Theoret. Chim. Acta (Berl.) 54, 1–14 (1979)

THEORETICA CHIMICA ACTA

Original Investigations

Molecular Orbital Theory of the Electronic Structures of One-Dimensional Molecular Crystals

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A non-empirical tight-binding LCAO SCF MO treatment of one-dimensional molecular crystals based on the SCF perturbation theory is presented. The simpler version of this method at the level of the CNDO/2 approximation is also given.

Key words: One-dimensional molecular crystals – Crystals, one-dimensional molecular ~

1. Introduction

In recent years there has been a considerable interest in the chemical and physical properties of one-dimensional materials such as tetracyanoquinodimethane (TCNQ) charge-transfer salts, $K_2[Pt(CN)_4]Br_{0.3} \cdot 3H_2O$ mixed-valence complex, polymeric sulfur nitride $(SN)_x$, and so on in the field of solid-state science [1, 2]. Quantum-chemical treatments of the electronic structures of these materials have been achieved with the use of the tight-binding LCAO SCF MO method [3–6]. Almost all of the calculations, however, are based on methods for treating polymers composed of an infinite repetition of unit cells along *one* direction (main chain direction). Indeed, this approach is justified as a starting point owing to the week interactions in the remaining two lattice-vector directions (let us denote these simply as interchain interactions), but a more accurate treatment should include the interchain interactions in the next step, since these interactions seem to have a subtle influence on the electronic structures of the main chains and on the cooperative phenomena manifesting themselves in one-dimensional materials [7]. An orthodox approach to satisfy this requirement is to calculate the three-dimensional crystal orbitals with the use of the method established by Ladik *et al.* some time ago [8]. However, the time required for the computation to accomplish the SCF procedure for the Fock equations in the three-dimensional Brillouin zone is too

0040-5744/79/0054/0001/$02.80

excessive and hence not practical for the present generation of computers, even at the level of the CNDO approximation [9]. Thus there have been no actual SCF calculations of crystals to the authors' knowledge.

An approach to the electronic structures of three-dimensional molecular crystals which avoids these tedious calculations has been reported by Santry *et al.* [10, 11]. This method is based on SCF perturbation theory, employing the Hamiltonian of a non-interacting molecule constituting a unit cell as the zeroth order and regarding all intercell interactions as the perturbation. However, it is not suitable for one-dimensional molecular crystals in which the intrachain interactions can no longer be treated as a perturbation.

In the present paper, we develop a specific non-empirical tight-binding LCAO SCF MO theory based on the SCF perturbation technique for a one-dimensional molecular crystal, the unit cell of which is of a closed shell structure. In this theory, the interactions between a unit cell in the main chain and those in the nearest neighbouring chains are regarded as the perturbation, with the main chain polymer as the unperturbed system. This approach can be applied not only to one-dimensional molecular crystals, but also to analyses of the interactions among polypeptide chains in order to investigate their higher structures.

2. Fock Equation of One-Dimensional Molecular Crystals

At first we begin by defining the lattice vectors of the one-dimensional molecular crystal and introducing the conventional Fock equation for the closed-shell tight-binding LCAO SCF MO calculation [8] for this system. Some notations used throughout this paper are also defined in this section.

An arbitrary unit cell in the system is defined by a linear combination of the three independent lattice translation vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, and $\boldsymbol{a}_3$ as

$$\boldsymbol{a} = j_1\boldsymbol{a}_1 + j_2\boldsymbol{a}_2 + j_3\boldsymbol{a}_3 \equiv [j_1, j_2, j_3], \tag{1}$$

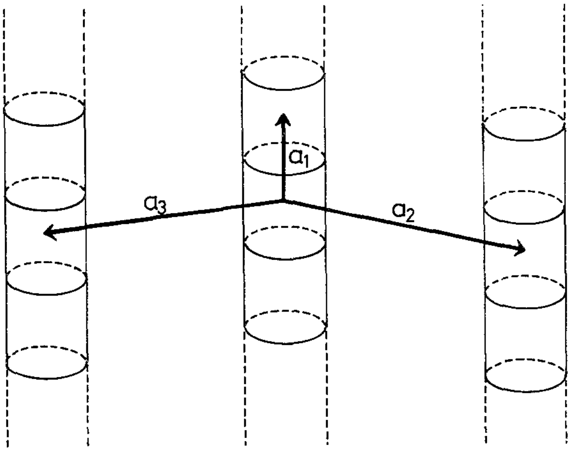

Fig. 1. Schematic representation of the unit cells and the lattice translation vectors in a one-dimensional molecular crystal. The direction along $\boldsymbol{a}_1$ is taken to that of the main chain

where the j_i's take all positive and negative integral values including zero. We refer to this unit cell as the $[j_1, j_2, j_3]$th cell, and take the [0, 0, 0]th one as the reference cell. It is supposed that there are $2N_i + 1$ cells along each direction of $\boldsymbol{a}_i$ without a loss of generality. As shown in Fig. 1, we choose the lattice translation along the main chain to be $\boldsymbol{a}_1$, and those along the interchain directions $\boldsymbol{a}_2$ and $\boldsymbol{a}_3$. In our one-dimensional molecular crystals, $|\boldsymbol{a}_1|$ is significantly smaller than $|\boldsymbol{a}_2|$ and $|\boldsymbol{a}_3|$. Each unit cell contains N_α nuclei whose charges are z_α and n atomic orbitals (AO's) assigned by the Greek letters μ, ν, ρ, and σ. It is to be noted that the vectors $\boldsymbol{a}_i$ are not necessarily orthogonal (triclinic system), and the corresponding reciprocal lattice vectors $\boldsymbol{K}_i$'s ($i = 1$, 2, and 3) are defined so that the relation

$$\boldsymbol{a}_i\boldsymbol{K}_j = 2\pi\delta_{ij}, \tag{2}$$

may be satisfied [12], namely,

$$\begin{aligned} \boldsymbol{K}_1 &= 2\pi \frac{\boldsymbol{a}_2 \times \boldsymbol{a}_3}{\boldsymbol{a}_1\cdot(\boldsymbol{a}_2 \times \boldsymbol{a}_3)} \\ \boldsymbol{K}_2 &= 2\pi \frac{\boldsymbol{a}_3 \times \boldsymbol{a}_1}{\boldsymbol{a}_2\cdot(\boldsymbol{a}_3 \times \boldsymbol{a}_1)}. \\ \boldsymbol{K}_3 &= 2\pi \frac{\boldsymbol{a}_1 \times \boldsymbol{a}_2}{\boldsymbol{a}_3\cdot(\boldsymbol{a}_1 \times \boldsymbol{a}_2)} \end{aligned} \tag{3}$$

Thus, any point in the first Brillouin zone can be defined by the wavevector $\boldsymbol{k} = (\boldsymbol{k}_1, \boldsymbol{k}_2, \boldsymbol{k}_3)$, where $\boldsymbol{k}_i$'s are the vectors along the directions of $\boldsymbol{K}_i$'s, respectively, under the condition,

$$\begin{aligned} -\frac{\pi}{\boldsymbol{a}_1} &< \boldsymbol{k}_1 < \frac{\pi}{\boldsymbol{a}_1} \\ -\frac{\pi}{\boldsymbol{a}_2} &< \boldsymbol{k}_2 < \frac{\pi}{\boldsymbol{a}_2}. \\ -\frac{\pi}{\boldsymbol{a}_3} &< \boldsymbol{k}_3 < \frac{\pi}{\boldsymbol{a}_3} \end{aligned} \tag{4}$$

In the tight-binding LCAO SCF MO method, a one-electron crystal orbital for the closed-shell structure is given with the aid of Bloch's theorem [13] as follows:

$$\begin{aligned} \psi_s(\boldsymbol{k}) = \frac{1}{\sqrt{N}} \sum_{j_1=0}^{\pm N_1} \sum_{j_2=0}^{\pm N_2} \sum_{j_3=0}^{\pm N_3} \sum_{\mu}^{n} \exp\,[i(j_1\boldsymbol{k}_1\boldsymbol{a}_1 + j_2\boldsymbol{k}_2\boldsymbol{a}_2 + j_3\boldsymbol{k}_3\boldsymbol{a}_3)] \\ \cdot C_{\mu s}(\boldsymbol{k})\chi_\mu(\boldsymbol{r} - \boldsymbol{a}), \end{aligned} \tag{5}$$

$$N = (2N_1 + 1)(2N_2 + 1)(2N_3 + 1), \tag{6}$$

where s specifies the energy level, $C_{\mu s}(\boldsymbol{k})$ the AO coefficient, $\chi_\mu(\boldsymbol{r} - \boldsymbol{a})$ the μth AO in the $[j_1, j_2, j_3]$th cell, and N the total number of unit cells. Note that $C_{\mu s}(\boldsymbol{k})$ is generally a complex number. The density matrix is defined for the wavevector $\boldsymbol{k}$ as

$$R_{\mu\nu}(\boldsymbol{k}) = \sum_{s}^{\mathrm{occ}} C_{\mu s}^{*}(\boldsymbol{k})C_{\nu s}(\boldsymbol{k}). \tag{7}$$

The total density matrix for the system is given by using Eq. (7) as

$$P_{\mu\nu}[j_1, j_2, j_3] = \frac{2}{N}\sum_{k_1}^{\mathrm{BZ}}\sum_{k_2}^{\mathrm{BZ}}\sum_{k_3}^{\mathrm{BZ}} \exp\,[i(j_1\boldsymbol{k}_1\boldsymbol{a}_1 + j_2\boldsymbol{k}_2\boldsymbol{a}_2 + j_3\boldsymbol{k}_3\boldsymbol{a}_3)]\cdot R_{\mu\nu}(\boldsymbol{k}), \tag{8}$$

where the summation of $\boldsymbol{k}$ in Eq. (8) extends over the first Brillouin zone, and is replaced by the integral form in the molecular crystal as follows:

$$\sum_{k_1}^{\mathrm{BZ}}\sum_{k_2}^{\mathrm{BZ}}\sum_{k_3}^{\mathrm{BZ}} \rightarrow \frac{N\boldsymbol{a}_1\cdot(\boldsymbol{a}_2 \times \boldsymbol{a}_3)}{8\pi^3}\iiint dk_1\, dk_2\, dk_3.$$

The density matrix element in Eq. (8) generally signifies the bond order between the μth AO in the [0, 0, 0]th cell and the νth AO in the $[j_1, j_2, j_3]$th cell. The crystal orbital in Eq. (5) is given as the solution of a set of the Fock equations of the system,

$$\sum_{\nu}^{n} [F_{\mu\nu}(\boldsymbol{k}) - \varepsilon_s(\boldsymbol{k})S_{\mu\nu}(\boldsymbol{k})]C_{\nu s}(\boldsymbol{k}) = 0 \quad (\mu = 1, 2, \ldots, n), \tag{9}$$

where $\varepsilon_s(\boldsymbol{k})$ is the energy level of the crystal orbital at $\boldsymbol{k}$, describing the energy band over the Brillouin zone. $F_{\mu\nu}(\boldsymbol{k})$ is the Fock matrix element defined as follows.

$$F_{\mu\nu}(\boldsymbol{k}) = \sum_{j_1=0}^{\pm N_1}\sum_{j_2=0}^{\pm N_2}\sum_{j_3=0}^{\pm N_3} \exp\,[i(j_1\boldsymbol{k}_1\boldsymbol{a}_1 + j_2\boldsymbol{k}_2\boldsymbol{a}_2 + j_3\boldsymbol{k}_3\boldsymbol{a}_3)] \cdot\{H_{\mu\nu}[j_1, j_2, j_3] + G_{\mu\nu}[j_1, j_2, j_3]\}, \tag{10}$$

$$H_{\mu\nu}[j_1, j_2, j_3] = \langle \chi_\mu[0, 0, 0]|h^c|\chi_\nu[j_1, j_2, j_3]\rangle, \tag{11}$$

$$h^c = -\frac{1}{2}\nabla^2 - \sum_{j_1=0}^{\pm N_1}\sum_{j_2=0}^{\pm N_2}\sum_{j_3=0}^{\pm N_3}\sum_{\alpha}^{N_\alpha} \frac{Z_\alpha}{|\boldsymbol{r} - \boldsymbol{R}_\alpha[j_1, j_2, j_3]|}, \tag{12}$$

$$\begin{aligned} G_{\mu\nu}[j_1, j_2, j_3] = {} & \sum_{\rho}^{n}\sum_{\sigma}^{n}\sum_{j_1'=0}^{\pm N_1}\sum_{j_2'=0}^{\pm N_2}\sum_{j_3'=0}^{\pm N_3}\sum_{j_1''=0}^{\pm N_1}\sum_{j_2''=0}^{\pm N_2}\sum_{j_3''=0}^{\pm N_3} \\ & \Bigg[P_{\rho\sigma}[j_1'' - j_1', j_2'' - j_2', j_3'' - j_3'] \\ & \cdot\Bigg\{\Bigg\langle \chi_\mu[0, 0, 0]\chi_\nu[j_1, j_2, j_3]\Bigg|\frac{1}{r_{12}}\Bigg|\chi_\rho[j_1', j_2', j_3']\chi_\sigma[j_1'', j_2'', j_3'']\Bigg\rangle \\ & -\frac{1}{2}\Bigg\langle \chi_\mu[0, 0, 0]\chi_\sigma[j_1'', j_2'', j_3'']\Bigg|\frac{1}{r_{12}}\Bigg|\chi_\rho[j_1', j_2', j_3']\chi_\nu[j_1, j_2, j_3]\Bigg\rangle\Bigg\}\Bigg], \end{aligned} \tag{13}$$

where $\chi_\mu[j_1, j_2, j_3]$ and $\boldsymbol{R}_\alpha[j_1, j_2, j_3]$ denote the μth AO and the coordinate of the αth nucleus, respectively, in the $[j_1, j_2, j_3]$th cell. $S_{\mu\nu}(\boldsymbol{k})$ is the overlap matrix element defined as:

$$S_{\mu\nu}(\boldsymbol{k}) = \sum_{j_1=0}^{\pm N_1}\sum_{j_2=0}^{\pm N_2}\sum_{j_3=0}^{\pm N_3} \exp\,[i(j_1\boldsymbol{k}_1\boldsymbol{a}_1 + j_2\boldsymbol{k}_2\boldsymbol{a}_2 + j_3\boldsymbol{k}_3\boldsymbol{a}_3)]\cdot S_{\mu\nu}[j_1, j_2, j_3], \tag{14}$$

$$S_{\mu\nu}[j_1, j_2, j_3] = \langle \chi_\mu[0, 0, 0]|\chi_\nu[j_1, j_2, j_3]\rangle. \tag{15}$$

Since the set of the Fock equations of the usual one-dimensional polymers should be solved at 10 $\sim$ 20 $\boldsymbol{k}_1$ values in the one-dimensional Brillouin zone [14, 15], there are $10^3 \sim 20^3$ Fock matrices to be diagonalized for three-dimensional calculations for each SCF iteration. In the case of the one-dimensional molecular crystals, one can avoid the tedious calculations of this type with the use of the perturbation technique shown in the next section.

3. Perturbed Fock Submatrices

We expand the SCF matrix equation in Eq. (9) in a perturbation series as far as the second order:

$$F_{\mu\nu}(\boldsymbol{k}) = F^{(0)}_{\mu\nu}(\boldsymbol{k}) + \lambda F^{(1)}_{\mu\nu}(\boldsymbol{k}) + \lambda^2 F^{(2)}_{\mu\nu}(\boldsymbol{k}), \tag{16}$$

$$S_{\mu\nu}(\boldsymbol{k}) = S^{(0)}_{\mu\nu}(\boldsymbol{k}) + \lambda S^{(1)}_{\mu\nu}(\boldsymbol{k}) + \lambda^2 S^{(2)}_{\mu\nu}(\boldsymbol{k}). \tag{17}$$

The energy levels in Eq. (9) and AO coefficients in Eq. (5) are similarly expanded as

$$\varepsilon_s(\boldsymbol{k}) = \varepsilon_s^{(0)}(\boldsymbol{k}) + \lambda \varepsilon_s^{(1)}(\boldsymbol{k}) + \lambda^2 \varepsilon_s^{(2)}(\boldsymbol{k}), \tag{18}$$

$$C_{\mu s}(\boldsymbol{k}) = C^{(0)}_{\mu s}(\boldsymbol{k}) + \lambda C^{(1)}_{\mu s}(\boldsymbol{k}) + \lambda^2 C^{(2)}_{\mu s}(\boldsymbol{k}). \tag{19}$$

The perturbed density matrices for the wavevector $\boldsymbol{k}$ as far as the second order are given as follows.

$$R^{(0)}_{\mu\nu}(\boldsymbol{k}) = \sum_{s}^{\text{occ}} C^{*(0)}_{\mu s}(\boldsymbol{k}) C^{(0)}_{\nu s}(\boldsymbol{k}), \tag{20}$$

$$R^{(1)}_{\mu\nu}(\boldsymbol{k}) = \sum_{s}^{\text{occ}} \{C^{*(0)}_{\mu s}(\boldsymbol{k}) C^{(1)}_{\nu s}(\boldsymbol{k}) + C^{*(1)}_{\mu s}(\boldsymbol{k}) C^{(0)}_{\nu s}(\boldsymbol{k})\}, \tag{21}$$

$$R^{(2)}_{\mu\nu}(\boldsymbol{k}) = \sum_{s}^{\text{occ}} \{C^{*(0)}_{\mu s}(\boldsymbol{k}) C^{(2)}_{\nu s}(\boldsymbol{k}) + C^{*(1)}_{\mu s}(\boldsymbol{k}) C^{(1)}_{\nu s}(\boldsymbol{k}) + C^{*(2)}_{\mu s}(\boldsymbol{k}) C^{(0)}_{\nu s}(\boldsymbol{k})\}. \tag{22}$$

The perturbed total density matrices are given by using Eqs. (8), (20), (21), and (22) as:

$$P^{(0)}_{\mu\nu}[j_1, j_2, j_3] = \frac{2}{N} \sum_{\boldsymbol{k}_1}^{\text{BZ}} \sum_{\boldsymbol{k}_2}^{\text{BZ}} \sum_{\boldsymbol{k}_3}^{\text{BZ}} \exp{[i(j_1 \boldsymbol{k}_1 \boldsymbol{a}_1 + j_2 \boldsymbol{k}_2 \boldsymbol{a}_2 + j_3 \boldsymbol{k}_3 \boldsymbol{a}_3)]} \cdot R^{(0)}_{\mu\nu}(\boldsymbol{k}), \tag{23}$$

$$P^{(1)}_{\mu\nu}[j_1, j_2, j_3] = \frac{2}{N} \sum_{\boldsymbol{k}_1}^{\text{BZ}} \sum_{\boldsymbol{k}_2}^{\text{BZ}} \sum_{\boldsymbol{k}_3}^{\text{BZ}} \exp{[i(j_1 \boldsymbol{k}_1 \boldsymbol{a}_1 + j_2 \boldsymbol{k}_2 \boldsymbol{a}_2 + j_3 \boldsymbol{k}_3 \boldsymbol{a}_3)]} \cdot R^{(1)}_{\mu\nu}(\boldsymbol{k}), \tag{24}$$

$$P^{(2)}_{\mu\nu}[j_1, j_2, j_3] = \frac{2}{N} \sum_{\boldsymbol{k}_1}^{\text{BZ}} \sum_{\boldsymbol{k}_2}^{\text{BZ}} \sum_{\boldsymbol{k}_3}^{\text{BZ}} \exp{[i(j_1 \boldsymbol{k}_1 \boldsymbol{a}_1 + j_2 \boldsymbol{k}_2 \boldsymbol{a}_2 + j_3 \boldsymbol{k}_3 \boldsymbol{a}_3)]} \cdot R^{(2)}_{\mu\nu}(\boldsymbol{k}). \tag{25}$$

The final total density matrix is given by the sum of Eqs. (23), (24), and (25). In the present scheme, we employ the set of the isolated main chains along the $\boldsymbol{a}_1$ axis as the unperturbed system:

$$F^{(0)}_{\mu\nu}(\boldsymbol{k}) = \sum_{j_1=0}^{\pm M} \exp{[ij_1 \boldsymbol{k}_1 \boldsymbol{a}_1]} \{H^{(0)}_{\mu\nu}[j_1] + G^{(0)}_{\mu\nu}[j_1]\}, \tag{26}$$

where

$$H^{(0)}_{\mu\nu}[j_1] = \left\langle \chi_\mu[0, 0, 0] \right| -\frac{1}{2}\nabla^2 - \sum_{j_1=0}^{\pm M} \sum_{\alpha}^{N_\alpha} \frac{Z_\alpha}{|\boldsymbol{r} - \boldsymbol{R}_\alpha[j_1, 0, 0]|} \left| \chi_\nu[j_1, 0, 0], \right\rangle \tag{27}$$

$$G^{(0)}_{\mu\nu}[j_1] = \sum_{\rho}^{n}\sum_{\sigma}^{n}\sum_{j_1'=0}^{\pm M}\sum_{j_1''=0}^{\pm M}\Bigg[P^{(0)}_{\rho\sigma}[j_1''-j_1',0,0] \cdot\Bigg\{\Bigg\langle \chi_\mu[0,0,0]\chi_\nu[j_1,0,0]\Bigg|\frac{1}{r_{12}}\Bigg|\chi_\rho[j_1',0,0]\chi_\sigma[j_1'',0,0]\Bigg\rangle - \frac{1}{2}\Bigg\langle \chi_\mu[0,0,0]\chi_\sigma[j_1'',0,0]\Bigg|\frac{1}{r_{12}}\Bigg|\chi_\rho[j_1',0,0]\chi_\nu[j_1,0,0]\Bigg\rangle\Bigg\}\Bigg]. \tag{28}$$

The unperturbed overlap matrix is:

$$S^{(0)}_{\mu\nu}(\boldsymbol{k}) = \sum_{j_1=0}^{\pm M}\exp\,[ij_1\boldsymbol{k}_1\boldsymbol{a}_1]S_{\mu\nu}[j_1,0,0], \tag{29}$$

where $S_{\mu\nu}[j_1, 0, 0]$ is defined in Eq. (15). M in Eqs. (26), (27), and (28) indicates the number of neighbouring cells in the main chain interacting with the [0, 0, 0]th cell. The zeroth order total energy per unit cell is evaluated as follows.

$$E^{(0)} = \frac{1}{2}\sum_{\mu}^{n}\sum_{\nu}^{n}\sum_{j_1=0}^{\pm M}[P^{(0)}_{\mu\nu}[j_1,0,0]\{2H^{(0)}_{\mu\nu}[j_1] + G^{(0)}_{\mu\nu}[j_1]\}] + \sum_{\alpha<\alpha'}^{N\alpha}\frac{Z_\alpha Z_{\alpha'}}{|\boldsymbol{R}_\alpha[0,0,0]-\boldsymbol{R}_{\alpha'}[0,0,0]|} + \frac{1}{2}\sum_{j_1=0}^{\pm M}\sum_{\alpha}^{N\alpha}\sum_{\alpha'}^{N\alpha}\frac{Z_\alpha Z_{\alpha'}}{|\boldsymbol{R}_\alpha[0,0,0]-\boldsymbol{R}_{\alpha'}[j_1,0,0]|}. \tag{30}$$

It is to be noted that both of the zeroth order AO coefficients and the zeroth order energy levels at any point $\boldsymbol{k} = (\boldsymbol{k}_1, \boldsymbol{k}_2, \boldsymbol{k}_3)$ are equal to those at $(\boldsymbol{k}_1, \boldsymbol{0}, \boldsymbol{0})$, and that the zeroth order energy bands are flat toward the $\boldsymbol{k}_2$ and $\boldsymbol{k}_3$ axes. Hence, in actuality, one has only to solve a set of Fock equations of a main chain polymer, e.g., with $j_2 = j_3 = 0$, in order to get the unperturbed solution.

The interactions between a unit cell in the main chain and those in the nearest neighbouring chains are regarded as the first-order perturbation in Eqs. (16) and (17):

$$F^{(1)}_{\mu\nu}(\boldsymbol{k}) = F^{(1)}_{\mu\nu}[0,0,0] + \left(\sum_{j_2}\sum_{j_3}\right)\exp\,[i(j_2\boldsymbol{k}_2\boldsymbol{a}_2 + j_3\boldsymbol{k}_3\boldsymbol{a}_3)] \cdot F^{(1)}_{\mu\nu}[0,j_2,j_3] + \sum_{j_1=0}^{\pm M}\exp\,[ij_1\boldsymbol{k}_1\boldsymbol{a}_1]F^{(1)}_{\mu\nu}[j_1], \tag{31}$$

$$S^{(1)}_{\mu\nu}(\boldsymbol{k}) = \left(\sum_{j_2}\sum_{j_3}\right)\exp\,[i(j_2\boldsymbol{k}_2\boldsymbol{a}_2 + j_3\boldsymbol{k}_3\boldsymbol{a}_3)]S_{\mu\nu}[0,j_2,j_3]. \tag{32}$$

In Eqs. (31) and (32), $(\sum_{j2}\sum_{j3})$ means the summation with respect to the $[0, j_2, j_3]$th cell interacting with the [0, 0, 0]th cell. For example, in the tetragonal system shown in Fig. 2, this summation ranges over the [0, ±1, 0]th and the [0, 0, ±1]th cells. The first term in Eq. (31) represents the interchain interaction with two AO (μ and ν) centres existing in the [0, 0, 0]th cell as follows.

$$F^{(1)}_{\mu\nu}[0,0,0] = H^{(1)}_{\mu\nu}[0,0,0] + G^{(1)}_{\mu\nu}[0,0,0], \tag{33}$$

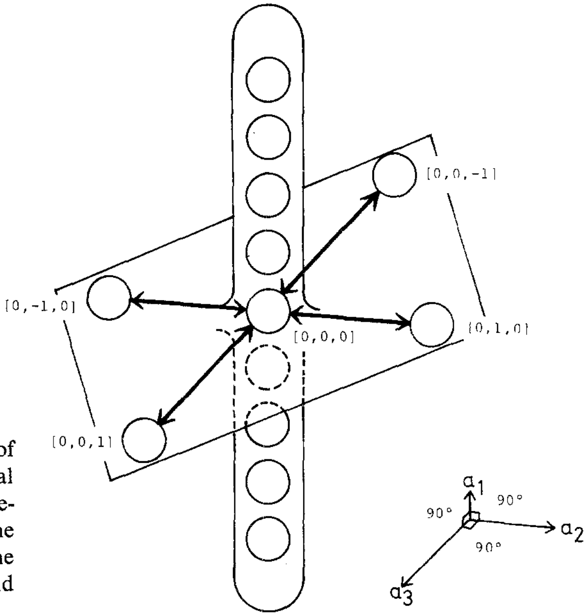

Fig. 2. Schematic representation of the cells interacting with the central reference cell in a tetragonal one-dimensional molecular crystal. The number of the interacting cells in the main chain (i.e., M in Eqs. (26) and so on) is 4 in this model.

where

$$H_{\mu\nu}^{(1)}[0,0,0] = \left\langle \chi_\mu[0,0,0] \middle| -\left(\sum_{j_2}\sum_{j_3}\right)\sum_{\alpha}^{N\alpha} \frac{Z_\alpha}{|\boldsymbol{r}-\boldsymbol{R}_\alpha[0,j_2,j_3]|} \middle| \chi_\nu[0,0,0] \right\rangle, \tag{34}$$

and

$$\begin{aligned} G_{\mu\nu}[0,0,0] = \sum_{\rho}^{n}\sum_{\sigma}^{n}\left(\sum_{j_2}\sum_{j_3}\sum_{j_2'}\sum_{j_3'}\right)\Bigg[& P_{\rho\sigma}^{(0)}[0,j_2'-j_2,j_3'-j_3] \\ & \cdot\left\{\left\langle \chi_\mu[0,0,0]\chi_\nu[0,0,0] \middle| \frac{1}{r_{12}} \middle| \chi_\rho[0,j_2,j_3]\chi_\sigma[0,j_2',j_3'] \right\rangle \right. \\ & \left. -\frac{1}{2}\left\langle \chi_\mu[0,0,0]\chi_\sigma[0,j_2',j_3'] \middle| \frac{1}{r_{12}} \middle| \chi_\rho[0,j_2,j_3]\chi_\nu[0,0,0] \right\rangle\right\}\Bigg]. \end{aligned} \tag{35}$$

In $G_{\mu\nu}^{(1)}[0,0,0]$, the summation as to j_2, j_3, j_2', and j_3' should be taken in the range of the nearest neighbouring interchain cells excluding the case of $j_2 = j_3 = j_2' = j_3' = 0$.

The second term in Eq. (31) is the interchain interaction term with two AO (μ and ν) centres belonging to the [0, 0, 0]th cell and the $[0, j_2, j_3]$th cell, respectively:

$$F_{\mu\nu}^{(1)}[0,j_2,j_3] = H_{\mu\nu}^{(1)}[0,j_2,j_3] + G_{\mu\nu}^{(1)}[0,j_2,j_3], \tag{36}$$

where

$$\begin{aligned} H_{\mu\nu}^{(1)}[0,j_2,j_3] = \Bigg\langle \chi_\mu[0,0,0] \Bigg| & -\frac{1}{2}\nabla^2 - \sum_{\alpha}^{N\alpha} Z_\alpha\left(\frac{1}{|\boldsymbol{r}-\boldsymbol{R}_\alpha[0,0,0]|}\right. \\ & \left. + \frac{1}{|\boldsymbol{r}-\boldsymbol{R}_\alpha[0,j_2,j_3]|}\right)\Bigg| \chi_\nu[0,j_2,j_3] \Bigg\rangle, \end{aligned} \tag{37}$$

and

$$G^{(1)}_{\mu\nu}[0, j_2, j_3] = \sum_{\rho}^{n} \sum_{\sigma}^{n} \left(\sum_{j_2'} \sum_{j_3'} \sum_{j_2''} \sum_{j_3''} \right) \Bigg[P^{(0)}_{\mu\nu}[0, j_2'' - j_2', j_3'' - j_3'] \cdot \Bigg\{ \left\langle \chi_\mu[0, 0, 0]\chi_\nu[0, j_2, j_3] \left| \frac{1}{r_{12}} \right| \chi_\rho[0, j_2', j_3']\chi_\sigma[0, j_2'', j_3''] \right\rangle - \frac{1}{2} \left\langle \chi_\mu[0, 0, 0]\chi_\sigma[0, j_2'', j_3''] \left| \frac{1}{r_{12}} \right| \chi_\rho[0, j_2', j_3']\chi_\nu[0, j_2, j_3] \right\rangle \Bigg\} \Bigg]. \tag{38}$$

In $G^{(1)}_{\mu\nu}[0, j_2, j_3]$, the summation as to j_2', j_3', j_2'', and j_3'' should be taken in the range of the nearest neighbouring interchain cells like that in Eq. (35), but on this occasion the case of $j_2' = j_3' = j_2'' = j_3'' = 0$ is included.

The third term in Eq. (31) is the intrachain coupled term resulting from the existence of the first-order perturbed density matrix:

$$F^{(1)}_{\mu\nu}[j_1] = \sum_{\rho}^{n} \sum_{\sigma}^{n} \sum_{j_1'=0}^{\pm M} \sum_{j_1''=0}^{\pm M} \Bigg[P^{(1)}_{\rho\sigma}[j_1'' - j_1', 0, 0] \cdot \Bigg\{ \left\langle \chi_\mu[0, 0, 0]\chi_\nu[j_1, 0, 0] \left| \frac{1}{r_{12}} \right| \chi_\rho[j_1', 0, 0]\chi_\sigma[j_1'', 0, 0] \right\rangle - \frac{1}{2} \left\langle \chi_\mu[0, 0, 0]\chi_\sigma[j_1'', 0, 0] \left| \frac{1}{r_{12}} \right| \chi_\rho[j_1', 0, 0]\chi_\nu[j_1, 0, 0] \right\rangle \Bigg\} \Bigg]. \tag{39}$$

In the present scheme, in which only the nearest neighbouring interchain interactions are taken into account, the second-order perturbed density matrix yields the second-order Fock submatrices as follows.

$$F^{(2)}_{\mu\nu}(\boldsymbol{k}) = F^{(2)}_{\mu\nu}[0, 0, 0] + \left(\sum_{j_2} \sum_{j_3} \right) \exp\,[i(j_2 \boldsymbol{k}_2 \boldsymbol{a}_2 + j_3 \boldsymbol{k}_3 \boldsymbol{a}_3)] \cdot F^{(2)}_{\mu\nu}[0, j_2, j_3] + \sum_{j_1=0}^{\pm M} \exp\,[ij_1 \boldsymbol{k}_1 \boldsymbol{a}_1] F^{(2)}_{\mu\nu}[j_1], \tag{40}$$

where

$$F^{(2)}_{\mu\nu}[0, 0, 0] = \sum_{\rho}^{n} \sum_{\sigma}^{n} \left(\sum_{j_2} \sum_{j_3} \sum_{j_2'} \sum_{j_3'} \right) \Bigg[P^{(1)}_{\rho\sigma}[0, j_2' - j_2, j_3' - j_3] \cdot \Bigg\{ \left\langle \chi_\mu[0, 0, 0]\chi_\nu[0, 0, 0] \left| \frac{1}{r_{12}} \right| \chi_\rho[0, j_2, j_3]\chi_\sigma[0, j_2', j_3'] \right\rangle - \frac{1}{2} \left\langle \chi_\mu[0, 0, 0]\chi_\sigma[0, j_2', j_3'] \left| \frac{1}{r_{12}} \right| \chi_\rho[0, j_2, j_3]\chi_\nu[0, 0, 0] \right\rangle \Bigg\} \Bigg], \tag{41}$$

$$F^{(2)}_{\mu\nu}[0, j_2, j_3] = \sum_{\rho}^{n} \sum_{\sigma}^{n} \left(\sum_{j_2'} \sum_{j_3'} \sum_{j_2''} \sum_{j_3''} \right) \Bigg[P^{(1)}_{\rho\sigma}[0, j_2'' - j_2', j_3'' - j_3'] \cdot \Bigg\{ \left\langle \chi_\mu[0, 0, 0]\chi_\nu[0, j_2, j_3] \left| \frac{1}{r_{12}} \right| \chi_\rho[0, j_2', j_3']\chi_\sigma[0, j_2'', j_3''] \right\rangle - \frac{1}{2} \left\langle \chi_\mu[0, 0, 0]\chi_\sigma[0, j_2'', j_3''] \left| \frac{1}{r_{12}} \right| \chi_\rho[0, j_2', j_3']\chi_\nu[0, j_2, j_3] \right\rangle \Bigg\} \Bigg], \tag{42}$$

and

$$F_{\mu\nu}^{(2)}[j_1] = \sum_{\rho}^{n} \sum_{\sigma}^{n} \sum_{j_1'=0}^{\pm M} \sum_{j_1''=0}^{\pm M} \Bigg[P_{\mu\nu}^{(2)}[j_1'' - j_1', 0, 0] \cdot \Bigg\{ \Bigg\langle \chi_\mu[0, 0, 0]\chi_\nu[j_1, 0, 0] \Bigg| \frac{1}{r_{12}} \Bigg| \chi_\rho[j_1', 0, 0]\chi_\sigma[j_1'', 0, 0] \Bigg\rangle - \frac{1}{2} \Bigg\langle \chi_\mu[0, 0, 0]\chi_\sigma[j_1'', 0, 0] \Bigg| \frac{1}{r_{12}} \Bigg| \chi_\rho[j_1', 0, 0]\chi_\nu[j_1, 0, 0] \Bigg\rangle \Bigg\} \Bigg]. \qquad (43)$$

The range of the summation as to various types of j_2 and j_3 in Eqs. (40), (41), and (42) are similar to those in Eqs. (31), (35), and (38), respectively. On the other hand, all of the second-order overlap matrix elements can be set as zero:

$$S_{\mu\nu}^{(2)}(\boldsymbol{k}) = 0, \qquad (44)$$

since, in the present scheme, it is supposed that there are no second-nearest neighbouring interchain interactions.

4. Solution to the Perturbed Fock Equation

The set of the perturbed Fock equations for each $\boldsymbol{k}$ made up of the submatrices in Eqs. (16) and (17) can be solved by a simple extension of the usual SCF perturbation theory [16]. It should be stressed that the present unperturbed system is degenerate in essence. We employ here the extended version, suitable for our system, of a conventional SCF perturbation theory for degenerate systems presented by O'Shea and Santry [11].

We introduce several notations for the ease of descriptions as follows.

$$\boldsymbol{S}_{st}^{(m)}(\boldsymbol{k}) = \sum_{\mu}^{n} \sum_{\nu}^{n} S_{\mu\nu}^{(m)}(\boldsymbol{k}) C_{\mu s}^{*(0)}(\boldsymbol{k}) C_{\nu t}^{(0)}(\boldsymbol{k}), \qquad (45)$$

$$\boldsymbol{F}_{st}^{(m)}(\boldsymbol{k}) = \sum_{\mu}^{n} \sum_{\nu}^{n} F_{\mu\nu}^{(m)}(\boldsymbol{k}) C_{\mu s}^{*(0)}(\boldsymbol{k}) C_{\nu t}^{(0)}(\boldsymbol{k}), \qquad (46)$$

$$\mathscr{F}_{st}^{(m)}(\boldsymbol{k}) = \boldsymbol{F}_{st}^{(m)}(\boldsymbol{k}) - \boldsymbol{S}_{st}^{(m)}(\boldsymbol{k}) \varepsilon_t^{(0)}(\boldsymbol{k}), \qquad (47)$$

$$A_{st}(\boldsymbol{k}) = \begin{cases} \mathscr{F}_{st}^{(1)}(\boldsymbol{k}) / (\varepsilon_t^{(0)}(\boldsymbol{k}) - \varepsilon_s^{(0)}(\boldsymbol{k})) & (s \neq t) \\ -\frac{1}{2} \boldsymbol{S}_{ss}^{(1)}(\boldsymbol{k}) & (s = t). \end{cases} \qquad (48)$$

Using these notations, the perturbed density matrices for the wavevector $\boldsymbol{k}$ in Eqs. (21) and (22) are evaluated as:

$$R_{\mu\nu}^{(1)}(\boldsymbol{k}) = \sum_{s}^{\mathrm{occ}} \sum_{t}^{\mathrm{vac}} \{ A_{ts}(\boldsymbol{k}) C_{\mu s}^{*(0)}(\boldsymbol{k}) C_{\nu t}^{(0)}(\boldsymbol{k}) + A_{ts}^{*}(\boldsymbol{k}) C_{\mu t}^{*(0)}(\boldsymbol{k}) C_{\nu s}^{(0)}(\boldsymbol{k}) \} - \sum_{s}^{\mathrm{occ}} \sum_{t}^{\mathrm{occ}} \boldsymbol{S}_{ts}^{(1)}(\boldsymbol{k}) C_{\mu s}^{*(0)}(\boldsymbol{k}) C_{\nu t}^{(0)}(\boldsymbol{k}), \qquad (49)$$

and

$$\begin{aligned}
R_{\mu\nu}^{(2)}(\boldsymbol{k}) = {} & \sum_{s}^{\mathrm{occ}}\sum_{t}^{\mathrm{vac}}\sum_{u}^{\mathrm{vac}} A_{ts}^{*}(\boldsymbol{k})A_{us}(\boldsymbol{k})C_{\mu t}^{*(0)}(\boldsymbol{k})C_{\nu u}^{(0)}(\boldsymbol{k}) + \sum_{s}^{\mathrm{occ}}\sum_{t}^{\mathrm{occ}} C_{\mu s}^{*(0)}(\boldsymbol{k})C_{\nu t}^{(0)}(\boldsymbol{k}) \\
& \times \Bigg\{ - \sum_{u}^{\mathrm{vac}} A_{tu}(\boldsymbol{k})A_{su}^{*}(\boldsymbol{k}) + \sum_{u}^{\mathrm{all}} \boldsymbol{S}_{su}^{(1)}(\boldsymbol{k})\boldsymbol{S}_{ut}^{(1)}(\boldsymbol{k}) - \boldsymbol{S}_{ts}^{(2)}(\boldsymbol{k}) \Bigg\} \\
& + \sum_{s}^{\mathrm{occ}}\sum_{t}^{\mathrm{vac}} \Bigg[\!\!\Bigg[C_{\mu s}^{*(0)}(\boldsymbol{k})C_{\nu t}^{(0)}(\boldsymbol{k}) \Bigg[\Bigg\{ \mathscr{F}_{ts}^{(2)}(\boldsymbol{k}) - \sum_{u}^{\mathrm{occ}} A_{tu}(\boldsymbol{k})\mathscr{F}_{us}^{(1)}(\boldsymbol{k}) \\
& \qquad - \sum_{u}^{\mathrm{all}} \boldsymbol{S}_{tu}^{(1)}(\boldsymbol{k})\mathscr{F}_{us}^{(1)}(\boldsymbol{k}) + \sum_{u}^{\mathrm{vac}} A_{us}(\boldsymbol{k})\mathscr{F}_{tu}^{(1)}(\boldsymbol{k}) \Bigg\} \Bigg/ (\varepsilon_{s}^{(0)}(\boldsymbol{k}) \\
& \qquad - \varepsilon_{t}^{(0)}(\boldsymbol{k})) - \sum_{u}^{\mathrm{occ}} A_{tu}(\boldsymbol{k})\boldsymbol{S}_{us}^{(1)}(\boldsymbol{k}) \Bigg] + C_{\mu t}^{*(0)}(\boldsymbol{k})C_{\nu s}^{(0)}(\boldsymbol{k}) \\
& \qquad \times \Bigg[\Bigg\{ \mathscr{F}_{ts}^{*(2)}(\boldsymbol{k}) - \sum_{u}^{\mathrm{occ}} A_{tu}^{*}(\boldsymbol{k})\cdot\mathscr{F}_{us}^{*(1)}(\boldsymbol{k}) - \sum_{u}^{\mathrm{all}} \boldsymbol{S}_{tu}^{*(1)}(\boldsymbol{k})\mathscr{F}_{us}^{*(1)}(\boldsymbol{k}) \\
& \qquad\quad + \sum_{u}^{\mathrm{vac}} A_{us}^{*}(\boldsymbol{k})\mathscr{F}_{tu}^{*(1)}(\boldsymbol{k}) \Bigg\} \Bigg/ (\varepsilon_{s}^{(0)}(\boldsymbol{k}) - \varepsilon_{t}^{(0)}(\boldsymbol{k})) \\
& \qquad - \sum_{u}^{\mathrm{occ}} A_{tu}^{*}(\boldsymbol{k})\boldsymbol{S}_{us}^{*(1)}(\boldsymbol{k}) \Bigg] \Bigg]\!\!\Bigg].
\end{aligned} \tag{50}$$

The perturbed total density matrices can be evaluated with the use of Eqs. (24) and (25). The calculations of $P_{\mu\nu}^{(1)}[j_1, j_2, j_3]$ and $P_{\mu\nu}^{(2)}[j_1, j_2, j_3]$ must be iterative, since these quantities are involved in $F_{\mu\nu}^{(1)}(\boldsymbol{k})$ and $F_{\mu\nu}^{(2)}(\boldsymbol{k})$. The practical procedures for the iterative calculation are given as follows:

1. A first-order calculation is performed by first evaluating $F_{\mu\nu}^{(1)}(\boldsymbol{k})$ from Eq. (31) with $P_{\mu\nu}^{(1)}[j_1, 0, 0]$ equal to zero.

2. Using $P_{\mu\nu}^{(1)}[j_1, 0, 0]$ obtained with the use of Eqs. (24) and (49) from the previous $F_{\mu\nu}^{(1)}(\boldsymbol{k})$, $F_{\mu\nu}^{(1)}(\boldsymbol{k})$ is evaluated again and new values for $P_{\mu\nu}^{(1)}[j_1, 0, 0]$ are calculated.

3. Procedure 2 is repeated until the values of $P_{\mu\nu}^{(1)}[j_1, 0, 0]$ are constant.

4. Subsequently, a second-order calculation is performed by first evaluated $P_{\mu\nu}^{(2)}[j_1, 0, 0]$ in Eq. (25) from $R_{\mu\nu}^{(2)}(\boldsymbol{k})$ in Eq. (50) setting $\mathscr{F}_{ts}^{(2)}(\boldsymbol{k})$ equal to zero. To calculate $R_{\mu\nu}^{(2)}(\boldsymbol{k})$, the values of $P_{\mu\nu}^{(1)}[j_1, j_2, j_3]$ obtained in Procedure 3 are used.

5. Using this $P_{\mu\nu}^{(2)}[j_1, j_2, j_3]$, $F_{\mu\nu}^{(2)}(\boldsymbol{k})$ is calculated by Eq. (40) and new values for $P_{\mu\nu}^{(2)}$ $[j_1, j_2, j_3]$ are obtained by Eqs. (50) and (25).

6. Procedure 5 is repeated until the values of $P_{\mu\nu}^{(2)}[j_1, 0, 0]$ are constant.

7. Using the thus-obtained $P_{\mu\nu}^{(1)}[j_1, j_2, j_3]$ and $P_{\mu\nu}^{(2)}[j_1, j_2, j_3]$, the correction for the energy level, $\varepsilon_{s}^{(1)}(\boldsymbol{k})$ and $\varepsilon_{s}^{(2)}(\boldsymbol{k})$, and that for the total energy per unit cell, $E^{(1)}$ and $E^{(2)}$, are obtained as follows:

$$\varepsilon_{s}^{(1)}(\boldsymbol{k}) = \mathscr{F}_{ss}^{(1)}(\boldsymbol{k}), \tag{51}$$

$$\begin{aligned}\varepsilon_s^{(2)}(\boldsymbol{k}) = {} & \mathscr{F}_{ss}^{(2)}(\boldsymbol{k}) - \boldsymbol{S}_{ss}^{(1)}(\boldsymbol{k})\varepsilon_s^{(1)}(\boldsymbol{k}) + (\mathscr{F}_{st}^{(1)}(\boldsymbol{k}) \\ & - \boldsymbol{S}_{st}^{(0)}(\boldsymbol{k})\varepsilon_s^{(1)}(\boldsymbol{k}))\left(\sum_t^{\mathrm{vac}} A_{ts}(\boldsymbol{k}) - \frac{1}{2}\sum_t^{\mathrm{occ}} \boldsymbol{S}_{ts}^{(1)}(\boldsymbol{k})\right),\end{aligned} \tag{52}$$

$$\begin{aligned}E^{(1)} = {} & \frac{1}{2}\sum_{\mu}^{n}\sum_{\nu}^{n}\Bigg[\sum_{j_1=0}^{\pm M}\{P_{\mu\nu}^{(0)}[j_1, 0, 0]F_{\mu\nu}^{(1)}[j_1] + P_{\mu\nu}^{(1)}[j_1, 0, 0] \\ & \cdot(2H_{\mu\nu}^{(0)}[j_1] + G_{\mu\nu}^{(0)}[j_1])\} + P_{\mu\nu}^{(0)}[0, 0, 0](2H_{\mu\nu}^{(1)}[0, 0, 0] \\ & + G_{\mu\nu}^{(1)}[0, 0, 0])\Bigg] + \frac{1}{2}\left(\sum_{j_2}\sum_{j_3}\right)\sum_{\alpha}^{N_\alpha}\sum_{\alpha'}^{N_\alpha}\frac{Z_\alpha Z_{\alpha'}}{|\boldsymbol{R}_\alpha[0, 0, 0] - \boldsymbol{R}_{\alpha'}[0, j_2, j_3]|},\end{aligned} \tag{53}$$

and

$$\begin{aligned}E^{(2)} = {} & \frac{1}{2}\sum_{\mu}^{n}\sum_{\nu}^{n}\Bigg[\sum_{j_1=0}^{\pm M}\{P_{\mu\nu}^{(0)}[j_1, 0, 0]F_{\mu\nu}^{(2)}[j_1] + P_{\mu\nu}^{(1)}[j_1, 0, 0] \\ & \cdot F_{\mu\nu}^{(1)}[j_1] + P_{\mu\nu}^{(2)}[j_1, 0, 0](2H_{\mu\nu}^{(0)}[j_1] + G_{\mu\nu}^{(0)}[j_1])\} \\ & + P_{\mu\nu}^{(0)}[0, 0, 0]F_{\mu\nu}^{(2)}[0, 0, 0] + P_{\mu\nu}^{(1)}[0, 0, 0](2H_{\mu\nu}^{(1)}[0, 0, 0] \\ & + G_{\mu\nu}^{(1)}[0, 0, 0]) + \left(\sum_{j_2}\sum_{j_3}\right)\{P_{\mu\nu}^{(1)}[0, j_2, j_3](2H_{\mu\nu}^{(1)}[0, j_2, j_3] \\ & + G_{\mu\nu}^{(1)}[0, j_2, j_3])\}\Bigg].\end{aligned} \tag{54}$$

In Eqs. (51)–(54), only the final forms are shown. The summation as to j_2 and j_3 in Eqs. (53) and (54) is similar to that in Eqs. (31) and (32).

5. Perturbed Fock Submatrices under the CNDO/2 Version

Several non-empirical tight-binding LCAO SCF MO calculations have been performed of polymers such as polyethylene[17, 18], polyacetylene[19,20], and polysulfur nitride[3,4]. In almost all of these calculations, however, only the nearest neighbouring intercell interactions are taken into account and, hence, the results obtained are somewhat unreliable[21]. Therefore, at the present stage, one still can not disregard semi-empirical versions such as the CNDO approximation [9], in which the intercell interactions are included up to a considerably long-range distance[6,14,15]. In this section, we present the forms of the perturbed Fock submatrices under the CNDO/2 approximation[9].

The forms of $H_{\mu\nu}^{(0)}[j_1]$ in Eq. (27) and $G_{\mu\nu}^{(0)}[j_1]$ in Eq. (28) are the same as those in the usual CNDO/2 version of the tight-binding LCAO SCF MO method for polymers [14,15]. The first-order submatrices $H_{\mu\nu}^{(1)}[j_1, j_2, j_3]$, $G_{\mu\nu}^{(1)}[j_1, j_2, j_3]$, and $F_{\mu\nu}^{(1)}[j_1]$ in Eqs. (34) ~ (39) are simplified as follows:

$$H_{\mu\nu}^{(1)}[0, 0, 0] = \begin{cases} 0 & (\mu \neq \nu) \\ -\left(\sum_{j_2}\sum_{j_3}\right)\sum_{\rho}^{n} Z_\rho \gamma_{\mu[0,0,0]\rho[0,j_2,j_3]} & (\mu = \nu), \end{cases} \tag{55}$$

$$G^{(1)}_{\mu\nu}[0, 0, 0] = \begin{cases} 0 \quad (\mu \neq \nu) \\ \left(\sum_{j_2} \sum_{j_3}\right) \sum_{\rho}^{n} P^{(0)}_{\rho\rho}[0, 0, 0]\gamma_{\mu[0,0,0]\rho[0,j_2,j_3]} \quad (\mu = \nu), \end{cases} \tag{56}$$

$$H^{(1)}_{\mu\nu}[0, j_2, j_3] = \beta_{\mu\nu} S_{\mu\nu}[0, j_2, j_3], \tag{57}$$

$$G^{(1)}_{\mu\nu}[0, j_2, j_3] = 0, \tag{58}$$

$$F^{(1)}_{\mu\nu}[0] = \begin{cases} -\frac{1}{2} P^{(1)}_{\nu\mu}[0, 0, 0]\gamma_{\mu[0,0,0]\nu[0,0,0]} \quad (\mu \neq \nu) \\ \sum_{j_1=0}^{\pm M} \sum_{\rho}^{n} P^{(1)}_{\rho\rho}[0, 0, 0]\gamma_{\mu[0,0,0]\rho[j_1,0,0]} \\ \qquad\qquad -\frac{1}{2} P^{(1)}_{\mu\mu}[0, 0, 0]\gamma_{\mu[0,0,0]\mu[0,0,0]} \quad (\mu = \nu), \end{cases} \tag{59}$$

$$F^{(1)}_{\mu\nu}[j_1] = -\frac{1}{2} P^{(1)}_{\nu\mu}[-j_1, 0, 0]\gamma_{\mu[0,0,0]\nu[j_1,0,0]} \quad (j_1 \neq 0). \tag{60}$$

In the above equations, the summation as to j_2 and j_3 is the same as that in Eqs. (31) and (32). Z_ρ represents the core charge of the atom to which AOρ belongs, and $\gamma_{\mu[j_1,j_2,j_3]\nu[j'_1,j'_2,j'_3]}$ the two-centre electron repulsion between AO μ in the $[j_1, j_2, j_3]$th cell and AO ν in the $[j'_1, j'_2, j'_3]$th cell evaluated by:

$$\gamma_{\mu[j_1,j_2,j_3]\nu[j'_1,j'_2,j'_3]} = \left\langle \chi_{sA}[j_1, j_2, j_3]\chi_{sA}[j_1, j_2, j_3] \left| \frac{1}{r_{12}} \right| \right. \\ \left. \chi_{sB}[j'_1, j'_2, j'_3]\chi_{sB}[j'_1, j'_2, j'_3] \right\rangle, \tag{61}$$

where χ_{sA} and χ_{sB} denote the valence shell s AO's on atom A and B, to which AO μ and AO ν belong, respectively. $\beta_{\mu\nu}$ is the bonding parameter between AO's μ and ν.

The second-order submatrices in Eqs. (41), (42), and (43) are similarly simplified as follows:

$$F^{(2)}_{\mu\nu}[0, 0, 0] = \begin{cases} 0 \quad (\mu \neq \nu) \\ \left(\sum_{j_2} \sum_{j_3}\right) \sum_{\rho}^{n} P^{(1)}_{\rho\rho}[0, 0, 0]\gamma_{\mu[0,0,0]\rho[0,j_2,j_3]} \quad (\mu = \nu), \end{cases} \tag{62}$$

$$F^{(2)}_{\mu\nu}[0, j_2, j_3] = -\frac{1}{2} P^{(1)}_{\nu\mu}[0, -j_2, -j_3]\gamma_{\mu[0,0,0]\nu[0,j_2,j_3]}, \tag{63}$$

$$F^{(2)}_{\mu\nu}[0] = \begin{cases} -\frac{1}{2} P^{(2)}_{\nu\mu}[0, 0, 0]\gamma_{\mu[0,0,0]\nu[0,0,0]} \quad (\mu \neq \nu) \\ \sum_{j_1=0}^{\pm M} \sum_{\rho}^{n} P^{(2)}_{\rho\rho}[0, 0, 0]\gamma_{\mu[0,0,0]\rho[j_1,0,0]} \\ \qquad\qquad -\frac{1}{2} P^{(2)}_{\mu\mu}[0, 0, 0]\gamma_{\mu[0,0,0]\mu[0,0,0]} \quad (\mu = \nu), \end{cases} \tag{64}$$

$$F^{(2)}_{\mu\nu}[j_1] = -\frac{1}{2}P^{(2)}_{\nu\mu}[-j_1, 0, 0]\gamma_{\mu[0,0,0]\nu[j_1,0,0]} \quad (j_1 \neq 0). \tag{65}$$

Furthermore, in this CNDO/2 approximation, the overlap matrix elements $S_{\mu\nu}[j_1, j_2, j_3]$ in Eqs. (14) and (17) are reduced to:

$$S_{\mu\nu}[j_1, j_2, j_3] = \begin{cases} \delta_{\mu\nu} & (j_1 = j_2 = j_3 = 0) \\ 0 & (\text{otherwise}). \end{cases} \tag{66}$$

Using this equation, for example, the first-order quantities in Eqs. (45) and (47) are simplified as follows.

$$S^{(1)}_{st}(\boldsymbol{k}) = 0, \tag{67}$$

$$\mathscr{F}^{(1)}_{st}(\boldsymbol{k}) = F^{(1)}_{st}(\boldsymbol{k}). \tag{68}$$

6. Concluding Remarks

We have developed a non-empirical tight-binding LCAO SCF MO treatment of one-dimensional molecular crystals. The present approach enables the calculations to obtain the valuable informations on the electronic processes of the one-dimensional molecular crystals as well as the biopolymers.

The third-order treatment of further neighbouring interchain interactions might be required for unusually strongly interacting chains. But even in such situations, the present second-order calculations will provide valuable results of the semi-quantitative level. Practical applications of the present treatment to several problems of the one-dimensional molecular crystals will be discussed elsewhere.

Acknowledgement. This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan (No. 255315).

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Received April 4, 1979