Interpretation of Energy Bands of Regular Quasi-One-Dimensional Systems in Terms of Local Structure

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Received 16 November 1999; revised 13 September 2000; accepted 31 October 2000

ABSTRACT: A new approach to investigate one-electron spectra of regular quasi-one-dimensional systems is suggested. It is based on an inverted order of operations that differs from the traditional solid-state theory, interchain interactions are taken into account before the intrasubchain ones (subchains correspond here to subsets of translationally equivalent atomic orbitals). The block-diagonalization transformation for matrices [V. Gineityte, Int J Quantum Chem 68, 119 (1998)] is used to perform the first step of the approach. Given that the intersubchain interactions are sufficiently weak, the nonzero blocks of the transformed one-electron Hamiltonian matrix correspond to separate subchains of the initial chain and thereby play the role of effective Hamiltonian matrices for separate energy bands influenced by the interband interaction. Elements of these matrices describe effective interactions between atomic orbitals (AOs) of the given subchain that consist of their direct interactions and of indirect interactions by means of the nearest AOs of other subchains. Moreover, separate additive increments of the dispersion relation depend on particular local effective interactions of AOs. As a result, the approach suggested is especially efficient for interpretation of dispersion curves in terms of local constitution of the system. © 2001 John Wiley & Sons, Inc. Int J Quantum Chem 81: 321–331, 2001

Key words: quasi-one-dimensional systems; one-electron spectra; dispersion curves; direct (through-space) and indirect (through-bond) interactions of AOs

Introduction

Studies of one-electron states (energy bands) of polymers and other extended quasi-one-dimensional systems are usually based on solution of eigenvalue equations for the relevant one-electron Hamiltonian or Fockian matrices represented in the basis of atomic orbitals (AOs). To simplify the problem, cyclic boundary conditions are most commonly imposed on the chain under study. As a result, concepts and methods of the solid-state theory [1, 2] are applied for investigation of the energy bands of polymers [3–12], e.g., the quasi-momentum vector **k**, the dispersion relation, etc.

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Given that an elementary cell of our translationally symmetric chain contains M AOs, M subchains of equivalent basis functions may be revealed there. On this basis, two types of interactions (resonance parameters) may be distinguished, viz. the intrasubchain parameters and the intersubchain ones.

The first step of the standard theory of energy bands of polymers [3–12] consists in taking into account the translational symmetry of the chain and thereby the intrasubchain resonance parameters. The usual way of doing this lies in passing to the basis of the Bloch functions for each set of equivalent AOs separately. As a consequence, M energy bands are obtained, each of them corresponding to an isolated subchain and being most usually described by a cos-like curve.

Regard for resonance parameters of the intersubchain type makes the second step of the conventional theory. To this end, an $M \times M$-dimensional $\mathbf{k}$-dependent square block of the transformed Hamiltonian matrix corresponding to an elementary cell is diagonalized for certain values of the quasi-momentum vector $\mathbf{k}$. As a result, the final dispersion curves of the system under study follow from a $\mathbf{k}$-dependent interaction of M cos-like curves being referred to as the interband interaction.

The above-described classical approach forms the basis of efficient numerical methods for calculation of band structures, including the most popular Hartree–Fock crystal orbital method [5–7].

Interpretation of dispersion curves in terms of local constitution of the chain also is an important part of the investigation of quasi-one-dimensional systems [3]. However, just the relations between these curves and local interorbital interactions are rather involved and difficult to analyze in the framework of the conventional solid-state theory. The main reason for that consists in the delocalized nature of the Bloch functions [2, 3]. As a consequence, the interband interaction becomes directly related to interaction of delocalized subsystems (subchains) of equivalent AOs.

In this connection, development of alternative theories of one-electron spectra of regular quasi-one-dimensional systems becomes of interest.

The experience of dealing with eigenvalue equations for matrices shows that it is the decision on the first step when solving the problem that determines the terms in which the results are expressed and interpreted [13]. In this connection, we are about to suggest in this study an new approach to investigation of energy bands of regular quasi-one-dimensional systems. The approach is based on an inverted order of operations against that of the standard theory, namely taking into account the intersubchain interactions with regard to the intrasubchain ones. To perform the above-specified initial step, we will invoke the block-diagonalization transformation for matrices proposed recently [14–18] and being equivalent to the so-called eigenblock equation [15]. Choice of just this procedure is based on the following expectations.

Application of the block-diagonalization transformation to the common one-electron model Hamiltonian matrix of alkanes in the basis of bonding and antibonding bond orbitals (BOs) [14, 15] allowed us to obtain a new Hamiltonian matrix in the form of a direct sum of two nonzero blocks (eigenblocks) corresponding to subsets of bonding BOs and antibonding BOs, respectively. At the same time, the eigenblocks proved to imbibe the initial interactions between BOs of different types. It should be added here that an evident analogy may be traced between subspaces of bonding and antibonding BOs of alkanes and those of equivalent AOs within chains of regular constitution.

An explicit perturbative solution of the block-diagonalization problem has been obtained in Refs. [14–18] in the particular case of weak intersubset interaction. To be able to apply this solution, we will dwell on regular quasi-one-dimensional systems described by large differences in Coulomb parameters of individual subchains as compared to the intersubchain resonance parameters. It should be mentioned, however, that the case of two quasi-degenerate subsets of orbitals also may be treated algebraically [15, 19]. This case also will be discussed separately.

Thus, the first step of our approach will consist in transforming the initial $N \times N$-dimensional one-electron Hamiltonian matrix $\mathbf{H}$ of a regular quasi-one-dimensional chain containing K elementary cells ($N = M \times K$) into a block-diagonal form defined as a direct sum of M individual $K \times K$-dimensional blocks (eigenblocks). Given that the intersubchain interaction is weak, each of these eigenblocks is likely to correspond to a separate subchain of our chain as was the case with alkanes [14, 15].

Inasmuch as each subchain of equivalent AOs gives birth to an energy band containing K levels [1–3], the eigenblocks of the relevant matrix $\mathbf{H}$ may be expected to play the role of effective model Hamiltonian matrices for separate energy bands influenced by the interband interaction. Then an explicit examination of the interband interaction seems to be feasible before the final diagonalization of the matrix **H** and thereby before passing to the delocalized description of the system. This, in turn, offers a possibility of interpretation of the final dispersion curves in terms of local constitution of the chain. Just the above-described expectations are verified in this work.

To this end, we start with a brief description of the block-diagonalization procedure for Hamiltonian (Fockian) matrices. Thereupon, we turn to interpretation of eigenblocks in terms of local constitution of a regular chain. Finally, some particular examples are considered in a detail.

Block-Diagonalization Transformation for Hamiltonian Matrices of Regular Quasi-One-Dimensional Chains

Let us consider a regular quasi-one-dimensional system containing $N = M \times K$ basis orbitals (AOs) $\{\varphi\}$. Let us enumerate these orbitals in such a way that the first K AOs $\varphi_{1,r}$ $(r = 1, 2, \ldots, K)$ refer to the first subchain; the subsequent K AOs $\varphi_{2,r}$ $(r = 1, 2, \ldots, K)$ correspond to the second subchain, etc.

Let us assume now that the intersubchain resonance parameters are first-order terms as compared to differences in Coulomb parameters of separate subchains. Then the initial model Hamiltonian matrix **H** of our system may be presented as a sum of zero-order and first-order matrices, i.e.

$$\mathbf{H} = \mathbf{H}_{(0)} + \mathbf{V}. \tag{1}$$

The zero-order term $\mathbf{H}_{(0)}$ is assumed to be a block-diagonal matrix of the form [16, 17]

$$\mathbf{H}_{(0)} = \begin{vmatrix} \mathbf{E}_{(0)1} & \mathbf{0} & \mathbf{0} & \ldots & \mathbf{0} \\ \mathbf{0} & \mathbf{E}_{(0)2} & \mathbf{0} & \ldots & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{E}_{(0)3} & \ldots & \mathbf{0} \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \ldots & \mathbf{E}_{(0)M} \end{vmatrix}, \tag{2}$$

where $\mathbf{E}_{(0)k}$, $k = 1, 2, \ldots, M$ are $K \times K$-dimensional submatrices (blocks), each of them containing the intrasubchain resonance parameters of the respective subchain along with Coulomb ones. It is seen that zero-order intrasubchain interactions are allowed here in contrast to intersubchain interactions.

The first-order term **V** of Eq. (1) also may be divided into $K \times K$-dimensional blocks describing the intrasubchain interactions (the diagonal blocks) and the intersubchain ones (the off-diagonal blocks), i.e.,

$$\mathbf{V} = \begin{vmatrix} \mathbf{V}_{11} & \mathbf{V}_{12} & \mathbf{V}_{13} & \ldots & \mathbf{V}_{1M} \\ \mathbf{V}_{21} & \mathbf{V}_{22} & \mathbf{V}_{23} & \ldots & \mathbf{V}_{2M} \\ \mathbf{V}_{31} & \mathbf{V}_{32} & \mathbf{V}_{33} & \ldots & \mathbf{V}_{3M} \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ \mathbf{V}_{M1} & \mathbf{V}_{M2} & \mathbf{V}_{M3} & \ldots & \mathbf{V}_{MM} \end{vmatrix}. \tag{3}$$

The block-diagonalization transformation for the matrix **H** takes the form [14–17]

$$\mathbf{H}' = \mathbf{C}^{+}\mathbf{H}\mathbf{C} = \begin{vmatrix} \mathbf{E}_{1} & \mathbf{0} & \mathbf{0} & \ldots & \mathbf{0} \\ \mathbf{0} & \mathbf{E}_{2} & \mathbf{0} & \ldots & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{E}_{3} & \ldots & \mathbf{0} \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \ldots & \mathbf{E}_{M} \end{vmatrix}, \tag{4}$$

where $\mathbf{E}_k$, $k = 1, 2, \ldots, M$ are the $K \times K$-dimensional eigenblocks [15] of this matrix and **C** is an unitary matrix, i.e.,

$$\mathbf{C}^{+}\mathbf{C} = \mathbf{I}. \tag{5}$$

The superscript + here and below denotes the Hermitian-conjugate (transposed) matrix, and **I** is the unit matrix of the respective dimension. As with the Hamiltonian matrix **H**, the transformation matrix **C** also may be divided into $K \times K$-dimensional submatrices $\mathbf{C}_{mk}$ $(m, k = 1, 2, \ldots, M)$.

To obtain a perturbative solution of the matrix problem defined by Eqs. (4) and (5) [14–18], the entire eigenblocks $\mathbf{E}_k$ and the submatrices $\mathbf{C}_{mk}$ of the matrix **C** have been sought in the form of power series, i.e.,

$$\mathbf{E}_k = \mathbf{E}_{(0)k} + \mathbf{E}_{(1)k} + \mathbf{E}_{(2)k} + \cdots \tag{6}$$

and

$$\mathbf{C}_{mk} = \mathbf{C}_{(0)mk} + \mathbf{C}_{(1)mk} + \mathbf{C}_{(2)mk} + \cdots. \tag{7}$$

The zero-order members of Eq. (6) coincide with the initial blocks $\mathbf{E}_{(0)k}$ of Eq. (2), while the zero-order term of Eq. (7) equals to

$$\mathbf{C}_{(0)mk} = \mathbf{I}\delta_{mk}. \tag{8}$$

The first-order corrections to the eigenblocks, in turn, coincide with the respective diagonal blocks of the perturbation matrix **V**, i.e.,

$$\mathbf{E}_{(1)k} = \mathbf{V}_{kk}. \tag{9}$$

The second-order corrections of Eq. (6) $\mathbf{E}_{(2)k}$ have been expressed as follows [17]:

$$\mathbf{E}_{(2)k} = \frac{1}{2}\sum_{i}(1 - \delta_{ki})\big(\mathbf{V}_{ik}^{+}\mathbf{C}_{(1)ik} + \mathbf{C}_{(1)ik}^{+}\mathbf{V}_{ik}\big), \tag{10}$$

where the submatrices $\mathbf{C}_{(1)ik}$ $(i \neq k)$ meet the matrix equations

$$\mathbf{E}_{(0)i}\mathbf{C}_{(1)ik} - \mathbf{C}_{(1)ik}\mathbf{E}_{(0)k} + \mathbf{V}_{ik} = \mathbf{0}. \tag{11}$$

The third-order corrections $\mathbf{E}_{(3)k}$ also may be obtained as described in Ref. [17]. The final expression takes the form

$$\mathbf{E}_{(3)k} = \frac{1}{2}\sum_{i}(1-\delta_{ki})\big(\mathbf{V}_{ik}^{+}\mathbf{C}_{(2)ik} + \mathbf{C}_{(2)ik}^{+}\mathbf{V}_{ik}\big), \tag{12}$$

where the submatrices $\mathbf{C}_{(2)ik}$ $(i \neq k)$ follow from solution of the matrix equation

$$\mathbf{E}_{(0)i}\mathbf{C}_{(2)ik} - \mathbf{C}_{(2)ik}\mathbf{E}_{(0)k} + \mathbf{W}_{ik} = \mathbf{0} \tag{13}$$

and

$$\mathbf{W}_{ik} = \sum_{j}\mathbf{V}_{ij}\mathbf{C}_{(1)jk} - \mathbf{C}_{(1)ik}\mathbf{V}_{kk}. \tag{14}$$

No problems arise in the way of obtaining also the higher order corrections to eigenblocks as described in Refs. [16, 17]. The principal solutions of matrix equations such as those of Eqs. (11) and (13) have been discussed in Ref. [17].

Let us dwell now on the particular case when the zero-order blocks $\mathbf{E}_{(0)k}$, $k = 1, 2, \ldots, M$ are diagonal matrices. This evidently implies first-order magnitude of both intra- and intersubchain resonance parameters.

As a result of both the diagonality requirement for blocks $\mathbf{E}_{(0)k}$ and the regular constitution of subchains, these submatrices become actually proportional to K-dimensional unit matrices, i.e.,

$$\mathbf{E}_{(0)k} = \varepsilon_{(0)k}\mathbf{I}, \tag{15}$$

where $\varepsilon_{(0)k}$ is a constant coinciding with the one-electron energy of equivalent AOs $\varphi_{k,r}$ $(r = 1, 2, \ldots, K)$ of the kth subset. We then obtain

$$\mathbf{C}_{(1)ik} = \frac{1}{\varepsilon_{(0)k} - \varepsilon_{(0)i}}\mathbf{V}_{ik}, \qquad \mathbf{C}_{(2)ik} = \frac{1}{\varepsilon_{(0)k} - \varepsilon_{(0)i}}\mathbf{W}_{ik}, \tag{16}$$

where $\mathbf{W}_{ik}$ is defined by Eq. (14) [The expressions of Eq. (16) refer to $i \neq k$, whereas $\mathbf{C}_{(1)ik} = \mathbf{0}$ for any k.]

After substituting Eq. (16) into Eqs. (10) and (12), the corrections $\mathbf{E}_{(2)k}$ and $\mathbf{E}_{(3)k}$ take the form

$$\mathbf{E}_{(2)k} = \sum_{i(\neq k)}\frac{1}{\varepsilon_{(0)k} - \varepsilon_{(0)i}}\mathbf{V}_{ki}\mathbf{V}_{ik} \tag{17}$$

and

$$\begin{aligned}\mathbf{E}_{(3)k} = {} & \sum_{i(\neq k)}\sum_{j(\neq k)}\frac{1}{(\varepsilon_{(0)k} - \varepsilon_{(0)i})(\varepsilon_{(0)k} - \varepsilon_{(0)j})}\mathbf{V}_{ki}\mathbf{V}_{ij}\mathbf{V}_{jk} \\ & - \frac{1}{2}\sum_{i(\neq k)}\frac{1}{(\varepsilon_{(0)k} - \varepsilon_{(0)i})^{2}}[\mathbf{V}_{ki}\mathbf{V}_{ik}\mathbf{V}_{kk} \\ & + \mathbf{V}_{kk}\mathbf{V}_{ki}\mathbf{V}_{ik}].\end{aligned} \tag{18}$$

The expressions of Eqs. (17) and (18) formally resemble those of the usual Rayleigh–Schrödinger perturbation theory (RSPT) [20, 21]. However, entire submatrices of the first-order matrix $\mathbf{V}$ arise in Eqs. (17) and (18) instead of its particular elements.

The analogy between our perturbative solution and the usual RSPT [17] embraces also the quasi-degenerate case. To show this, let us assume that the ith and jth subchains consists of AOs of similar energies so that the difference $\mathbf{E}_{(0)i} - \mathbf{E}_{(0)j}$ may be considered as a small matrix relatively to $\mathbf{V}_{ij}$. Let us confine ourselves to the case of large interactions between pairs of AOs inside the same elementary cell.

Basis orbitals $\varphi_{i,r}$ and $\varphi_{j,s}$ belonging to the ith and jth subsets $(i \neq j)$ always may be enumerated in such a way that the intracell resonance parameters take diagonal positions within the matrix $\mathbf{V}_{ij}$. As with diagonal elements of blocks $\mathbf{E}_{(0)k}$, the elements $V_{ij,rr}$ also may be assumed to be uniform. Let us take them equal to unit for simplicity. We then obtain

$$\mathbf{V}_{ij} = \mathbf{I} + \mathbf{\Omega}_{ij}, \tag{19}$$

where $\mathbf{\Omega}_{ij}$ is a small matrix.

Let us turn now to the basis of intracell bonding and antibonding combinations of pairs of AOs defined as follows:

$$\psi_{b,r} = \frac{1}{\sqrt{2}}(\varphi_{i,r} + \varphi_{j,r}), \qquad \psi_{a,r} = \frac{1}{\sqrt{2}}(\varphi_{i,r} - \varphi_{j,r}) \tag{20}$$

and denoted by subscripts b and a, respectively.

The relevant $2K \times 2K$-dimensional transformation matrix $\mathbf{U}$ evidently contains four K-dimensional unit matrices, viz.

$$\mathbf{U} = \frac{1}{\sqrt{2}}\begin{vmatrix}\mathbf{I} & \mathbf{I} \\ \mathbf{I} & -\mathbf{I}\end{vmatrix}. \tag{21}$$

As a result of this transformation, a new Hamiltonian matrix block containing four subblocks follows. Now the intersubset block equals to

$$\mathbf{\Lambda} = \tfrac{1}{2}\big(\mathbf{E}_{(0)i} - \mathbf{E}_{(0)j} + \mathbf{\Omega}_{ij} - \mathbf{\Omega}_{ij}^{+}\big), \tag{22}$$

and it may be considered as a small matrix as compared to the new difference between the intrasubset blocks

$$\mathbf{E}_{b} - \mathbf{E}_{a} = 2\mathbf{I} + \mathbf{\Omega}_{ij} + \mathbf{\Omega}_{ij}^{+}. \tag{23}$$

This result indicates that the total transformed Hamiltonian matrix complies with the requirements of the above-outlined perturbation theory. Hence, eigenblocks corresponding to the bonding subset of orbitals $\{\psi_b\}$ and to the antibonding one $\{\psi_a\}$ may be obtained using Eqs. (1)–(18).

Interpretation of Eigenblocks of The Hamiltonian Matrix and of Their Particular Elements

Let us consider the expressions shown in Eqs. (6), (9), (17), and (18) in a more detail. It is seen that the principal contributions to eigenblocks $\mathbf{E}_k$ coincide with respective intrasubchain blocks $\mathbf{E}_{(0)k} + \mathbf{V}_{kk}$ of the initial model Hamiltonian matrix $\mathbf{H}$ in accordance with Eqs. (6) and (9). Hence, correspondence of any eigenblock $\mathbf{E}_k$ to the respective (kth) subchain is beyond any doubt. It is also seen that the second- and the third-order increments to eigenblocks imbibe the intersubchain interactions described by matrices $\mathbf{V}_{ik}$ ($i \neq k$).

In the case of a weak intersubchain (interband) interaction, an energy band is known to correspond to each subchain of equivalent AOs [1–3]. Thus, the eigenblocks $\mathbf{E}_k$ defined by Eqs. (17) and (18) are nothing more than the effective model Hamiltonian matrices for separate energy bands influenced by the interband interaction.

Now, let us consider the influence of the intersubchain interaction upon the individual elements of the eigenblock $\mathbf{E}_k$. An element of this eigenblock corresponding to AOs $\varphi_{k,p}$ and $\varphi_{k,q}$ may be presented in the form

$$\begin{aligned} E_{k,pq} &= \varepsilon_{(0)k}\delta_{pq} + V_{kk,pq} \\ &\quad + \sum_{i(\neq k)} \frac{1}{\varepsilon_{(0)k} - \varepsilon_{(0)i}} \sum_r V_{ki,pr} V_{ik,rq} \\ &\quad + \sum_{i(\neq k)} \sum_{j(\neq k)} \frac{1}{(\varepsilon_{(0)k} - \varepsilon_{(0)i})(\varepsilon_{(0)k} - \varepsilon_{(0)j})} \\ &\quad \times \sum_{r,s} V_{ki,pr} V_{ij,rs} V_{jk,sq} \\ &\quad - \frac{1}{2} \sum_{i(\neq k)} \frac{1}{(\varepsilon_{(0)k} - \varepsilon_{(0)i})^2} \sum_{r,s} [V_{ki,pr} V_{ik,rs} V_{kk,sq} \\ &\quad + V_{kk,pr} V_{ki,rs} V_{ik,sq}]. \end{aligned} \tag{24}$$

In the case of an off-diagonal element ($p \neq q$), the principal (first-order) contribution to $E_{k,pq}$ coincides with the resonance parameter between AOs $\varphi_{k,p}$ and $\varphi_{k,q}$, i.e.,

$$E_{(1)k,pq} = V_{kk,pq} \equiv \langle \varphi_{k,p} | \hat{H} | \varphi_{k,q} \rangle \tag{25}$$

and represents the direct (through-space) interaction of the above-mentioned AOs. Again, the second-order increment to the same element takes the form

$$E_{(2)k,pq} = \sum_{i(\neq k)} \frac{1}{\varepsilon_{(0)k} - \varepsilon_{(0)i}} \sum_r \langle \varphi_{k,p} | \hat{H} | \varphi_{i,r} \rangle \langle \varphi_{i,r} | \hat{H} | \varphi_{k,q} \rangle \tag{26}$$

and describes the indirect interaction of the same AOs by means of AOs of other subchains, the latter playing the role of mediators. It is evident that the second-order increment to the eigenblock $\mathbf{E}_k$ takes a nonzero value if the AO $\varphi_{i,r}$ interacts directly both with $\varphi_{k,p}$ and $\varphi_{k,q}$.

Similarly, the third-order terms of Eq. (24) may be shown to represent the indirect interactions of the same AOs by means of two mediators. It is noteworthy that AOs both of the subchain under consideration (i.e., the kth one) and of other subchains are able to play the role of mediators in this case, provided that the mediators interact directly both with each other and with AOs under consideration. For example, the AOs $\varphi_{k,r}$ and $\varphi_{i,s}$ of the kth and ith subchain, respectively, play the role of mediators of the indirect interaction described by the last increment of Eq. (24).

Hence, an off-diagonal element $E_{k,pq}$ ($p \neq q$) of the eigenblock $\mathbf{E}_k$ describes the effective interaction between AOs $\varphi_{k,p}$ and $\varphi_{k,q}$ of the kth subchain, which consists of the direct interaction of the above-mentioned two AOs and of various types of their indirect interactions. Basis orbitals of the other subchains are necessarily involved in the indirect interactions of AOs $\varphi_{k,p}$ and $\varphi_{k,q}$.

It may be also easily seen that the diagonal element $E_{k,pp}$ of the kth eigenblock describes the effective one-electron energy of the AO $\varphi_{k,p}$ of the kth subchain under the influence of other subchains. Indeed, the zero-order increment to $E_{k,pp}$ equal to $\varepsilon_{(0)k}$ coincides with the energy of an isolated AO $\varphi_{k,p}$ whereas the remaining terms describe the correction to this energy owing to the presence of other subchains. Given that the entire Coulomb parameters are included into the zero-order Hamiltonian matrix $\mathbf{H}_{(0)}$ of Eq. (2), the equality $V_{kk,pp} = 0$ may be accepted. Again, the increments of the second and of the subsequent orders to an element $E_{k,pp}$ may be shown to represent the indirect self-interactions of the AO $\varphi_{k,p}$ by means of other AOs.

It should be noted here that the concept of direct and indirect interactions of basis orbitals was originally introduced [22–24] for saturated organic molecules. Bond orbitals played the role of basis functions in this case, and the interactions were referred to as through-space and through-bond ones. Now, this concept acquires a new application in the theory of energy bands of quasi-one-dimensional systems.

Let us turn again to Eqs. (24)–(26). Resonance parameters, and thereby the direct interactions of AOs, are known to decrease rapidly when the distance between the two involved AOs grows (see, e.g., [25]). Thus, the first-order increment to the element $E_{k,pq}$ shown in Eq. (25) is essentially local in nature. As far as the second-order increment is concerned, only the AOs $\varphi_{i,r}$ situated in the nearest neighborhood of both $\varphi_{k,p}$ and $\varphi_{k,q}$ are able to play the role of efficient mediators in the second-order (indirect) interaction. The same evidently refers to the third-order terms. Hence, both $E_{k,pq}$ and $E_{k,pp}$ are determined mainly by the structure of the nearest neighborhood of the AOs $\varphi_{k,p}$ and $\varphi_{k,q}$, and of the AO $\varphi_{k,p}$, respectively.

It is seen, therefore, that the intersubchain interaction turns into an effective intrasubchain interaction after performing the block-diagonalization procedure. It is essential that no turning to delocalized orbitals (such as Bloch functions) is required here. As a consequence, the intersubchain interaction that was essentially local in nature remains local also after block-diagonalization. How this local interaction exerts influence upon the energy bands will be considered in the next section.

Studies of Particular Examples

For the sake of simplicity, let us dwell in this section on quasi-one-dimensional chains containing two AOs within an elementary cell and thereby two subchains ($M = 2$). Then the subscripts i, j, and k of Eqs. (15)–(18) may be replaced by numbers 1 and 2, corresponding to the first and the second subchain, respectively. If the reference point is chosen in the middle of the energy gap between AOs of the first and the second subchain and this gap is taken equal to the double negative energy unit in addition, the matrices $\mathbf{E}_{(0)1}$ and $\mathbf{E}_{(0)2}$ take the following simple form:

$$\mathbf{E}_{(0)1} = \mathbf{I}, \qquad \mathbf{E}_{(0)2} = -\mathbf{I}. \tag{27}$$

From Eqs. (15), (17), (18), and (27) we then obtain

$$\begin{aligned}\mathbf{E}_1 = \mathbf{I} + \mathbf{V}_{11} + \tfrac{1}{2}\mathbf{V}_{12}\mathbf{V}_{12}^{+} - \tfrac{1}{8}\big(\mathbf{V}_{11}\mathbf{V}_{12}\mathbf{V}_{12}^{+}\\ + \mathbf{V}_{12}\mathbf{V}_{12}^{+}\mathbf{V}_{11} - 2\mathbf{V}_{12}\mathbf{V}_{22}\mathbf{V}_{12}^{+}\big) + \cdots,\end{aligned} \tag{28}$$

$$\begin{aligned}\mathbf{E}_2 = -\mathbf{I} + \mathbf{V}_{22} - \tfrac{1}{2}\mathbf{V}_{12}^{+}\mathbf{V}_{12} - \tfrac{1}{8}\big(\mathbf{V}_{22}\mathbf{V}_{12}^{+}\mathbf{V}_{12}\\ + \mathbf{V}_{12}^{+}\mathbf{V}_{12}\mathbf{V}_{22} - 2\mathbf{V}_{12}^{+}\mathbf{V}_{11}\mathbf{V}_{12}\big) + \cdots.\end{aligned} \tag{29}$$

These expressions will be applied now for investigation of particular subchains.

INTERACTION OF TWO ENERGY BANDS ORIGINATING FROM *ns* AND *n′s* AOS

Let us start with a regular chain of uniform atoms, each of them containing two AOs of the *s* type, e.g., $ns = 1s$, $n's = 2s$. These AOs evidently build up an elementary cell of the chain. In accordance with the above-specified energy reference point and the (negative) energy unit, the zero-order energies of the *ns* and *n′s* AOs will be taken equal to 1 and −1, respectively.

Let γ and β stand for resonance parameters of the intersubchain-type corresponding to pairs of AOs of the same atom and of the nearest-neighboring atoms, respectively, as shown in Figure 1(a). When

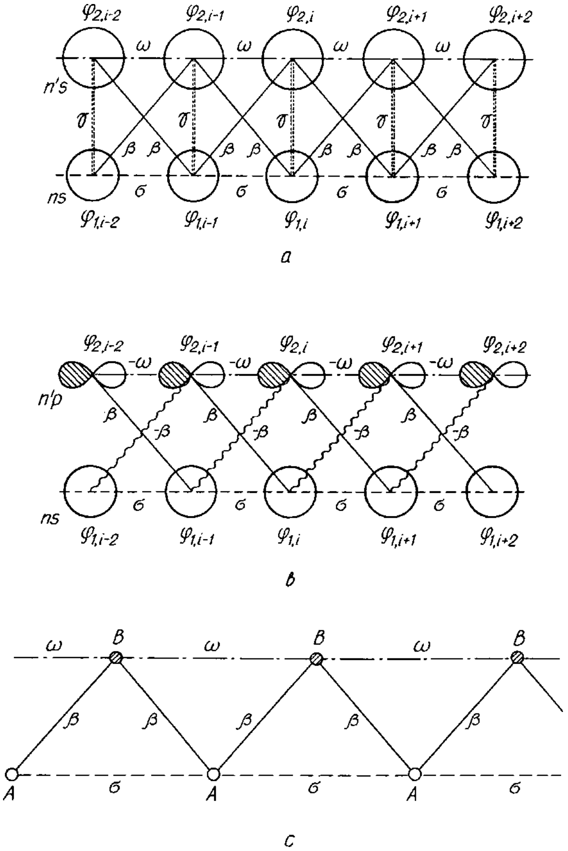

FIGURE 1. Examples of regular quasi-one-dimensional chains studied in this work. Chains consisting of uniform atoms, each of them containing two AOs are shown in diagrams (a) and (b). Atoms of the chain (a) are described by two AOs of the *s*-type (*ns* and *n′s*), while those of the chain (b) contain an *ns* AO and an *n′p* AO. The last picture (c) represents an alternating chain consisting of atoms of two types *A* and *B*, each of them described by a single AO. Greek letters (β, γ, ω, and σ) stand for various types of resonance parameters.

expressed in our negative energy units, these parameters are positive, i.e., $\gamma > 0$, $\beta > 0$. The intrasubchain resonance parameters for the nearest pairs of *ns* AOs will be denoted by σ ($\sigma > 0$), whereas those for the nearest-neighboring *n′s* AOs will be designated by ω ($\omega > 0$).

Using the above-introduced designations, the elements of submatrices $\mathbf{V}_{11}$, $\mathbf{V}_{22}$, and $\mathbf{V}_{12}$ of the first-order matrix $\mathbf{V}$ may be represented in the form

$$V_{11,ij} = \sigma(\delta_{i,j+1} + \delta_{i,j-1}), \qquad V_{22,ij} = \omega(\delta_{i,j+1} + \delta_{i,j-1}), \tag{30}$$

$$V_{12,ij} = V^{+}_{12,ij} = \beta(\delta_{i,j+1} + \delta_{i,j-1}) + \gamma\delta_{ij}. \tag{31}$$

Equations (30) and (31) should be substituted into the expressions for eigenblocks $\mathbf{E}_1$ and $\mathbf{E}_2$ shown in Eqs. (28) and (29). Then the elements of these eigenblocks ($E_{1,ij}$ and $E_{2,ij}$) become of the following constitution:

$$E_{1,ij} = \left(1 + \beta^2 + \tfrac{1}{2}\gamma^2\right)\delta_{ij} + (\sigma + \beta\gamma)(\delta_{i,j+1} + \delta_{i,j-1}) + \tfrac{1}{2}\beta^2(\delta_{i,j+2} + \delta_{i,j-2}) + \cdots, \tag{32}$$

$$E_{2,ij} = \left(-1 + \beta^2 + \tfrac{1}{2}\gamma^2\right)\delta_{ij} + (\omega - \beta\gamma)(\delta_{i,j+1} + \delta_{i,j-1}) - \tfrac{1}{2}\beta^2(\delta_{i,j+2} + \delta_{i,j-2}) + \cdots, \tag{33}$$

where terms to within the second order are included.

The influence of the intersubchain interaction upon the intrasubchain Hamiltonian matrix elements may be easily seen from Eqs. (32) and (33). Thus, one-electron energies of the *ns* AOs are increased by

$$\Delta = \beta^2 + \tfrac{1}{2}\gamma^2 \tag{34}$$

under the influence of the *n′s* AOs, whereas those of *n′s* AOs are decreased accordingly. The correction Δ of Eq. (34) originates from the second-order increment of Eq. (28) and describes the indirect self-interactions of the *ns* (*n′s*) AOs by means of the *n′s* (*ns*) AOs. Alternatively, it may be interpreted as the total "repulsion" of the given AO (e.g., $\varphi_{1i} = ns$) from the three nearest AOs of the second subchain (φ_{2i}, $\varphi_{2,i-1}$, and $\varphi_{2,i+1}$). It is evident that just the above-mentioned three AOs interact with the AO φ_{1i} directly.

Furthermore, the interactions between the nearest-neighboring AOs of the first subchain (e.g., φ_{1i} and $\varphi_{1,i+1}$) becomes increased by $\beta\gamma$ owing to the indirect interaction of these AOs by means of two AOs of the second subchain (φ_{2i} and $\varphi_{2,i+1}$, respectively), whereas that between the nearest AOs of the second subchain is decreased by $\beta\gamma$.

The most important peculiarity of the elements $E_{1,ij}$ and $E_{2,ij}$, however, consists in the emergence of a new effective interactions between the second-neighboring pairs of AOs of the first subchain under the influence of the second subchain and vice versa. For example, an interaction equal to $\frac{1}{2}\beta^2$ arises between AOs φ_{1i} and $\varphi_{1,i+2}$ of the first subchain owing to their indirect interactions by means of AOs $\varphi_{2,i+1}$ situated in between the former and playing the role of the only mediator.

It is noteworthy that the effective model Hamiltonian matrices $\mathbf{E}_1$ and $\mathbf{E}_2$ represented by elements $E_{1,ij}$ and $E_{2,ij}$ describe rather simple chains containing effective bonds between the first-neighboring and the second-neighboring pairs of AOs. As a result, the well-known methods of obtaining the dispersion relations for simple chains (see, e.g., [26]) may be applied here.

Given that terms of the solid-state theory [2, 3] are chosen (namely, the quasi-momentum vector $\mathbf{k}$ and the elementary cell's position vector $\mathbf{a}$), the approximate dispersion relations for the two energy bands of our system take the form

$$\varepsilon_1(\mathbf{k}) = (1 + \Delta) + 2(\sigma + \beta\gamma)\cos(\mathbf{ka}) + \beta^2\cos(2\mathbf{ka}) + \cdots, \tag{35}$$

$$\varepsilon_2(\mathbf{k}) = -(1 + \Delta) + 2(\omega - \beta\gamma)\cos(\mathbf{ka}) - \beta^2\cos(2\mathbf{ka}) + \cdots. \tag{36}$$

These relations should be compared to those of isolated subchains of the initial chain, viz.

$$\varepsilon_1^{\circ}(\mathbf{k}) = 1 + 2\sigma\cos(\mathbf{ka}), \qquad \varepsilon_2^{\circ}(\mathbf{k}) = -1 + 2\omega\cos(\mathbf{ka}). \tag{37}$$

The dispersion curves $\varepsilon_1(\mathbf{k})$, $\varepsilon_2(\mathbf{k})$, $\varepsilon_1^{\circ}(\mathbf{k})$, and $\varepsilon_2^{\circ}(\mathbf{k})$ are shown in Figure 2.

To be able to interpret separate peculiarities of these curves in terms of local interactions, an evident interrelation between terms of Eqs. (32) and (33), on the one hand, and those of Eqs. (35) and (36), on the other hand, should be used along with the above-discussed local interpretation of the former.

Thus, the first $\mathbf{k}$-vector-independent terms of Eqs. (35) and (36) are directly related to effective energies of AOs described by the parameter Δ of Eq. (34). Similarly, the coefficients of the cos(**ka**)-like terms originate from the effective interactions between the nearest-neighboring pairs of AOs determined by sums $\sigma + \beta\gamma$ and $\omega - \beta\gamma$ for the first and for the second subchain, respectively. Finally, the "weights" of the cos(2**ka**)-like increments

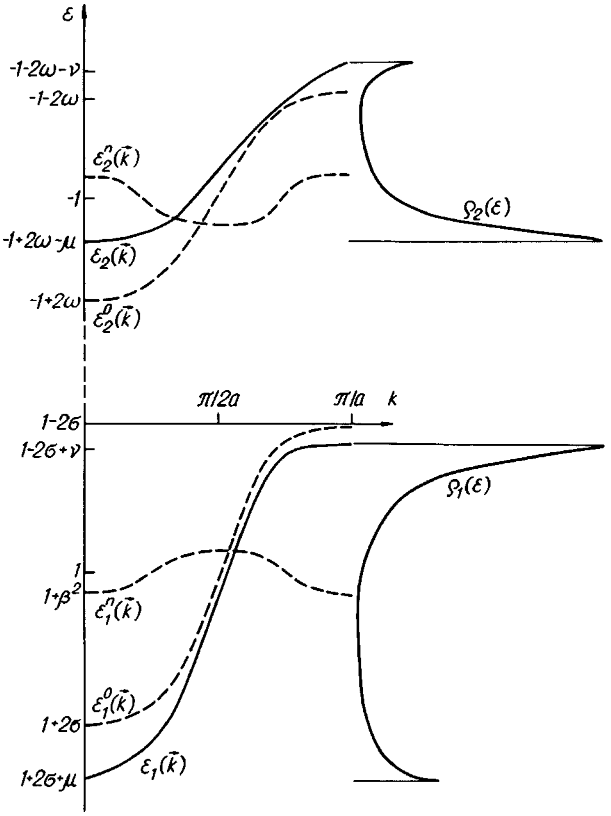

FIGURE 2. Diagram representing the formation of the final dispersion curves $\varepsilon_1(\mathbf{k})$ and $\varepsilon_2(\mathbf{k})$ of the regular quasi-one-dimensional chain displayed in Figure 1(a). The simple cos(**ka**)-like curves $\varepsilon_1^\circ(\mathbf{k})$ and $\varepsilon_2^\circ(\mathbf{k})$ correspond to isolated subchains of the chain under study and represent the dispersion relations of Eq. (37). The cos(2**ka**)-like curves $\varepsilon_1^n(\mathbf{k})$ and $\varepsilon_2^n(\mathbf{k})$ represent the new terms arising within Eqs. (35) and (36) owing to the interband interaction. The expressions for parameters μ and ν in terms of the initial resonance parameters β, γ, ω, and σ are shown in Eq. (40). The level density functions $\rho_1(\varepsilon)$ and $\rho_2(\varepsilon)$ corresponding to the dispersion curves $\varepsilon_1(\mathbf{k})$ and $\varepsilon_2(\mathbf{k})$, respectively, are shown in the right part of the picture.

depend on the relative value of the new effective interaction between the second-neighboring pairs of AOs.

As a result, the final dispersion curves prove to be made up of three additive components, each of them referring to a definite type of effective interorbital interaction. This principal conclusion forms the basis for interpretation of the observed dispersion curves in terms of local interactions. For example, alteration in the band's width is described by the following parameter:

$$\theta = \varepsilon_1(0) - \varepsilon_1(\pi/a) = -\big(\varepsilon_2(0) - \varepsilon_2(\pi/a)\big) = 4\beta\gamma, \tag{38}$$

which is proportional to the indirect interaction between the nearest-neighboring pairs of AOs. It is seen that the total width of the first band is increased by θ, whereas that of the second band is reduced by θ as compared to respective values for isolated subchains.

In this context, the influence of the new effective interaction between the second-neighboring pairs of AOs upon the final dispersion curves deserves particular attention. Indeed, the new cos(2**ka**)-like contribution arising within Eqs. (35) and (36) determines some significant changes in the shapes of the final dispersion curves as compared to the simple cos(**ka**)-like shape.

In particular, the lower part of the first band and the upper part of the second band become streched after adding the cos(2**ka**)-containing term, whereas the upper part of the first band and the lower part of the second band become compressed under the influence of the same term. If we turn to the density of states $\rho(\varepsilon)$ is defined as follows:

$$\rho(\varepsilon) = \left|\frac{\partial k}{\partial \varepsilon}\right|. \tag{39}$$

An increased density of states corresponds to the compressed regions of the final dispersion curves, and decreased values of the function $\rho(\varepsilon)$ refer to the streched parts of these curves.

The above-discussed examples demonstrate the existance of direct relations between separate characteristics of dispersion curves and individual effective interactions. On the other hand, there are some features of dispersion curves that originate from a simultaneous action of different interorbital interactions. The so-called interband "repulsion" may be mentioned here as an example.

Thus, comparison of curves $\varepsilon_1(\mathbf{k})$ and $\varepsilon_2(\mathbf{k})$ to $\varepsilon_1^\circ(\mathbf{k})$ and $\varepsilon_2^\circ(\mathbf{k})$, respectively, shows that curve $\varepsilon_1(\mathbf{k})$ is shifted downward vs. $\varepsilon_1^\circ(\mathbf{k})$, whereas $\varepsilon_2(\mathbf{k})$ is shifted upward vs. $\varepsilon_2^\circ(\mathbf{k})$. This phenomenon proves to be determined by superposition of various types of interorbital interactions. In particular, the interband repulsion energies μ and ν corresponding to $k = 0$ and $k = \pi/a$, respectively, are related to the above-described interorbital interaction parameters as follows:

$$\mu = \Delta + 2\beta\gamma + \beta^2, \qquad \nu = \Delta - 2\beta\gamma + \beta^2. \tag{40}$$

It is seen that all types of effective interactions (viz. the self-interactions of AOs, the effective interactions between the first-neighboring pairs of AOs and those between their second-neighboring pairs) participate in the interband repulsion.

INTERACTION OF ENERGY BANDS ORIGINATING FROM *ns* AOS AND *n′p* AOS

Let us consider now another chain of uniform atoms, each of them containing an *ns* AO and an *n′p* AO as shown in Figure 1(b). The main difference of this system from the previous one consists in the emergence of both positive and negative resonance parameters. In addition, the equality $\gamma = 0$ may be assumed for this chain.

As a result, a minus sign arises within the new expression for elements $V_{22,ij}$ of the matrix $\mathbf{V}_{22}$, whereas those of the matrix $\mathbf{V}_{11}$ may be taken from Eq. (30). The elements $V_{12,ij}$ of the matrix $\mathbf{V}_{12}$, in turn, take the form

$$V_{12,ij} = -V^{+}_{12,ij} = \beta(\delta_{i,j-1} + \delta_{i,j+1}). \tag{41}$$

Then the final expressions for elements of eigenblocks E_1 and E_2 are

$$\begin{aligned} E_{1,ij} = {} & \bigl(1+\beta^2\bigr)\delta_{ij} + \sigma(\delta_{i,j-1} + \delta_{i,j+1}) \\ & - \tfrac{1}{2}\beta^2(\delta_{i,j-2} + \delta_{i,j+2}) + \cdots , \end{aligned} \tag{42}$$

$$\begin{aligned} E_{1,ij} = {} & -\bigl(1+\beta^2\bigr)\delta_{ij} - \omega(\delta_{i,j-1} + \delta_{i,j+1}) \\ & - \tfrac{1}{2}\beta^2(\delta_{i,j-2} + \delta_{i,j+2}) + \cdots . \end{aligned} \tag{43}$$

Accordingly, the dispersion relations take the form

$$\begin{aligned} \varepsilon_1(\mathbf{k}) = {} & \bigl(1+\beta^2\bigr) + 2\sigma\cos\bigl(\mathbf{ka}\bigr) \\ & - \beta^2\cos(2\mathbf{ka}) + \cdots , \end{aligned} \tag{44}$$

$$\begin{aligned} \varepsilon_2(\mathbf{k}) = {} & -\bigl(1+\beta^2\bigr) + 2\omega\cos\bigl(\mathbf{ka}\bigr) \\ & - \beta^2\cos(2\mathbf{ka}) + \cdots \end{aligned} \tag{45}$$

for the *ns* band and for the *n′p* band, respectively.

Let us compare the dispersion relations of Eqs. (35) and (44) that describe the *ns* band under the influence of an *n′s* band and of an *n′p* band, respectively.

It is seen that the most essential difference between Eqs. (35) and (38) consists in opposite signs of their cos(2**ka**)-like terms. This peculiarity is evidently due to different signs of indirect interactions between the second-neighboring pairs of *ns* AOs by means of an *n′s* AO and by means of an *n′p* AO (both of them being localized in between the two *ns* AOs). The negative cos(2**ka**)-containing term of Eq. (44) gives rise to an increased density of states in the lower part of the band ($k \approx 0$) and to a reduced density of states in the upper part of the band ($k \approx \pi/a$) in contrast to the function $\rho_1(\varepsilon)$ of Figure 2.

ALTERNATING CHAIN CONTAINING BOTH FIRST- AND SECOND-NEIGHBORING RESONANCE PARAMETERS

Let us consider now a chain made up of atoms of two different types (*A* and *B*), each of them represented by a single AO. Atoms are assumed to be situated in such a way that each atom possesses two neighbors *A* and two neighbors *B*, as shown in Figure 1(c).

Equation (30) for elements of matrices $\mathbf{V}_{11}$ and $\mathbf{V}_{22}$ is valid for this chain as well, while the elements of the intersubchain block $\mathbf{V}_{12}$ are

$$V_{12,ij} = \beta(\delta_{i,j} + \delta_{i,j-1}), \qquad V^{+}_{12,ij} = \beta(\delta_{i,j} + \delta_{i,j+1}). \tag{46}$$

Substituting Eqs. (30) and (46) into Eqs. (28) and (29) indicates that no cos(2**ka**)-containing terms arise to within the second-order terms inclusive in contrast to the chains (a) and (b). After taking into account the third-order terms of Eqs. (28) and (29) as well, the elements of the first eigenblock $\mathbf{E}_1$ take the form

$$\begin{aligned} E_{1,ij} = {} & \bigl[1 + \beta^2 + \tfrac{1}{2}\beta^2(\omega - \sigma)\bigr]\delta_{ij} \\ & + \bigl[\sigma + \tfrac{1}{2}\beta^2 + \tfrac{1}{2}\beta^2(\omega - \sigma)\bigr](\delta_{i,j-1} + \delta_{i,j+1}) \\ & + \tfrac{1}{4}\beta^2(\omega - \sigma)(\delta_{i,j-2} + \delta_{i,j+2}) + \cdots , \end{aligned} \tag{47}$$

and the respective dispersion relation $\varepsilon_1(\mathbf{k})$ is

$$\begin{aligned} \varepsilon_1(\mathbf{k}) = {} & \bigl[1 + \beta^2 + \tfrac{1}{2}\beta^2(\omega - \sigma)\bigr] \\ & + 2\bigl[\sigma + \tfrac{1}{2}\beta^2 + \tfrac{1}{2}\beta^2(\omega - \sigma)\bigr]\cos(\mathbf{ka}) \\ & + \tfrac{1}{2}\beta^2(\omega - \sigma)\cos(2\mathbf{ka}) + \cdots . \end{aligned} \tag{48}$$

It is seen that the sign of the third-order cos(2**ka**)-containing term depends on the relative values of the intrasubchain resonance parameters ω and σ. As a result, the density of states $\rho_1(\varepsilon)$ corresponding to the dispersion function $\varepsilon_1(\mathbf{k})$ of Eq. (48) resembles the function $\rho_1(\varepsilon)$ of Figure 2 if $\omega > \sigma$. In the opposite case ($\omega < \sigma$), the shape of the density function under discussion resembles that of the function $\rho_2(\varepsilon)$ of Figure 2. If an equality $\omega = \sigma$ is valid, a cos(**ka**)-like shape of the dispersion curve of Eq. (48) follows. Emergence of the difference $\omega - \sigma$ in Eqs. (47) and (48) and thereby the above-discussed results may be accounted for by the presence of terms of different signs within the third-order increments to the eigenblocks $\mathbf{E}_1$ and $\mathbf{E}_2$ as shown in Eqs. (28) and (29).

On the whole, the results of this section demonstrate the efficiency our approach for interpretation of the principal characteristics of energy bands of regular quasi-one-dimensional systems in terms of local constitution of the chain. Thus, the dispersion relations, the density of states, and the interband interaction are among characteristics of the above-mentioned type.

Relations of Approach Suggested to Other Theories and Methods: Concluding Remarks

1. Let us start with the relation of the present approach to the standard solid-state theory [1–3].

As already mentioned, the two ways of investigation of quasi-one-dimensional systems differ in the relative order of taking into account the intra- and intersubchain interactions. Hence, the respective final numerical results may be expected to coincide with one another provided that these are obtained at the same level of approximation.

The very block-diagonalization problem for matrices shown in Eq. (4) may be formulated for any Hermitian matrix **H**, where $\mathbf{E}_k$, $k = 1, 2, \ldots, M$ are eigenblocks of any dimension [17]. This problem, however, is considerably less explored than the diagonalization problem. The question whether or not a general (nonperturbative) solution of the problem of Eq. (4) may be obtained also is still open.

In the present form, the approach suggested is based on a perturbative solution of the block-diagonalization problem. In particular, the case described by Eqs. (15)–(18) corresponds to a power series with respect to both intra- and intersubchain resonance parameters. Hence, coincidence of our final numerical results to those of the standard theory may be expected if an analogous power series is invoked in the latter case as well.

To verify this expectation, let us turn again to the chain of Figure 1(a) and consider it by means of the usual solid-state theory [1–3]. Two delocalized Bloch functions $\Psi_1(\mathbf{k})$ and $\Psi_2(\mathbf{k})$ corresponding to subchains of the *ns* and *n′s* AOs, respectively, may be obtained in this case. The relevant two-dimensional **k**-dependent Hamiltonian matrix block takes the form

$$\mathbf{H}(\mathbf{k}) = \begin{vmatrix} 1 + 2\sigma\cos(\mathbf{ka}) & \gamma + 2\beta\cos(\mathbf{ka}) \\ \gamma + 2\beta\cos(\mathbf{ka}) & -1 + 2\omega\cos(\mathbf{ka}) \end{vmatrix}, \qquad (49)$$

and the exact dispersion relation

$$\begin{aligned} \varepsilon_{1,2}(\mathbf{k}) = {} & (\omega + \sigma)\cos(\mathbf{ka}) \\ & \pm \left\{1 + \gamma^2 + 2\left[(\sigma - \omega) + 2\beta\gamma\right]\cos(\mathbf{ka}) \right. \\ & \left. + \left[4\beta^2 + (\sigma - \omega)^2\right]\cos^2(\mathbf{ka})\right\}^{1/2} \qquad (50) \end{aligned}$$

may be easily obtained after solving the respective two-dimensional secular problem. Accordingly, the final energy bands may be interpreted as a result of a **k**-dependent interaction of two cos(**ka**)-like dispersion curves, each of them corresponding to a delocalized subsystem (subchain). Nevertheless, if we expand the square root of Eq. (50) into power series with respect to resonance parameters β, γ, σ, and ω, the relations of Eqs. (35) and (36) follow.

Both the advantages and weak points of the new approach vs. the standard one reveal themselves on the basis of this simple example. Thus, despite its limitations caused by the application of the perturbation theory, the new approach offers additional possibilities for interpretation of the final results. As the above analysis shows, it allows us to interpret the separate increments of the dispersion relation in terms of local (direct and indirect) interactions of AOs and thereby in terms of local structure of the chain.

2. Let us dwell now on the relation of the present approach to the so-called noncanonical theory of molecular orbitals (MOs) [17, 18].

To this end, let us consider the particular case of the block-diagonalization problem of Eq. (4) for systems like those of Figure 1 containing $N = 2K$ basis orbitals and the same total number of electrons. Then the zero off-diagonal blocks of the transformed matrix **H** coincide with the occupied-vacant intersubset blocks. As a result, the problem of Eq. (4) is nothing more than the matrix form of the Brillouin theorem for noncanonical MOs, the latter following from matrix **C**. In the case of a regular system, the localized crystalline orbitals (Wannier functions [27, 28]) are likely to be among noncanonical MOs. One-electron density matrix (bond order matrix) also may be easily obtained on the basis of the transformation matrix **C** [18]. Hence, for the above-specified systems our approach coincides with the noncanonical theory of MOs.

3. The approach developed in this work yields effective Hamiltonian matrices for separate subspaces of the total space of AOs. In this respect, certain analogy may be traced between

this approach and the Löwdin's partitioning technique [29–32]. The principal difference between these procedures, however, consists in the fact that an eigenvalue-dependent effective Hamiltonian matrix and thereby the secular problem of an iterative nature was obtained in Refs. [29–32] in contrast to our case.

Nevertheless, in the case of two subsets certain relations may be established between these problems after additional assumptions. If the eigenvalue arising within the Löwdin's effective Hamiltonian matrix is taken equal to 1 and the matrix $[2\mathbf{I}-\mathbf{V}_{22}]^{-1}$ is expanded into power series with respect to $\mathbf{V}_{22}$, the resulting eigenvalue-independent Hamiltonian matrix coincides with that of Eq. (28) to within the second-order terms inclusive.

4. Comparison of the present approach to the reduction procedure of Ref. [13] also deserves attention, as $K \times K$-dimensional effective Hamiltonian matrices have been obtained there as well. Let us start with the main differences of these approaches.

The eigenvalue-dependent effective Hamiltonian matrices of Ref. [13] describe the whole chain under study and not its separate subchains. Moreover, quite extended fragments of the chain and not separate AOs correspond to diagonal elements of these matrices. Finally, no conditions of perturbative nature have been imposed when performing the reduction procedure.

It is also noteworthy that both approaches yield coinciding results for some simple chains containing AOs described by sufficiently different Coulomb parameters. The quasi-one-dimensional alternating chain described in Ref. [13] and containing AOs of two types represented by Coulomb parameters α_1 and α_2 is among the above-mentioned chains. To show this, no more is required to take Eq. (14a) of Ref. [13] and substitute $\alpha_1 = -1$, $\alpha_2 = 1$ and $\beta = \gamma$, $\varepsilon = 1$ into this relation.

On the whole, both the results of this work and of Ref. [13] indicate that a straightforward solution of the secular problem for the matrix $\mathbf{H}$ is hardly the most efficient way of qualitative investigation of electronic structures of extended systems. Indeed, the primary block-diagonalization of the matrix $\mathbf{H}$ described in this work and lowering of the dimension of the secular problem by means of elimination of certain coefficients of the matrix $\mathbf{C}$ suggested in Ref. [13] both yield new results that are usefull for interpretation of one-electron spectra of the above-mentioned systems.

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