbf{b}^f(\mathbf{k}) = \epsilon(\mathbf{k},f)\mathbf{b}^f(\mathbf{k}) . \tag{20a}$$

For the purpose of the later calculations, it is advantageous to separate the real and imaginary parts of the matrices. We obtain from (18a)

$$\begin{aligned} \mathrm{Re}[\mathbf{F}_0(\mathbf{k})] = \mathbf{S}_0(\mathbf{k})^{-1/2}(&\mathrm{Re}[\mathbf{V}^T(\mathbf{k})] \\ &\times\{\mathrm{Re}[\mathbf{F}'(\mathbf{k})]\,\mathrm{Re}[\mathbf{V}(\mathbf{k})] \\ &-\mathrm{Im}[\mathbf{F}'(\mathbf{k})]\,\mathrm{Im}[\mathbf{V}(\mathbf{k})]\} \\ &+\mathrm{Im}[\mathbf{V}^T(\mathbf{k})]\{\mathrm{Re}[\mathbf{F}'(\mathbf{k})]\,\mathrm{Im}[\mathbf{V}(\mathbf{k})] \\ &+\mathrm{Im}[\mathbf{F}'(\mathbf{k})]\,\mathrm{Re}[\mathbf{V}(\mathbf{k})]\})\mathbf{S}_0(\mathbf{k})^{-1/2} , \end{aligned} \tag{18b}$$

$$\begin{aligned} \mathrm{Im}[\mathbf{F}_0(\mathbf{k})] = \mathbf{S}_0(\mathbf{k})^{-1/2}(&\mathrm{Re}[\mathbf{V}^T(\mathbf{k})] \\ &\times\{\mathrm{Re}[\mathbf{F}'(\mathbf{k})]\,\mathrm{Im}[\mathbf{V}(\mathbf{k})] \\ &+\mathrm{Im}[\mathbf{F}'(\mathbf{k})]\mathrm{Re}[\mathbf{V}(\mathbf{k})]\} \\ &-\mathrm{Im}[\mathbf{V}^T(\mathbf{k})]\{\mathrm{Re}[\mathbf{F}'(\mathbf{k})]\,\mathrm{Re}[\mathbf{V}(\mathbf{k})] \\ &-\mathrm{Im}[\mathbf{F}'(\mathbf{k})]\,\mathrm{Im}[\mathbf{V}(\mathbf{k})]\})\mathbf{S}_0(\mathbf{k})^{-1/2} , \end{aligned} \tag{18c}$$

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[11] The first Brillouin zones of a crystal with a specific symmetry are usually given in terms of the Cartesian coordinates of $\mathbf{k}$. On the other hand, we can characterize the elementary cells most easily with the aid of the lattice vectors $\mathbf{R}_\mathbf{q}$ expressed in terms of the unit vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$, which are not necessarily orthogonal. We need therefore the transformation (16).

[12] P.-O. Löwdin, J. Chem. Phys. **18**, 365 (1950).

[13] Since $\mathbf{S}_0(\mathbf{k})$ is real and diagonal, the matrix $\mathbf{S}_0(\mathbf{k})^{-1/2}$ is also real and diagonal, and its nonzero elements are $[\mathbf{S}_0(\mathbf{k})^{-1/2}]_f{}^f = [\mathbf{S}_{0f}{}^f(\mathbf{k})]^{-1/2}$.

where $\mathbf{V}^T(\mathbf{k})$ denotes the transpose of the matrix $\mathbf{V}(\mathbf{k})$, and where, from Eq. (11b), we find

$$\mathrm{Re}[\mathbf{F}'(\mathbf{k})]=\sum_{\mathbf{q}}^{\pm\infty}\cos(\mathbf{k}\cdot\mathbf{R}_\mathbf{q})\mathbf{F}(\mathbf{q}),\qquad(11\mathrm{c})$$

and

$$\mathrm{Im}[\mathbf{F}'(\mathbf{k})]=\sum_{\mathbf{q}}^{\pm\infty}\sin(\mathbf{k}\cdot\mathbf{R}_\mathbf{q})\mathbf{F}(\mathbf{q}).\qquad(11\mathrm{d})$$

Having calculated the matrices $\mathrm{Re}[\mathbf{F}_0(\mathbf{k})]$ and $\mathrm{Im}[\mathbf{F}_0(\mathbf{k})]$ we can rewrite (20a) in a real form

$$\begin{pmatrix}\mathrm{Re}[\mathbf{F}_0(\mathbf{k})] & -\mathrm{Im}[\mathbf{F}_0(\mathbf{k})]\\ \mathrm{Im}[\mathbf{F}_0(\mathbf{k})] & \mathrm{Re}[\mathbf{F}_0(\mathbf{k})]\end{pmatrix}\begin{pmatrix}\mathrm{Re}[\mathbf{b}^f(\mathbf{k})]\\ \mathrm{Im}[\mathbf{b}^f(\mathbf{k})]\end{pmatrix}=\epsilon(\mathbf{k},f)\begin{pmatrix}\mathrm{Re}[\mathbf{b}^f(\mathbf{k})]\\ \mathrm{Im}[\mathbf{b}^f(\mathbf{k})]\end{pmatrix}\qquad(20\mathrm{b})$$

B. SCF LCAO Formalism

1. The Hamiltonian of the whole polymer may be written

$$\mathcal{H}=\sum_{\mu=1}^{n_e(2N+1)^3}H_0{}^\mathrm{c}(\mu)+\tfrac{1}{2}\sum_{\mu,\nu=1}^{n_e(2N+1)^3}\frac{1}{r_{\mu\nu}};$$

$$H_0{}^\mathrm{c}(\mu)=-\tfrac{1}{2}\Delta_\mu+\sum_{\mathbf{q}}\sum_{j=1}^{n_a}V^\mathrm{c}(\mathbf{q},j;\mu),\qquad(21)$$

where the Greek letters μ, ν refer to the electrons, n_e denotes the number of electrons within the elementary cell explicitly taken into account, and $V^\mathrm{c}(\mathbf{q},j;\mu)$ means the core potential acting on the μth electron due to the jth atom of the elementary cell characterized by $\mathbf{R}_\mathbf{q}$; finally, n_a is the number of atoms in the elementary cell. After carrying out a Roothaan[7]-type procedure,[14] we obtain a hypermatrix in the form of (5) for the determination of the different one-electron energy levels of the polymer. However, it is not necessary to give all the elements of this hypermatrix, because, applying the unitary transformation described in the previous section, we obtain again the transformed hypermatrix in a block-diagonal form in which the nonzero submatrices $\mathbf{F}'(\mathbf{p})$ may be expressed with the aid of the submatrices $\mathbf{F}(\mathbf{q})$ of the hypermatrix $\mathbf{F}$ [see Eqs. (11a) and (13)]. The elements of $\mathbf{F}(\mathbf{q})$ we can specify in this case[7] as

$$F_f{}^g(\mathbf{q})=\langle\chi^{\mathbf{0}f}(1)|H_0{}^\mathrm{c}(1)+\sum_{\mathbf{r}}\sum_{h=1}^{n^*}[J(\mathbf{r},h;1)-K(\mathbf{r},h;1)]|\chi^{\mathbf{q}g}(1)\rangle,\qquad(22\mathrm{a})$$

where

$$J(\mathbf{r},h;\mu)\varphi(\mu)=\langle\varphi^{\mathbf{r}h}(\nu)|r_{\mu\nu}{}^{-1}|\varphi^{\mathbf{r}h}(\nu)\rangle\varphi(\mu),\qquad(22\mathrm{b})$$

$$K(\mathbf{r},h;\mu)\varphi(\mu)=\langle\varphi^{\mathbf{r}h}(\nu)|r_{\mu\nu}{}^{-1}|\varphi(\nu)\rangle\varphi^{\mathbf{r}h}(\mu),\qquad(22\mathrm{c})$$

and n^* denotes the number of molecular orbitals (MOs) which would be filled by the n_e electrons coming from *one* elementary cell. Substituting into (22b) and (22c) the LCAO MOs and forming the charge-bond order matrix of the three-dimensional polymer

$$\mathsf{P}=2\sum_{\mathbf{r}}\sum_{h=1}^{n^*}\mathbf{C}^{\mathbf{r}h}(\mathbf{C}^{\mathbf{r}h})^\dagger,\qquad(23)$$

we obtain, after simple calculations, the expression

$$F_f{}^g(\mathbf{q})=H_f{}^g(\mathbf{q})+\mathrm{Tr}[\mathsf{PG}(\mathbf{0},f;\mathbf{q},g)],\qquad(24\mathrm{a})$$

where

$$H_f{}^g(\mathbf{q})=\langle\chi^{\mathbf{0}f}(1)|H_0{}^\mathrm{c}(1)|\chi^{\mathbf{q}g}(1)\rangle,\qquad(24\mathrm{b})$$

and

$$G_{\mathbf{s}i}{}^{\mathbf{t}j}(\mathbf{0},f;\mathbf{q},g)=\langle\chi^{\mathbf{0}f}(1)\chi^{\mathbf{s}i}(2)|r_{12}{}^{-1}|\chi^{\mathbf{t}j}(2)\chi^{\mathbf{q}g}(1)\rangle-\tfrac{1}{2}\langle\chi^{\mathbf{0}f}(1)\chi^{\mathbf{s}i}(2)|r_{12}{}^{-1}|\chi^{\mathbf{q}g}(2)\chi^{\mathbf{t}j}(1)\rangle;\qquad(24\mathrm{c})$$

$$\mathrm{Tr}[\mathsf{PG}(\mathbf{0},f;\mathbf{q},g)]=\sum_{\mathbf{t}}\sum_{j=1}^{n}\mathbf{P}_{\mathbf{t}j}\mathbf{G}^{\mathbf{t}j}(\mathbf{0},f;\mathbf{q},g).\qquad(24\mathrm{d})$$

Further, the elements of the column vectors $\mathbf{G}^{\mathbf{t}j}(\mathbf{0},f;\mathbf{q},g)$ are defined by the expression (24c).

2. To write down in detail the elements of the matrices $\mathbf{F}(\mathbf{q})$, however, we now have to take into account that in (24a) we have the expression of the matrix P which contains the original hypervectors $\mathbf{C}^{\mathbf{r}h}$. Taking into account that according to Eq. (8) $\mathbf{D}^{\mathbf{r}h}=\mathsf{U}^\dagger\mathbf{C}^{\mathbf{r}h}$ and therefore

$$\mathbf{C}^{\mathbf{r}h}=\mathsf{U}\mathbf{D}^{\mathbf{r}h},\qquad(25)$$

and considering further the definition (7) of the submatrices of U and the definition (23) of the hypermatrix P, after a simple calculation we obtain

$$\mathbf{P}_\mathbf{t}{}^\mathbf{s}=2(2N+1)^{-3}\sum_{\mathbf{r}}\sum_{h=1}^{n^*}\mathbf{d}^h(\mathbf{r})[\mathbf{d}^h(\mathbf{r})]^\dagger\times\exp[2\pi i\mathbf{r}(\mathbf{t}-\mathbf{s})/(2N+1)],\qquad(26)$$

where the vectors $\mathbf{d}^h(\mathbf{r})$ can be obtained from Eq. (10a). In the case of $N\to\infty$ we can go over again from the discrete-level system to the continuous-band description and, using the same notation as in Eqs. (10b)–(12b), (15), and (16), obtain the final result

$$\mathbf{P}_\mathbf{t}{}^\mathbf{s}=2\int_{-1/2}^{1/2}\int_{-1/2}^{1/2}\int_{-1/2}^{1/2}\sum_{h=1}^{n^*}\mathbf{d}^h(\mathbf{k})\times[\mathbf{d}^h(\mathbf{k})]^\dagger e^{i\mathbf{k}(\mathbf{R}_\mathbf{t}-\mathbf{R}_\mathbf{s})}d\mathbf{k},\qquad(27\mathrm{a})$$

where[15] $d\mathbf{k}$ is a shorthand notation for $dk_1dk_2dk_3$. In this case the form (24a) of the elements of the matrices

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[14] It is assumed, here and in what follows, that our system is a closed-shell system.

[15] It should be mentioned that we can sum over the bands which correspond to the filled levels of the monomer, as we did in the derivation of the expression (26), only if the bands do not overlap. In the case of organic polymers, however, this is usually the case.

$\mathbf{F}(\mathbf{q})$ remains unchanged, but we have to sum in (24d) over all the three components of $\mathbf{t}$ from $-\infty$ to $+\infty$. Further, we have to keep in mind that in this case $\mathbf{P}$ and $\mathbf{G}(0,f;\mathbf{q},g)$ are infinite matrices and that the number of different $\mathbf{H}(\mathbf{q})$ and $\mathbf{G}(0,f;\mathbf{q},g)$ matrices is also infinite.

3. In connection with the overlap problem we have to notice that in the SCF case in Eq. (24a) we have defined the elements of the matrices $\mathbf{F}(\mathbf{q})$ in terms of the vectors $\mathbf{d}^h(\mathbf{k})$ according to Eq. (27a). Therefore, taking into account the identity $\mathbf{d}^h(\mathbf{k})=\mathbf{V}(\mathbf{k})\mathbf{S}_0(\mathbf{k})^{-1/2}\mathbf{b}^h(\mathbf{k})$ [see Eq. (19)], we can substitute in Eq. (27a)

$$\mathbf{d}^h(\mathbf{k})[\mathbf{d}^h(\mathbf{k})]^\dagger=\mathbf{V}(\mathbf{k})\mathbf{S}_0(\mathbf{k})^{-1/2} \times\mathbf{b}^h(\mathbf{k})[\mathbf{b}^h(\mathbf{k})]^\dagger\mathbf{S}_0(\mathbf{k})^{-1/2}\mathbf{V}^\dagger(\mathbf{k}). \quad (28)$$

By forming the real and imaginary parts of matrix $\mathbf{F}'(\mathbf{k})$ [which we have to substitute into (18b) and (18c) in the SCF case], seemingly we have to take into account Eqs. (24a), (27a) and (28) in addition to Eq. (11b). We should observe, however, that the second term in Eq. (24a) corresponds to Coulomb and exchange integrals, which are real quantities. Therefore they also have to remain real after the transformations (25) and (28), respectively. Thus the matrices $\mathbf{F}(\mathbf{q})$ are real matrices, and therefore Eqs. (11c) and (11d) hold also in the SCF case.

III. NEAREST-NEIGHBOR APPROXIMATION

1. In the case of the nearest-neighbor approximation we have to sum, in Eq. (11b) of $\mathbf{F}'(\mathbf{k})$ and Eq. (12b) of $\mathbf{S}'(\mathbf{k})$, respectively, only over the nearest neighbors:

$$\mathbf{F}'(\mathbf{k})\approx\sum_{\mathbf{q}}^{(\text{n.n.})} e^{i\mathbf{k}\cdot\mathbf{R}_\mathbf{q}}\mathbf{F}(\mathbf{q}), \quad (29a)$$

$$\mathbf{S}'(\mathbf{k})\approx\sum_{\mathbf{q}}^{(\text{n.n.})} e^{i\mathbf{k}\cdot\mathbf{R}_\mathbf{q}}\mathbf{S}(\mathbf{q}), \quad (30a)$$

where the upper index (n.n.) of the sums indicates that the summations should be extended only for the elementary cell and its nearest neighbors. The summations (29a) and (30a) also contain, of course, the matrices $\mathbf{F}(0)$ and $\mathbf{S}(0)$, respectively, corresponding to the *intra*-elementary-cell interactions and overlaps, respectively. Further, in this case the approximate form of $\mathbf{S}'(\mathbf{k})$ given by Eq. (30a) should be used also in Eqs. (17a)–(19) and (28). If we also want to take into account the second or third neighbors, etc., we have to extend the summations in (29a) and (30a) to these neighbors as well.

2. In the nearest-neighbor approximation we can also simplify the matrix elements $F_f{}^g(\mathbf{q})$ by extending the summations in (24d) only to nearest neighbors. (The other terms give contributions quickly decreasing with distance.) Introducing this further approximation, according to (21), (24a), (24b), and (24d) we have

$$F_f{}^g(\mathbf{q})=\langle\chi^{0f}(1)|-\tfrac{1}{2}\Delta_1 -\sum_{\mathbf{p}}^{(\text{n.n.})}\sum_{j=1}^{na}\left[\frac{Z_j}{|\mathbf{r}_1-\mathbf{R}_{\mathbf{p}j}|}-V^{\text{c.e.}}(\mathbf{p},j;1)\right]|\chi^{\mathbf{q}g}(1)\rangle + \sum_{\mathbf{s},\mathbf{t}}^{(\text{n.n.})}\sum_{i,j=1}^{n} P_{\mathbf{t}j}{}^{\mathbf{s}i}G_{\mathbf{s}i}{}^{\mathbf{t}j}(0,f;\mathbf{q},g)$$
$$\text{for}\quad \mathbf{t}-\mathbf{s},\ \mathbf{s}-\mathbf{q},\ \mathbf{q}-\mathbf{t}\neq(\text{s.n.}), \quad (31a)$$

where (s.n.) is an abbreviation for second neighbors. Here in the one-electron integral we have separated the core potential $V^c(\mathbf{p},j;1)$ into the two terms $-(Z_j/|\mathbf{r}_1-\mathbf{R}_{\mathbf{p}j}|)+V^{\text{c.e.}}(\mathbf{p},j;1)$ of which the first term gives the interaction of the electron having the position vector $\mathbf{r}_1$ with the jth nucleus in the elementary cell characterized by the lattice vector $\mathbf{R}_\mathbf{p}$ (the nucleus has the position vector $\mathbf{R}_{\mathbf{p}j}$ and its nuclear charge is Z_j), while the second term is the interaction of the electron with the core electrons of the jth atom in the elementary cell determined by $\mathbf{R}_\mathbf{p}$. Further, we have to keep in mind that in this case the infinite matrices $\mathbf{G}(0,f;\mathbf{q},g)$ have only a finite number of nonzero submatrices, and the number of different nonzero $\mathbf{H}(\mathbf{q})$ and $\mathbf{G}(0,f;\mathbf{q},g)$ matrices is also finite.

IV. ANALYSIS OF THE ELEMENTS OF MATRIX F(*q*) IN THE NEAREST-NEIGHBOR APPROXIMATION FOR A LINEAR CHAIN

1. To simplify the analysis of the elements of the matrix $\mathbf{F}(\mathbf{q})$, we rewrite (27) and (31a) for the case of a linear chain. We obtain then for the charge-bond order matrix within the elementary cell:

$$\mathbf{P}_s{}^s=\mathbf{P}^0=\frac{1}{\pi}\int_{-\pi}^{\pi}\sum_{h=1}^{n^*}\mathbf{d}^h(\kappa)[\mathbf{d}^h(\kappa)]^\dagger d\kappa, \quad (27b)$$

where $\kappa=2\pi k_1$ (the vector $\mathbf{k}$ is simply $\mathbf{k}=k_1\mathbf{b}_1$ in this case) and the bond order matrix between the nearest-neighbor elementary cells is

$$\mathbf{P}_{s\pm1}{}^s=\mathbf{P}^\pm=\frac{1}{\pi}\int_{-\pi}^{\pi}\sum_{h=1}^{n^*}\mathbf{d}^h(\kappa)[\mathbf{d}^h(\kappa)]^\dagger e^{\pm i\kappa}d\kappa. \quad (27c)$$

With these expressions we can write (31a) in the following form:

$$F_f{}^g(q)=\langle\chi^{0f}(1)|-\tfrac{1}{2}\Delta_1 -\sum_{j=1}^{na}\left[\frac{Z_j}{|\mathbf{r}_1-\mathbf{R}_j{}^0|}+\frac{Z_j}{|\mathbf{r}_1-\mathbf{R}_j{}^+|}+\frac{Z_j}{|\mathbf{r}_1-\mathbf{R}_j{}^-|} -V^{\text{c.e.}}(0,j;1)-V^{\text{c.e.}}(1,j;1)-V^{\text{c.e.}}(-1,j;1)\right] \times|\chi^{qg}(1)\rangle+\sum_{\substack{s,t=-1\\ t-s,s-q,q-t\neq2}}^{1}\sum_{i,j=1}^{n}P_{tj}{}^{si}G_{si}{}^{tj}(0,f;q,g), \quad (31b)$$

where now q is only a scalar integer. We have introduced the notation $\mathbf{R}_j^0$, $\mathbf{R}_j^+$, and $\mathbf{R}_j^-$ for the position vector of the jth nucleus in the elementary cell where we have put the origin of our coordinate system, and in the right (+) and left (−) neighboring cell, respectively. For a linear chain, Eqs. (29a) and (30a) also become simpler:

$$\mathbf{F}'(\kappa)\approx\mathbf{F}(0)+e^{i\kappa}\mathbf{F}(1)+e^{-i\kappa}\mathbf{F}(-1) \tag{29b}$$

and

$$\mathbf{S}'(\kappa)\approx\mathbf{S}(0)+e^{i\kappa}\mathbf{S}(1)+e^{-i\kappa}\mathbf{S}(-1)\,, \tag{30b}$$

respectively.

2. It is advantageous at this stage to subdivide the n atomic orbitals of the elementary cell into subsets of orbitals provided by the different atoms of the elementary cell. If we have n_a atoms in the elementary cell and we denote by m_j the number of orbitals provided by the jth atom, we can write

$$n=\sum_{j=1}^{n_a} m_j.$$

Further, we can now rewrite, for a scalar integer q only, the row vector (3a) characterizing the qth elementary cell in the form

$$\chi^q=(\chi^{q1},\cdots,\chi^{qj},\cdots,\chi^{qn_a}) \tag{32a}$$

with subvectors

$$\chi^{qj}=(\chi^{qj1},\cdots,\chi^{qj\alpha},\cdots,\chi^{qjm_j})\,. \tag{32b}$$

Making this further subdivision of our basis, we can indicate also in the elements of matrices **F**, **P**, and **G** the different atoms and their different orbitals. Thus an element of $\mathbf{F}(\mathbf{q})$ will have the form

$$F_{j\alpha}{}^{l\beta}(q)=\langle\chi^{0j\alpha}(1)|\mathcal{H}_1|\chi^{ql\beta}(1)\rangle + \sum_{\substack{s,t=-1\\ t-s\neq 2}}^{1}\ \sum_{u,v=1}^{n_a}\ \sum_{\gamma=1}^{m_u}\ \sum_{\delta=1}^{m_v} P_{tv\delta}{}^{su\gamma} \times G_{su\gamma}{}^{tv\delta}(0,j,\alpha;\,q,l,\beta)\,, \tag{33}$$

and in the expressions (27b) and (27c) of the charge-bond order matrix the column vector $\mathbf{d}^h(\kappa)$ has the elements $d_{u\gamma}{}^h(\kappa)$. Furthermore,

$$G_{su\gamma}{}^{tv\delta}(0,j,\alpha;\,q,l,\beta) =\langle\chi^{0j\alpha}(1)\chi^{su\gamma}(2)|r_{12}{}^{-1}|\chi^{tv\delta}(2)\chi^{ql\beta}(1)\rangle -\tfrac{1}{2}\langle\chi^{0j\alpha}(1)\chi^{su\gamma}(2)|r_{12}{}^{-1}|\chi^{ql\beta}(2)\chi^{tv\delta}(1)\rangle. \tag{34}$$

Here we have used the symbolic notation $\mathcal{H}_1$ for the integrand of the first term of (31b). Further, the indices j, l, v, and u refer to the atoms and the Greek indices α, β, γ, and δ to the orbitals of these atoms. For example, $F_{j\alpha}{}^{l\beta}(q)$ is an interaction matrix element between the αth AO of the jth atom in the elementary cell characterized by 0 and the βth AO of the lth atom in the elementary cell characterized by q.

3. Introducing this notation we can classify the elements of $\mathbf{F}(q)$ as follows:

(i) $F_{j\alpha}{}^{j\alpha}(0)$, intra-atomic diagonal term;

(ii) $F_{j\alpha}{}^{j\beta}(0)$, $\alpha\neq\beta$, intra-atomic off-diagonal terms (interaction terms between different AO's centered on the same atom);

(iii) $F_{j\alpha}{}^{j'\beta}(0)$, $j\neq j'$, interaction terms between AO's centered on different atoms j and j' of the same kind within the same elementary cell;

(iv) $F_{j\alpha}{}^{l\beta}(0)$, $j\neq l$, interaction terms between AO's centered on atoms of different kinds within the same elementary cell;

(v) $F_{j\alpha}{}^{j'\beta}(\pm 1)$, interaction terms between AO's centered on atoms of the same kind belonging to neighboring cells; and finally

(vi) $F_{j\alpha}{}^{l\beta}(\pm 1)$, $j\neq l$, interaction terms between AO's centered on atoms of different kinds belonging to neighboring elementary cells.

In the interatomic cases (iii), (iv), (v), and (vi), we can distinguish further between matrix elements corresponding to chemical bonds of the polymer and much smaller matrix elements which correspond to interactions between orbitals which do not form a chemical bond with each other.

4. If we substitute into (33) the expression (34) and the expression of $\mathcal{H}_1$ given in (31b), we can derive the expression for the different elements of $\mathbf{F}(q)$ in terms of a number of integrals. To do this, however, we need to specify the potentials $V^{\text{c.e.}}(p,j;1)$ ($p=0,\pm 1$) occurring in (31b). If we suppose in the first rough approximation that the exchange between the core electrons and the valence electrons is negligible, and if we also neglect exchange effects between the core electrons, we obtain the very simple expression

$$V^{\text{c.e.}}(p,j;1)=\sum_{\alpha=1}^{n_j{}^c}\langle\chi^{pj\alpha}(2)|r_{12}{}^{-1}|\chi^{pj\alpha}(2)\rangle\,, \tag{35}$$

where $n_j{}^c$ denotes the number of orbitals of core electrons in the jth atom.

After doing this, we shall have one-electron integrals due to the kinetic-energy operator and to the potentials of the nuclei in $\mathcal{H}_1$, and two-electron integrals due to the core-electron potentials $V^{\text{c.e.}}(p,j;1)$ [Eq. (35)] and the Coulomb and exchange terms in Eq. (34). The kinetic-energy integrals will be either one-center integrals [in the cases (i) and (ii)] or two-center integrals [in the cases (iii)–(vi)]. Using Slater-type orbitals, all these can be evaluated analytically. For the nuclear-interaction one-electron integrals we obtain one-center, two-center, and three-center integrals. [The last have the form

$$\langle\chi^{0j\alpha}(1)|Z_v/|\mathbf{r}_1-\mathbf{R}_v{}^p||\chi^{ql\beta}(1)\rangle,$$

where $j\neq v$, $j\neq l$ and $v\neq l$ if both p and q are zero.] The evaluation of the one-center and both the homo- and heteronuclear two-center nuclear-interaction integrals is well known in the case of Slater-type orbitals,[16] and methods have also been developed for the calculation of three-center integrals of these types.[17]

The integrals corresponding to the interaction between the valence electrons and the core electrons, if we use Eq. (48) for $V^{\text{c.e.}}(p,j;1)$, will again be one-center, two-center, and three-center integrals, the last having the general form

$$\langle\chi^{0l\beta}(1)\chi^{pj\alpha}(2)|r_{12}^{-1}|\chi^{pj\alpha}(2)\chi^{su\gamma}(1)\rangle,$$

where $j\neq u$, $j\neq l$, and $u\neq l$ if both p and s are zero. In the case of Slater-type orbitals the calculations of one-center and homonuclear two-center integrals is well known,[18] and there are also methods for the evaluation of the heteronuclear two-center[19] as well as of the three-center integrals.[17,20]

Finally, we have a great number of different two-electron integrals coming from the Coulomb and the exchange terms in (34). Here we have one-, two-, three-, and four-center integrals. In the case of the four-center integrals, j, u, v, and l are generally all different numbers in Eq. (34). Also in this case, the calculation of the one-center and of the homo- and heteronuclear Coulomb, exchange, and hybrid-type two-center integrals with Slater-type orbitals is well known,[18,19] and recently methods have been developed for calculating the three- and four-center integrals.[17,20]

To perform an actual SCF LCAO calculation for the determination of the energy-band structure of a linear chain without neglecting any of these integrals is an enormous task, but with the aid of large computers it is not impossible. If, however, we want to neglect some terms to simplify the matter, we have to study in detail the dependence of these integrals on the distances occurring in the nearest-neighbor approximation, and on the form of the valence-shell orbitals that are explicitly taken into account. (It is clear, for instance, that completely different situations arise if we take into account only π orbitals, or only σ orbitals, or both.) Unfortunately, this cannot be done in the general case, but only for a given linear chain.

V. CONCLUDING REMARKS

1. The general formalism developed in the present paper is applicable to numerical calculations, at least on large computers. Calculations of this kind are in progress, and in further papers we shall present numerical examples referring especially to the influence of the various terms classified in 3 of Sec. III on the band structure of polymers.

Here, as a final remark, we wish to give only some formulas which are particularly useful for the analysis of the shapes of the bands which are obtained from Eq. (10b), namely, the derivatives of the eigenvalues and of the eigenvectors of the matrix $\mathbf{F}'(\mathbf{k})$ with respect to the components of $\mathbf{k}$.

For the sake of simplicity we shall consider explicitly only the dependence on one parameter k_1. Let us rewrite Eq. (10b) in the form

$$\mathbf{F}'(\mathbf{k})\mathbf{d}(\mathbf{k})=\mathbf{S}'(\mathbf{k})\mathbf{d}(\mathbf{k})\boldsymbol{\varepsilon}(\mathbf{k}),\qquad(36)$$

where $\mathbf{d}(\mathbf{k})$ is a square matrix formed from the complex eigenvectors $\mathbf{d}^f(\mathbf{k})$, and the diagonal matrix $\boldsymbol{\varepsilon}(\mathbf{k})$ has as elements the different $\epsilon(\mathbf{k},f)$ eigenvalues. Differentiating this equation and multiplying on the left by $\mathbf{d}^\dagger(\mathbf{k})$, we obtain

$$\begin{aligned}\mathbf{d}^\dagger(\mathbf{k})\frac{\partial\mathbf{F}'(\mathbf{k})}{\partial k_1}\mathbf{d}(\mathbf{k})&\\ =\mathbf{d}^\dagger(\mathbf{k})\frac{\partial\mathbf{S}'(\mathbf{k})}{\partial k_1}\mathbf{d}(\mathbf{k})\boldsymbol{\varepsilon}(\mathbf{k})&+\mathbf{d}^\dagger(\mathbf{k})\mathbf{S}'(\mathbf{k})\frac{\partial\mathbf{d}(\mathbf{k})}{\partial k_1}\boldsymbol{\varepsilon}(\mathbf{k})\\ &-\boldsymbol{\varepsilon}(\mathbf{k})\mathbf{d}^\dagger(\mathbf{k})\mathbf{S}'(\mathbf{k})\frac{\partial\mathbf{d}(\mathbf{k})}{\partial k_1}+\frac{\partial\boldsymbol{\varepsilon}(\mathbf{k})}{\partial k_1},\qquad(37)\end{aligned}$$

where use has been made of the condition

$$\mathbf{d}^\dagger(\mathbf{k})\mathbf{S}'(\mathbf{k})\mathbf{d}(\mathbf{k})=\mathbf{I}\qquad(38)$$

and of Eq. (36). Taking the diagonal elements of Eq. (37), we find immediately

$$\frac{\partial\epsilon(\mathbf{k},f)}{\partial k_1}=[\mathbf{d}^f(\mathbf{k})]\left[{}^\dagger\frac{\partial\mathbf{F}'(\mathbf{k})}{\partial k_1}-\epsilon(\mathbf{k},f)\frac{\partial\mathbf{S}'(\mathbf{k})}{\partial k_1}\right]\mathbf{d}^f(\mathbf{k}).\qquad(39)$$

Actually, sometimes the complex matrices we consider in the present paper may have degenerate eigenvalues. As is customary, we must then apply the usual techniques of degenerate perturbation theory.

Since the complex matrices $\mathbf{F}$ and $\mathbf{S}$ have, in the case of a linear chain in the nearest-neighbor approximation, the simple form $\mathbf{A}(\kappa)=\mathbf{A}(0)+\mathbf{A}(1)e^{i\kappa}+\mathbf{A}(-1)e^{-i\kappa}$ ($\mathbf{A}=\mathbf{F}$ or $\mathbf{S}$) and the matrices $\mathbf{S}(p)$ and $\mathbf{F}(p)$ do not depend on κ, we can write simply

$$\begin{aligned}\partial\mathbf{A}(\kappa)/\partial\kappa=&-\sin\kappa[\mathbf{A}(1)+\mathbf{A}(-1)]\\ &+i\cos\kappa[\mathbf{A}(1)-\mathbf{A}(-1)],\quad(\mathbf{A}=\mathbf{F}\text{ or }\mathbf{S}),\qquad(40)\end{aligned}$$

which can be substituted into Eq. (39).

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