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Energy Band Structure of Polymer Chains with Screw Axes of Symmetry

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The general relations concerning the energy band structure of quasi-one-dimensional crystals possessing screw axes are obtained. The π-electron energy bands of an infinite polyene chain are considered within the SCF tight binding approximation.

Key words: Energy band structure of polymers – Infinite polyene chain – One-dimensional crystals

1. Introduction

There is a number of systems which can be treated approximately as quasi-one-dimensional crystals. Some of them such as the DNA molecules and polypeptide chains, are of a great practical interest. Others, such as infinite polyene chains, are often used as shooting-range for testing different theoretical constructions which can not be studied in the three-dimensional case (for instance, see Ref. [1]). These facts cause a great interest for studying such systems.

In the present paper we obtain some general relations concerning the energy band structure of quasi-one-dimensional crystals with a screw symmetry (Section 2). These relations are applicable to exciton, phonon or electron energy bands. In Section 3 we use the results obtained for studying the energy bands of an infinite polyene chain within the tight binding approximation.

The problem of the electronic structure of conjugated chains is under consideration during a long time. The main results obtained by the well known π-electronic methods are reviewed in Ref. [1]. One of these results concerns the fact that a simple band theory leads to the metallic properties of an infinite polyene chain with equal C–C bond lengths or, alternatively, the Hartree-Fock energy levels of π-electrons in this system form a half-filled zone. In order to obtain a forbidden band between the energy levels occupied in the ground state and vacant levels one must perturb the initial symmetry of the chain [2, 3] or take into account electron correlations [4, 5] or, at last, consider both effects simultaneously [6]. Unlike these results of π-electronic treatments, the SCF LCAO CNDO [7] and *ab initio* [8] calculations give other than zero value of the forbidden gap between a conduction and valence bands of the regular polyene chain with equal C–C distances. We explain this discrepancy in Section 3.

2. The Energy Band Structure of One-Dimensional Crystals with a Screw Symmetry

Let us suppose that the wave function of a crystal state with the wave number k in the l-th energy band is given by

$$\psi_l(k)=\sum_{\lambda=1}^{\Lambda} C_{\lambda l}(k)\varphi_\lambda(k), \tag{1}$$

where $-\pi \leqq k \leqq \pi$. The functions $\{\varphi_\lambda(k)\}$ form an orthonormalized basis set. The explicit form of $\varphi_\lambda(k)$ is non-essential for the present. But we shall assume that

$$T_{an}\varphi_\lambda(k)=e^{ikn}\varphi_\lambda(k), \tag{2}$$

where T_{an} is the operator of the translation by the vector na, a is one-dimensional lattice constant and $n=0, \pm 1, \pm 2, \ldots$. For instance, we can see such $\varphi_\lambda(k)$ as

$$\varphi_\lambda(k)=\frac{1}{\sqrt{M}}\sum_m e^{ikm} X_{m\lambda} \tag{3}$$

where the letter m numbers different elementary cells, λ labels the different basis functions $X_{m\lambda}$ with the same m. $M\rightarrow\infty$ is the total number of unit cells, $k=2\pi j/M$. In the theory of molecular excitons the functions $X_{m\lambda}$ are treated as the states,of a whole crystal with an excitation on the $m\lambda$-th molecule [9]. As far as it concerns the SCF tight binding approximation, $\varphi_\lambda(k)$ is a Bloch orbital and $X_{m\lambda}$ is the λ-th AO within the m-th elementary cell [7, 8, 10–13]. The values of $C_{\lambda l}(k)$ are defined by the system of equations

$$\frac{dE}{dC^*_{\lambda l}(k)}=H_{\lambda\mu}(k)C_{\mu l}(k)=\varepsilon_l(k)C_{\lambda l}(k), \tag{4}$$

where $\lambda=1,2,\ldots,\Lambda$; E is the total energy, $H_{\lambda\mu}(k)$ are the matrix elements of Hamiltonian. Solving Eqs. (4) we obtain Λ eigenvalues ε_l and Λ eigenvectors $\{C_{1l}, C_{2l}, \ldots C_{\Lambda l}\}$ for each the value of $k=(-\pi,\pi)$. The eigenvalues $\varepsilon_l(k)$ form Λ Brillouin zones. Moreover, $\varepsilon_l(k)$ is a continuous function of k [10].

Now we consider the one-dimensional crystal possessing a screw symmetry axis of the N-th order C_N ($N=2,3,\ldots$). We assume that the functions $\varphi_\lambda(k)$ can be distributed between $F=\Lambda/N$ groups $\{\varphi_{af}\}$ in such a way that

$$\langle\varphi_{af}|\,T_{R_N}|\varphi_{bp}\rangle=\delta_{fp}t_{ab}, \tag{5}$$

where T_{R_N} is the operator of rotation about C_N. This operation can be treated as the translation by one N-th of the lattice constant and successive rotation by $2\pi/N$, or vice versa. If Eq. (5) is valid we can transform the initial basis set $\{\varphi_\lambda\}=\{\varphi_{af}\}$ so that

$$\begin{aligned} T_{R_N}[\varphi_{af}(k)]&=\pm\varphi_{a-1,f}(k), \quad (a\neq 1)\\ T_{R_N}[\varphi_{1f}(k)]&=\pm e^{ik}\varphi_{Nf}(k). \end{aligned} \tag{6a}$$

It will be assumed that the sign in the right of Eqs. (6a) depends on the index f only. In terms of the functions $X_{m,af}$ Eqs. (6a) can be written as

$$\begin{aligned} T_{R_N}X_{m,a,f}&=\pm X_{m,a-1,f},\\ T_{R_N}X_{m,1,f}&=\pm X_{m-1,N,f}. \end{aligned} \tag{6b}$$

Using Eqs. (6) we can construct the eigenfunctions of the operators $(\boldsymbol{T}_{R_N})^m$ $(m=0, 1, 2, \ldots)$. It can be shown that the functions

$$f_i(k) = \sum_{a=1}^{N} S_{ai}(k)\varphi_{af}(k)$$

satisfy the equations

$$(\boldsymbol{T}_{R_N})^m f_i(k) = (\lambda_{ki})^m f_i(k) \tag{7}$$

if

$$\begin{aligned} S_{ai}(k) &= \frac{1}{\sqrt{N}} e^{i\theta} ki^{a}, \theta_{ki} = \frac{k}{N} + 2i\pi/N\,, \qquad (i=0, 1, 2, \ldots N-1) \\ \lambda_{ki} &= \exp(i\theta_{ki})\,. \end{aligned} \tag{8}$$

The functions f_i are orthonormalized. In the case of one dimension the operator $(\boldsymbol{T}_{R_N})^m$ does commute with the translation operator $\boldsymbol{T}_{an}$. As far as the Hamiltonian commutes with all the symmetry transformations, we can rewrite Eq. (1) as the following

$$\psi_l(k) = \psi_{ti}(k) \quad \sum_{af} S_{ai}(k)\, U_{ft}(k)\varphi_{af}(k)\,. \tag{9}$$

So, the number of independent values $C_{\lambda l} = C_{af,ti}$ in Eqs. (4) is reduced by N^2 times due to the screw symmetry. Because of this, there is a dependence between eigenvalues $\varepsilon_{ti}(k)$. $(i=0, 1, 2, \ldots, N-1)$ for all the values of k and t.

Using Eq. (9) we obtain for the eigenvalues of Eqs. (4)

$$\varepsilon_{ti}(k) = \sum_{a,b=1}^{N} S^*_{ai}(k) S_{bi}(k) F_{ab}(t, k)\,, \tag{10}$$

where

$$F_{ab}(t, k) = \sum_{p,f=1}^{F} U^*_{ft}(k)\, U_{pt}(k) H_{af,bp}(k)\,. \tag{11}$$

Now we mention the following properties of Eqs. (4) [10]

$$\varepsilon_l(k) = \varepsilon^*_l(k) = \varepsilon_{l'}(-k) = \varepsilon_{l''}(k+2\pi)\,. \tag{12}$$

As a consequence, the matrix $\boldsymbol{F}(t, k)$ should satsify the equations

$$F_{ab}(t, k) = F^*_{ba}(t, k) = F_{ab}(t, k+2\pi) = F^*_{ab}(t, -k) \tag{13}$$

Let us study the structure of bands $\varepsilon_{ti}(k)$. First of all we consider such pairs ε_{ti} and ε_{tj} that $i+j=Nm$ $(m=0, \pm 1, \ldots)$. Then, $\theta_{-k,j} = \theta_{ki} + 2\pi m$ and from Eqs. (7)–(13) it follows that

$$\varepsilon_{tj}(-k) = \varepsilon_{ti}(k)\,, \qquad (i+j=Nm) \tag{14}$$

So, the graphs of $\varepsilon_{ti}(k)$ and $\varepsilon_{t,N-i}(k)$ intersect at the point $k=0$. The number of doubly degenerated eigenvalues equals to $(N-2)/2$ for even N and $(N-1)/2$ for odd N. If $j \neq N-i$ then $\varepsilon_{ti}(0) \neq \varepsilon_{tj}(0)$. Using Eq. (10) we can conclude that among $\varepsilon_{ti}(k=0)$ $(i=0, 1, 2, \ldots, N-1)$ there are n_0 different numbers where $n_0 = (N+2)/2$ (N is even) or $n_0 = (N+1)/2$ (N is odd). Alternatively speaking, the initial level ε_t splits up into n_0 levels. In the case of molecular excitons this effect is known as

Davydov splitting. This splitting is caused by the presence of N identical molecules within unit cell (see Ref. [9]).

Using Eqs. (7)–(13) we can write also that

$$\begin{aligned} &\varepsilon_{tj}(-\pi)=\varepsilon_{ti}(\pi) \qquad (j=i+1+Nm) \\ &\varepsilon'_{tj}(k=\pi-0)=\varepsilon'_{ti}(k=-\pi+0)\,, \end{aligned} \tag{15}$$

where $\varepsilon'_l(k)\equiv d\varepsilon_l(k)/dk$. Equations (14) and (15) lead to

$$\begin{aligned} \varepsilon_{t,N-i-1}(\pi)&=\varepsilon_{t,i}(\pi)\,, \\ \varepsilon_{t,N+1-i}(-\pi)&=\varepsilon_{t,i}(-\pi)\,. \end{aligned} \tag{16}$$

Thus, each of the energy bands $\varepsilon_{ti}(k)$ (except the case when $i=N\pm 1-i$) contacts with an other band at the point $k=\pm\pi$. It follows from Eqs. (15)–(16) that there are n_π different values among $\varepsilon_{ti}(k)$ $(i=0, 1, \ldots, N-1)$, where $n_\pi=N/2$ (N is even) or $n_\pi=(N+1)/2$ for odd N and $k=\pm\pi$. The results obtained above show also that we can build up a fictitious band $\varepsilon_t(k)$ from N bands $\varepsilon_{ti}(k)$. The continuous function $\varepsilon_t(k)$ can be constructed in the following manner. Let us introduce a wave number $q=k/N$. According to Eqs. (1), (3), (8) and (9) we write

$$\psi_{tj}(k)=\psi_t(q+2\pi j/N)\,, \qquad |q|\leqq\frac{\pi}{N} \tag{17}$$

where

$$\psi_t(q)=\sum_{a,f,n}\frac{1}{\sqrt{MN}}\,U_{ft}(k)\,X_{n,af}\,e^{iq(nN+a)} \tag{18}$$

For $-\pi\leqq q\leqq\pi$ we define $\psi_t(q)$ as

$$\psi_t(q)=\begin{cases} \psi_{tj}(k)\,, & \dfrac{(2j-1)\pi}{N}\leqq q\leqq\dfrac{(2j+1)\pi}{N} \\[2ex] \psi_{t,N-j}(k)\,, & -\dfrac{(2j+1)\pi}{N}\leqq q\leqq-\dfrac{(2j-1)\pi}{N}\,. \end{cases} \tag{19}$$

Due to Eq. (10) the corresponding energy levels are given by

$$\varepsilon_t(q)=\begin{cases} \varepsilon_{tj}(k)\,, \\ \varepsilon_{t,N-j}(k)\,. \end{cases} \tag{20}$$

Using the expression (19) instead of (1) we just take into account the screw symmetry. Besides, the order of the secular problem (4) is reduced by N times.

Equations (14)–(20) are valid in general. One can use them for studying exciton, phonon, electron or other energy bands of one-dimensional crystals with a screw symmetry.

In order to illustrate the relations given above we consider now some examples. Let us suppose that one-dimensional crystal possesses the screw axis of the 6-th order. For sake of simplicity we consider the case $F=1$ and use the approximation of the nearest neighbours:

$$\langle X_{ma}|\boldsymbol{H}|X_{nb}\rangle=\beta(\delta_{nm}\delta_{a,b-1}+\delta_{n+1,m}\delta_{a,1}\delta_{b,N}+\delta_{n-1,m}\delta_{a,N}\delta_{b,1})\,. \tag{21}$$

From Eqs. (14)–(16) it follows that

$$\langle \psi_j(k) | \boldsymbol{H} | \psi_i(k') \rangle = \delta_{kk'} \delta_{ij} \varepsilon j(k) ,$$

where

$$\varepsilon_j(k) = 2\beta \cos \theta_{kj} , \tag{22}$$

and δ_{ij} is a Kroneker delta-symbol. In the case under consideration Eqs. (14)–(16) give

$$\begin{aligned} \varepsilon_1(-k) &= \varepsilon_5(k), & \varepsilon_2(-k) &= \varepsilon_4(k) , \\ \varepsilon_0(k) &= \varepsilon_0(-k), & \varepsilon_3(-k) &= \varepsilon_3(k) , \\ \varepsilon_0(\pi) &= \varepsilon_5(\pi), & \varepsilon_1(\pi) &= \varepsilon_4(\pi) , \\ \varepsilon_2(\pi) &= \varepsilon_3(\pi), & \varepsilon_0(-\pi) &= \varepsilon_1(-\pi) , \end{aligned} \tag{23}$$

etc. Eq. (22) depends on the form of matrix elements (21), but Eqs. (23) are valid in general. From the energy bands (22) we can construct a new zone $\varepsilon(q) = 2\beta \cos q$ $(-\pi \leqq q \leqq \pi)$ in accordance with Eq. (20).

There is a number of the SCF tight binding calculations for regular polymer chains with the screw axis C_2. The energy band structure of polyenes $(CH{-}CH{=})_M$ is described in Ref. [7] (within the CNDO approximation) and Ref. [8] (*ab initio*). The energy bands of polyethylenes $(CH_2{-}CH_2{-})_M$ are given in Ref. [14]. In the case of the screw axis of the second order Eq. (16) has the form

$$\varepsilon_{t,0}(-\pi) = \varepsilon_{t,1}(-\pi) . \tag{24}$$

This effect can be easily observed on Fig. 3 in Ref. [14] and, as far as it concerned of polyene zones of the σ-type, on Figs. 1 in Refs. [7, 8]. The structure of π-electron energy bands of polyenes is discussed in detail in Section 3.

3. Energy Bands of an Infinite Polyene Chain

In this section we consider the energy band structure of the infinite polyene chain with equal C–C bond lengths (Fig. 1). For this purpose we shall use the SCF tight binding theory described in details elsewhere [10–13, 7, 8]. In the case of polyenes Bloch functions of the form (1) can be subdivided into two subsets: the functions of σ-type and the function of π-type. This σ-π separation enables one to consider the π-electron subsystem of polyenes neglecting its σ-electrons. We can note also that the lowest vacant and highest occupied energy levels in polyenes correspond to crystal orbitals of the π-type. The CNDO and *ab initio* calculations confirm this statement (see Refs. [7, 8]). So, to answer the question put in the Introduction it is sufficient to consider the π-electron energy bands of a regular polyene chain.

A polyene unit cell (Fig. 1) consists of two CH fragments labelled below by the indices A and B respectively. Using the minimal AO basis we can write π-electron functions in the form

$$\psi_l(k) = C_{Al}(k) \varphi_A(k) + C_{Bl}(k) \varphi_B(k) , \tag{25}$$

where $\varphi_\lambda(k)$ are defined by Eq. (3) if $X_{m\lambda}$ in (3) means the $2p_z$ orbital of the $m\lambda$-th carbon atom (Z-axis is normal to the plane of the chain). We shall use the CNDO

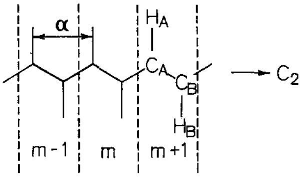

Fig. 1. The schematic diagram of an infinite polyene chain. The letters $m-1$, m, $m+1$ label the corresponding unit cells; a is the lattice constant. When all C–C bond lengths are equal this system possesses the screw axis of the second order – C_2 which runs through the centers of C–C bonds

approximation for the matrix elements of Hamiltonian. According to this approach only the following matrix elements do not vanish: the integrals of the Coulomb repulsion

$$\gamma_{m\lambda,n\lambda'} = \langle X^2_{m\lambda}(r_1)|\,|r_1 - r_2|^{-1}\,|r^2_{n\lambda'}(r_2)\rangle \tag{26}$$

and the core integrals

$$\beta_{m\lambda,n\lambda'} = \langle X_{m\lambda}(r)|\,\boldsymbol{h}(r)\,|X_{n\lambda'}(r)\rangle\,, \tag{27}$$

where $\boldsymbol{h}(r)$ is the operator of the kinetic and potential energy of a π-electron in the σ-core. We shall suppose also that

$$\beta_{m\lambda,n\lambda'} = \beta < 0 \tag{28}$$

when the $m\lambda$-th and $n\lambda'$-th atoms are the nearest neighbours, and that

$$\beta_{m\lambda,n\lambda'} = \alpha\delta_{mn}\delta_{\lambda\lambda'} \tag{29}$$

in other cases. We shall assume also that the π-electronic charge densities

$$2\sum_{k,l}|C_{\lambda l}(k)|^2 = 1 \tag{30}$$

on all the carbon atoms of the chain. It is easy to verify that under this assumption the σ-π separation is strictly valid within the CNDO approximation. Indeed, the energy expression of the CNDO method does not contain the exchange integrals between crystal orbitals of σ- and π-types. In the other hand, the Coulomb terms can be put equal to constants due to Eq. (30). As a consequence, Eq. (4) for the orbitals of π-type does not contain the values $C_{\lambda l_s}(k)$ where l_s refers to a σ-type zone.

Using the expressions (25)–(30) we can write Eqs. (4) in the form (the indices of zones are omitted)

$$\begin{aligned} C_B(k)\,[\beta(1+e^{-ik}) - a(k)] &= C_A(k)\,[\varepsilon(k) + W(k)]\,, \\ C_A(k)\,[\beta(1+e^{ik}) - a^*(k)] &= C_B(k)\,[\varepsilon(k) + W(k)]\,, \end{aligned} \tag{31}$$

where

$$\begin{aligned} W(k) &= \frac{1}{\pi}\int_{-\pi}^{\pi} V_{\lambda\lambda}(k-q)\,|C(q)|^2\,dq\,, \\ a(k) &= \frac{1}{\pi}\int_{-\pi}^{\pi} V_{AB}(k-q)\,C_B^*(q)\,C_A(q)\,dq\,, \\ V_{\lambda\lambda'}(k) &= \sum_n \gamma_{0\lambda,n\lambda'}e^{ikn}. \qquad (\lambda = A, B)\,. \end{aligned} \tag{32}$$

From Eq. (31) we obtain for the eigenvalues

$$\varepsilon_{1,2}(k) = -W(k) \mp \{4\beta^2 \cos^2 k/2 + |a(k)|^2 - 2\beta \operatorname{Re}[a(k)(1+\exp(ik/2))]\}^{1/2}. \tag{33}$$

The infinite polyene chain with equal C–C bond distances possesses the screw axis C_2 (see Fig. 1). From Eq. (24) it follows that each of the energy bands contacts with an other band at the points $k = \pm\pi$. Taking into account the fact that there is one π-electron on each of carbons, we can conclude that π-levels of the chain under consideration form a half-filled Brillouin zone. So, the SCF tight binding theory leads to metallic properties of an infinite polyene chain with equal C–C bonds.

Now we obtain the values of $\varepsilon_{1,2}(k)$ for π-bands in an explicit form. Equations (8)–(9) give

$$C_{Bj}(k) = C_{Aj}(k)\exp(i\theta_{kj}) = \pm C_{Aj}(k)e^{ik/2}. \tag{34}$$

Substituting Eq. (34) into (31) we can write

$$\varepsilon_{1,2}(k) = -W(k) \mp [2\beta\cos(k/2) - e^{ik/2}a(k)]. \tag{35}$$

In order to evaluate the Coulomb interaction in the system we suppose that

$$\gamma_{m\lambda;n\lambda'} = \gamma_1\delta_{mn}\delta_{\lambda\lambda'} + \frac{\gamma_2}{p}(1-\delta_{mn}\delta_{\lambda\lambda'}) \tag{36}$$

where p is the projection on the C_2 axis (Fig. 1) of the distance between the $m\lambda$-th and $n\lambda'$-th atoms in $a/2$ units. Simple calculations show that the difference between this approximation and more precise expressions is essential if the m_λ-th and n_λ-th atoms are the nearest neighbours. But the errors in the value of γ_{12} can be compensated by the reevaluation of the value of β (Ref. [5]). Using the approximation (36) we obtain

$$\begin{aligned}\varepsilon_{1,2}(k) = {} & \alpha + \frac{\gamma_1}{2} + 2\gamma_2\ln 2 \\ & \pm\left\{2\beta\cos k/2 + \frac{2\gamma_2}{\pi}\left[L\left(\frac{\pi}{4}+\frac{k}{4}\right) + L\left(\frac{\pi}{4}-\frac{k}{4}\right) - L\left(\frac{\pi}{2}\right)\right]\right\} \\ & -\frac{2\gamma_2}{\pi}L\left(\frac{\pi}{2}\right),\end{aligned} \tag{37}$$

where $L(x)$ is a Lobachevski function defined as (Ref. [15])

$$L(x) = -\int_0^x dt \ln\cos t. \tag{38}$$

Deriving Eq. (37) we take into account the relations (Ref. [15])

$$\sum_{n=1}^{\infty}\frac{1}{n}\cos nx = -\{\ln[2(1-\cos x)]\}/2, \tag{39}$$

$$\sum_{n=1}^{\infty}\frac{1}{2n-1}\cos(2n-1)x = \left(\ln\left|\operatorname{ctg}\frac{x}{2}\right|\right)\Big/2.$$

According to the results obtained in Section 2 we can perform the calculation of the $\varepsilon_j(k)$ in the alternative way. Namely, we can introduce a wave number $q=k/2$ and consider the chain with one CH fragment per unit cell. In this case, instead of Eq. (25), one can write down

$$\psi(q)=\frac{1}{\sqrt{2M}}\sum_n X_n e^{iqn}$$

and Eqs. (4) lead to the following expression $(-\pi\leqq k\leqq\pi)$

$$\varepsilon(k)=2\beta\cos k+\alpha+\frac{\gamma_1}{2}-\frac{\gamma_2}{2M}\sum_{k',n\neq 0}\frac{1}{n}e^{in(k-k')}. \tag{40}$$

It can be shown that in accordance with Eqs. (20)

$$\varepsilon(q=k/2)=\varepsilon_1(k),\ \varepsilon\left(q=-\frac{k}{2}+\pi\,\mathrm{sign}\,k\right)=\varepsilon_2(k). \tag{41}$$

One can see also that $\varepsilon_{1,2}(k)$ satisfy Eqs. (24). The following relation

$$\varepsilon_1(k)=-\varepsilon_2(k)+\mathrm{const}$$

known as the pairing theorem is a consequence of the approximations (27)–(29). It follows from the expression (37) that the Coulomb repulsion increases the widths of bands $\varepsilon_{1,2}(k)$ by the value of

$$\frac{2\gamma_2}{\pi}L\left(\frac{\pi}{2}\right)-2L\left(\frac{\pi}{4}\right)=\frac{2\gamma_2}{\pi}G \tag{42}$$

where G is a Catalan constant $(G=0.91596\ldots)$. Using Eqs. (37) and (38) we can obtain also that

$$|d\varepsilon_{1,2}(k)/dk|\to\infty \quad \text{when} \quad k\to\pm\pi. \tag{43}$$

It follows from Eq. (43) that the density of states which is proportional to $[d\varepsilon/dk]^{-1}$ vanishes on the Fermi surface. This effect of the Coulomb repulsion is well known for three dimensional crystals (for instance, see Ref. [16]).

The π-electron energy bands obtained for regular polyene chains in Refs. [7, 8] do not satisfy Eq. (24):

$$\Delta\varepsilon=\varepsilon_1(\pi)=\varepsilon_2(\pi)\neq 0. \tag{44}$$

Now we try to elucidate the origin of this inexactitude. This problem is also discussed in Refs. [17, 18].

Solving numerically Eqs. (4) one must truncate infinite series of the Coulomb integrals. Usually, such sums as in (32) are taken over a finite number of elementary cells. But, cutting off the interaction in such a way we disturb the symmetry invariance of the effective Hamiltonian under rotation around a screw axis. Indeed, such a rotation redistributes the atoms of the chain among the unit cells: the mA-th atom remains in the m-th cell and mB-th atom gets into the $(m+1)$-th cell (see Fig. 1 and Eqs. (6b)). As a consequence, the functions of the form (34) are not self-consistent and, generally speaking, the eigenvalues $\varepsilon_l(k)$ defined from Eq. (31) will not satisfy Eq. (24). Equation (31) can give a nonzero value of the energy gap (44) when $a(\pi)\neq 0$.

To illustrate this statement, we consider an example. Let us take into consideration only the interaction of the neighbouring unit cells. Using Eqs. (32), (34) and (36) we obtain

$$\begin{aligned} V_{AA}(k) &= V_{BB}(k) = (\gamma_2 \cos k)/2\,, \\ V_{AB}(k) &= \gamma_2 \left(1 + e^{-ik} + \frac{1}{3} e^{ik}\right), \\ a(k) &= \frac{4\gamma_2}{\pi} \exp(-ik/2)\left(2\cos\frac{k}{2} - \frac{1}{9} e^{i3k/2}\right). \end{aligned} \tag{45}$$

We can see that the value of $a(k)e^{ik/2}$ is complex. Therefore, the eigenvalues defined by Eq. (35) are not real, and the functions (34) are not self-consistent within the approximation (45).

Let us evaluate how the band gap (44) depends on the range of interaction. We do this for two cases. When the functions $C_{A,Bl}(k)$ satisfy Eq. (34) we obtain

$$\Delta\varepsilon(n) = 2(a^2 + 2a|\beta|)^{1/2} \approx \frac{\text{const}}{n} \tag{46}$$

where $a = a(\pi) = 4\gamma_2/(\pi n^2)$, the letter n in Eq. (46) means the range of interaction in $a/2$ units: If we take into account the interaction of the m-th cell with $(m \pm 1)$-th, $\dots, (m \pm p)$-th cells, $n = Np + 1 = 2p + 1$.

When, instead Eq. (34), $C_{Bl}(k) = -C_{Al}(k)$, the value of the gap (44) does not depend on n and equals $\Delta\varepsilon(n = 1)$. The self-consistent value of $\widetilde{\Delta\varepsilon}$ should satisfy the relation

$$\Delta\varepsilon(n) < \widetilde{\Delta\varepsilon}(n) < \Delta\varepsilon(n = 1)\,,$$

since due to Eqs. (31) $|C_{Al}(k)| = |C_{Bl}(k)|$. Thus, the gap value decreases slower than $1/n$ when n increases. On the other hand, numerical results of calculations change approximately as $1/n - 1/(n+1) \approx 1/n^2$ when we increase the number of interacting unit cells by one. As a result, the criterion of the convergence based on the comparison of the results for two successive values of $p = (n-1)/2$ can be wrong.

The results obtained in Refs. [7, 8] show that π-electron bands of polyenes $\varepsilon_l(k = \pi)$ are especially sensitive to such symmetry perturbations as described above. This effect can be explained in the following way. In the case of π-electronic bands we deal in fact with a half-filled zone of a metallic type and the zone states with energies close to the Fermi energy are nearly degenerate. Because of this, the correction to these levels is linear with respect to a small perturbation. Also, it should be noted that the contribution of these states into the total densities (30) is negligible (see Eq. (43)). As a consequence, a small perturbation of the symmetry properties of Eqs. (4) can result in a qualitatively wrong structure of the π-electron energy bands. This result can also be interpreted as the instability of the Hartree-Fock solution for π-bands of polyenes (see Ref. [18]).

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