Exactly solvable polymer models: polyphenylene

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A one-dimensional discrete model applicable for the description of the polymer polyphenylene is investigated. Its complete integrability in the class of finite-band potentials is proved. The deformation and the spectrum are obtained for an arbitrary occupation number ρ per molecule. It is shown that the Peierls effect leads to self-trapping of the electrons and to formation of polarons.

I. INTRODUCTION

Theoretical investigations of conducting polymers[1–4] show that the Peierls effect exerts a strong influence on their specific properties. A distinction is made between systems with pure and combined Peirels states. In a system with a pure Peierls state the gap in the electron spectrum is the result of spontaneous symmetry breaking in the system. An example of such a polymer is *trans*-$(CH)_x$. In systems with combined Peierls states the electron spectrum has, independently of the Peierls effect, a gap due to the polymer structure. An example of such a polymer is *cis*-$(CH)_x$. Previously proposed theoretical models are suitable for the description of the simplest polymers, such as polyacetylene, in which the band gap is small compared with the total bandwidth. The present paper is devoted to a model that describes the one-dimensional ($1D$) polymer polyphenylene, which has in its spectrum a large band gap $E_g \approx 3.5$ eV.[5] The continual approximation cannot be used in this case, and the discrete model is therefore considered. This polymer is of interest because experiments indicate that undoped samples are not paramagnetic.[5–7] It will be shown that polyphenylene is a dielectric of the combined type. We expect the Peierls effect to lead to self-trapping of the electrons and to formation of polarons.

The investigation reported here is based on the mathematical formalism described in the paper of Brazovskiĭ, Dzyaloshinskiĭ, and Krichever.[8]

II. FORMULATION OF MODEL. DETERMINATION OF GROUND STATE

1. The polymer polyphenylene consists of interconnected benzene molecules, as shown in Fig. 1. Each carbon atom has four valence electrons, three of which are on hybridized orbitals, make up σ bonds, and form low-lying filled bands. The remaining valence electrons (one per carbon atom) form π bonds, and the directions of their electron clouds are perpendicular to the molecule plane.

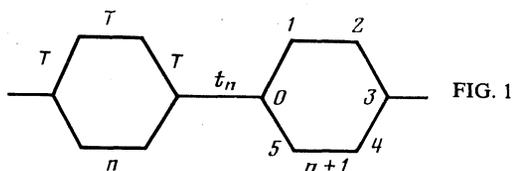FIG. 1

The Peierls effect is the result of an investigation between the electrons and the lattice deformations. It was shown by Brazovskiĭ *et al.*[9] that in the tight-binding approximation the electrons do not interact with the intramolecular oscillations, so that in this system the Peierls effect can occur via interaction with the intermolecular oscillations, i.e., via modulation of the hopping integrals t_n between the rings. Inside the benzene molecule, the hopping integral between neighboring sites has therefore a constant value T. It is assumed that T is of the same order as in polyacetylene, i.e., $T \approx 2.5$ eV.[3] The value of t_n can change either as a result of the bond length or as a result of rotation of the benzene ring through a certain angle about the longitudinal axis of the chain. Experiments[10,11] show that the lengths of the bonds between the molecules are approximately the same as in the molecules, and that neighboring molecules are rotated relative to one another through certain angles on the order of 10–30°. We assume therefore that the hopping integrals t_n will be modulated predominantly via rotation of the molecules or, in other words, that the Peierls effect is brought about by interaction of the electrons with rotational oscillations of the lattice (librons). When neighboring benzene molecules are rotated relative to one another the hopping integral between them decreases, in view of the decreased area of the overlap of the π-electron clouds; we shall therefore assume hereafter that $t_n \leqslant T$,

In the tight-binding approximation, with account taken of only the interaction between the nearest neighbors, the system Hamiltonian is

$$H = -\sum_n \left[t_n \psi_n^*(3)\,\psi_{n+1}(0) - \sum_{l=0} T\psi_n^*(l)\,\psi_n(l+1) \right] + \text{c. c.},$$

where

$$\psi_n(l) = A_n \cdot 6^{-\frac{1}{2}}(-1)^l + B_n \cdot 3^{-\frac{1}{2}}\cos(\pi l/3)$$
$$+ G_n \cdot 3^{-\frac{1}{2}}\cos(2\pi l/3) + D_n \cdot 6^{-\frac{1}{2}}$$
$$+ E_n \cdot 3^{-\frac{1}{2}}\sin(\pi l/3) + F_n \cdot 3^{-\frac{1}{2}}\sin(2\pi l/3), \qquad (1)$$

n is the number of the benzene molecule and l is the number of the molecule site (see Fig. 1). The wave function $\psi n(l)$ is made up as a linear combination of plane waves—the eigenfunctions of one benzene ring. For one benzene molecule, the electron spectrum and the wave functions are given by

$$E = -2T, \quad \varphi^{-2}(l) = 6^{-1/2},$$

$$E = -T, \quad \varphi^{-1}(l) = 3^{-1/2} \cos(\pi l/3), \quad \bar{\varphi}^{-1}(l) = 3^{-1/2} \sin(\pi l/3),$$

$$E = T, \quad \varphi^{1}(l) = 3^{-1/2} \cos(2\pi l/3), \quad \bar{\varphi}^{1}(l) = 3^{-1/2} \sin(2\pi l/3),$$

$$E = 2T, \quad \varphi^{2}(l) = (-1)^{l} \cdot 6^{-1/2}.$$

Since a neutral benzene ring contains six π electrons, in the ground state the levels $E = -2T$ are doubly occupied, $E = -T$ quadruply, and the levels $E = T$ and $E = 2T$ are free. When account is taken of the interaction between the rings, the discrete levels spread into bands. It can be seen from the structure of the Hamiltonian (1) that the term with the interaction does not contain the wave-function components $E_n \cdot 3^{-1/2} \sin(\pi l/3)$ and $F_n \cdot 3^{-1/2} \times \sin(2\pi l/3)$; therefore the levels corresponding to these functions remain discrete. Thus, the spectrum of the system has two discrete levels, $E = \pm T$, the level $E = -2T$ being $2N$-fold filled and the level $E = T$ empty. We discard hereafter in the wave function (1) the last two terms corresponding to the considered discrete levels.

We express the Schrödinger equation in terms of the variables

$$\alpha_n^{\pm} = 2^{-1/2}(D_n \pm A_n), \quad \beta_n^{\pm} = 2^{-1/2}(G_n \pm B_n).$$

It takes the form

$$\begin{pmatrix} -E & -2T & 0 & 0 \\ -2T & -E & 0 & 0 \\ 0 & 0 & -E & T \\ 0 & 0 & T & -E \end{pmatrix} \bar{\psi}_n$$

$$+ \begin{pmatrix} 0 & 0 & 0 & 0 \\ -\dfrac{t_n}{3} & 0 & -\dfrac{\sqrt{2}t_n}{3} & 0 \\ 0 & 0 & 0 & 0 \\ -\dfrac{\sqrt{2}t_n}{3} & 0 & -\dfrac{2t_n}{3} & 0 \end{pmatrix} \bar{\psi}_{n+1}$$

$$+ \begin{pmatrix} 0 & -\dfrac{t_{n-1}}{3} & 0 & -\dfrac{\sqrt{2}t_{n-1}}{3} \\ 0 & 0 & 0 & 0 \\ 0 & -\dfrac{\sqrt{2}t_{n-1}}{3} & 0 & -\dfrac{2t_{n-1}}{3} \\ 0 & 0 & 0 & 0 \end{pmatrix} \cdot \bar{\psi}_{n-1} = 0, \quad (2)$$

where the column $\bar{\psi}_n$ has the components $\bar{\psi}_n = (\alpha_n^+, \alpha_n^-, \beta_n^+, \beta_n^-)$. With the aid of (2) we can express the quantities $\alpha_n^{\pm}$ in terms of $\beta_n^{\pm}$:

$$\alpha_n^+ = -\frac{1}{\sqrt{2}} \frac{2T^2 + E^2}{4T^2 - E^2} \beta_n^+ + \frac{3}{\sqrt{2}} \frac{TE}{4T^2 - E^2} \beta_n^-,$$

$$\alpha_n^- = \frac{3}{\sqrt{2}} \frac{TE}{4T^2 - E^2} \beta_n^+ - \frac{1}{\sqrt{2}} \frac{2T^2 + E^2}{4T^2 - E^2} \beta_n^-. \quad (3)$$

Introducing the variables

$$\varphi_n^+ = -E\beta_n^+ + T\beta_n^-, \quad \varphi_n^- = T\beta_n^+ - E\beta_n^-;$$

We obtain from (2) with the aid of Eqs. (3) the following equivalent equation:

$$\varphi_{n+1} = S_n \varphi_n, \quad \varphi_n = \begin{pmatrix} \varphi_n^+ \\ \varphi_n^- \end{pmatrix}, \quad (4)$$

$$S_n = \begin{pmatrix} \dfrac{2T^3 t_n}{(E^2 - T^2)(E^2 - 4T^2)} & \dfrac{(3T^2 - E^2)E t_n}{(E^2 - T^2)(E^2 - 4T^2)} \\ -\dfrac{(3T^2 - E^2)E t_n}{(E^2 - T^2)(E^2 - 4T^2)} & -\dfrac{(3T^2 - E^2)^2 E^2 t_n}{2T^3(E^2 - T^2)(E^2 - 4T^2)} + \dfrac{(E^2 - T^2)(E^2 - 4T^2)}{2T^3 t_n} \end{pmatrix},$$

where $\det S_n \equiv 1$. For the components φ_n^+ and φ_n^- we easily obtain from Eq. (4)

$$\frac{\varphi_{n+1}^+}{t_n} + \frac{\varphi_{n-1}^+}{t_{n-1}} + \frac{(E^2 - T^2)}{2}\left(1 - \frac{E^2 - 4T^2}{t_{n-1}^2}\right)\varphi_n^+ = 0, \quad (5a)$$

$$\frac{\varphi_{n+1}^-}{t_n} + \frac{\varphi_{n-1}^-}{t_{n-1}} + \frac{(E^2 - T^2)}{2}\left(1 - \frac{E^2 - 4T^2}{t_n^2}\right)\varphi_n^- = 0. \quad (5b)$$

By specifying φ_0^+ and φ_0^- with the aid of (4), we can determine all the remaining φ_n^+ and φ_n^- for arbitrary values $E^2 \neq T^2$, $E^2 \neq 4T^2$. One can specify φ_0^+ and φ_1^+ and determine from (5) also φ_n^+ and φ_n^-. In analogy with Ref. 8, we shall solve Eqs. (4) and (5) with periodic coefficients $t_{n+N} = t_n$, with an aim at subsequently taking the limit as $N \to \infty$. Using (4), we get

$$\varphi_{n+N} = S_{N+n-1} S_{N+n-2} \ldots S_n \varphi_n = \hat{T}\varphi_n. \quad (6)$$

We seek the solution of Eq. (4) in the form of a Bloch wave, so that $\varphi_{n+N} = \Lambda\varphi_n$, where the eigenvalues Λ of the mono-dromy matrix T are determined from the equation

$$\Lambda^2 - 2Q(E)\Lambda + 1 = 0, \quad Q(E) = \frac{1}{2}\mathrm{Sp}\,\hat{T}. \quad (7)$$

The polynomial $Q(E)$ is of degree $4N$, and its leading terms are

$$Q(E) = \frac{\left[E^{4N} + E^{4N-2}\left(-5T^2 N - \sum_i t_i^2\right) + \ldots\right]}{2(2T^3)^N t_{N-1}\ldots t_0}. \quad (8)$$

As shown in Ref. 8, the end points of the spectrum are simple roots of the equation $Q^2(E) = 1$. If $E_1 < E_2 < \ldots E_{2q+2}$ satisfy the equations $Q^2(E_i) = 1$, the spectrum of the system contains q forbidden bands $E_{2k} < E < E_{2k+1}$ and $q + 1$ allowed bands $E_{2k-1} < E < E_{2k}$. In the forbidden bands we have $|Q(E)| < 1$ and $\Lambda(E) = \exp(ipN)$, where $p(E)$ is the momentum corresponding to an eigenstate with energy E. In the forbidden bands we have $|Q(E)| > 1$. We are interested in the case of finite q in the limit as $N \to \infty$. In this limit the

1050   Sov. Phys. JETP **59** (5), May 1984

S. I. Matveenko   1050

levels E fill densely the allowed bands, and we can transform from summation over the states to integration with respect to E:

$$\sum_E = \frac{2N}{2\pi} \int dp = \frac{2N}{\pi} \int \frac{dp}{dE} dE. \tag{9}$$

Account is taken here of the energy degeneracy in momentum $p \rightarrow -p$ and in spin. From (7) and from the definition of the momentum it follows[8] that

$$idp = \frac{1}{N} \frac{d\Lambda}{\Lambda} = \frac{N^{-1}dQ}{\pm(Q^2-1)^{1/2}} = \frac{4P(E)}{\pm R^{1/2}(E)}, \quad R = \prod_{i=1}^{2q+2} E - E_i, \tag{10}$$

where $P(E)$ is a polynomial of degree q. The sign of the square root in (10) is chosen such that $dp > 0$. It follows from the fact that in our case the polynomial contains only even powers of E that the spectrum is symmetric about the level $E = 0$. Therefore $R(E)$ and $P(E)$ are given by

$$R(E) = \prod_{k=1}^{q+1} (E^2 - E_k^2), \quad E_1 < E_2 < \ldots < E_{q+1},$$

$$P(E) = E^q + AE^{q-2} + BE^{q-4} + \ldots . \tag{11}$$

Since there are no eigenvalues of the operator H inside the forbidden bands, we have

$$\int_{E_{2k}}^{E_{2k+1}} \frac{dp}{dE} dE = 0, \quad k = 1, \ldots, \left[\frac{q-1}{2}\right]. \tag{12}$$

The system (12) enables us to find, in quadratures, the coefficients of the polynomial $P(E)$. The integrals with respect to the allowed bands are of the form

$$\frac{2}{\pi} \int dp = \frac{m_j}{N}, \quad \sum_j m_j = N, \tag{13}$$

where m_j is the number of levels in the jth band.

It follows from (10) that the differential p is single-valued on the Riemann surface Γ of the function $R^{1/2}(E)$. We shall represent such a surface as glued together of two E-plane sheets with cuts along the allowed bands. We assume that in the vicinity of $E \rightarrow \infty$ we have on the upper sheet $R^{1/2}(E) = E^{q+1} + O(E^{q-1})$, just as in Ref. 8. Then $dp > 0$ on the upper edges of the cuts on the lower sheet. The integration in the formulas that follow are along cycles that lie on the lower sheet of Γ and close the allowed bands.

From (7) and (8) and from the definition of the momentum p it follows that as $E \rightarrow \infty$ we have on the upper sheet the expansion

$$ip = N^{-1} \ln \Lambda = 4 \ln E - I_0 - I_2 E^{-2} - I_4 E^{-4} - \ldots, \tag{14}$$

where

$$I_0 = N^{-1} \ln (t_0 t_1 \ldots t_{N-1} \cdot (2T^3)^N),$$

$$I_2 = 5T^2 + \frac{1}{N} \sum_i t_i^2.$$

Comparing (14) with the expansion (10), we obtain expressions for the I_i in terms of the coefficients of the polynomial $P(E)$

$$I_0 = \lim_{E \rightarrow \infty} \left(4 \ln E - \int_{E_{q+1}}^{E} \frac{4P(E)}{|R^{1/2}(E)|} dE\right),$$

$$I_2 = 2A + s,$$

$$I_4 = \frac{1}{2} sA + B + \frac{1}{4} r + \frac{1}{8} s^2, \tag{15}$$

where

$$s = \sum_{i=1}^{q+1} E_i^2, \quad r = \sum_{i=1}^{q+1} E_i^4.$$

2. To continue, we need certain analytic properties of the Bloch functions φ_n^+ and φ_n^-. To each pair (Λ, E) satisfying Eq. (7) there corresponds a unique solution of Eq. (4), which is an eigensolution for the operator $\hat{T}: \varphi_{n+N} = \hat{T}\varphi_n$, and is normalized by the condition $\varphi_0^+ = 1$. This is called a Bloch solution. We then have for φ_n

$$\varphi_n = S_{n-1} \ldots S_0 \begin{pmatrix} 1 \\ \varphi_0^- \end{pmatrix} = \hat{T}\varphi_0, \tag{16}$$

where φ_0 is an eigenvector of the matrix

$$\hat{T} = \begin{pmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{pmatrix}, \quad \det T = 1,$$

so that $\varphi_0 = (\Lambda - T_{11})/T_{12}$. At each value of the energy E there are two functions φ_n corresponding to two different solutions of (7). The Bloch function is single-valued on the Riemann surface Γ of the function $(Q^2 - 1)^{1/2}$. As $E \rightarrow \infty$ the function φ_n has two asymptotic values, corresponding to two values of Λ, on the two Γ sheets:

$$\Lambda_1 \rightarrow \frac{E^{4N}}{(2T^3)^N t_0 \ldots t_{N-1}},$$

$$\varphi_0 \approx \begin{pmatrix} 1 \\ -\dfrac{E^5}{2T^3 (t_{N-1})^2} \end{pmatrix}, \quad \varphi_n \approx \begin{pmatrix} \dfrac{E^{4n} t_{n-1}}{(2T^3)^n t_{n-2} \ldots t_0 (t_{N-1}^2)} \\ -\dfrac{E^{4n+5}}{(2T^3)^{n+1} t_{n-1} \ldots t_0 (t_{N-1}^2)} \end{pmatrix},$$

$$\Lambda_2 \rightarrow \frac{(2T^3)^N t_0 \ldots t_{N-1}}{E^{4N}},$$

$$\varphi_0 \approx \begin{pmatrix} 1 \\ -\dfrac{2T^3 t_0^2}{E^5} \end{pmatrix}, \quad \varphi_n \approx \begin{pmatrix} \dfrac{(2T^3)^n t_{n-1} \ldots t_0}{E^{4n}} \\ -\dfrac{(2T^3)^{n+1} t_n^2 t_{n-1} \ldots t_0}{E^{4n+5}} \end{pmatrix}. \tag{17}$$

Away from infinity, φ_n is analytic everywhere except at the points γ at which $T_{12}(E) = 0$, where φ_n has poles. Since $\det T = 1 = T_{11}T_{22}$ at $E = \gamma$, we have $Q(\gamma) = (T_{11} + T_{22})/2 \geqslant 1$ and the poles γ of the function φ_n lie in forbidden bands. φ_n has in this case poles on only one sheet above the point γ, inasmuch as at $T_{12} = 0$ one of the roots is $\Lambda_1 = T_{11}$ and $\varphi_0 = (\Lambda - T_{11})/T_{12}$ has no pole.

The matrix S_n has singularities at $E = \pm T$ and $\pm 2T$, therefore the components φ_n^+ and φ_n^- of the wave function should be linearly dependent. It can be easily seen from (4) that

$$E = \pm T, \quad \varphi_n^+ = \mp \varphi_n^-; \quad E = \pm 2T, \quad \varphi_n^+ = \pm \varphi_n^-. \tag{18}$$

From (5a) and (5b) we obtain

$$E = \pm T, \quad \varphi_{n+1}^{\pm} = -(t_n/t_{n-1})\varphi_{n-1}^{\pm}, \tag{19}$$

$$\varphi_{n+1}^+=-\frac{t_n}{t_{n-1}}\varphi_{n-1}^+-\left(1+\frac{3T^2}{t_{n-1}^2}\right)\varphi_n^+=0,$$

$$E=\pm 2T,$$

$$\varphi_{n+1}^-=-\frac{t_n}{t_{n-1}}\varphi_{n-1}^--\left(1+\frac{3T^2}{t_n^2}\right)\varphi_n^-=0. \qquad (20)$$

It follows from (19) that at $E=T$ we have for even N

$$\Lambda_1=(-1)^{N/2}t_{N-1}t_{N-3}\ldots t_1/t_{N-2}t_{N-4}\ldots t_0, \qquad \Lambda_2=\Lambda_1^{-1}, \qquad (21a)$$

and for odd N

$$\Lambda_1=i, \qquad \varphi_0^+=1, \qquad \varphi_1^+=i(-1)^{(N+1)/2}t_1t_3\ldots t_{N-2}/t_2t_4\ldots t_{N-1},$$

$$\Lambda_2=-i, \qquad \varphi_0^+=1, \qquad (21b)$$

$$\varphi_1^+=-i(-1)^{(N+1)/2}t_1t_3\ldots t_{N-2}/t_2t_4\ldots t_{N-1}.$$

We shall be interested in the case when the levels $E=\pm T$, $\pm 2T$ lie in allowed bands. We therefore find from (21a) that at even N the following condition must be satisfied:

$$t_1t_3\ldots t_{N-1}=t_2t_4\ldots t_N. \qquad (22)$$

We consider for simplicity the case of odd N, so that the condition (22) is of no use to us.

We note next that at $E=0$, $\pm 3^{1/2}T$ the matrix S_n, meaning also T, is diagonal. Let, e.g., $E=0$. Then

$$\Lambda_1=\Pi(t_i/2T), \qquad \Lambda_2=\Lambda_1^{-1}.$$

As indicated above, we are interested in the case $t_i<T$. Therefore $|\Lambda_{1,2}|\neq 1$ and the level $E=0$ is always in the forbidden band. For the matrix $\hat{T}$ at $E=0$ we obtain the expression

$$\hat{T}=\begin{pmatrix} \Lambda_1 & Ef \\ Eh & \Lambda_2 \end{pmatrix} \qquad h,f=O(1).$$

The eigenfunctions φ_0 of the matrix $\hat{T}$ are

$$\Lambda=\Lambda_1, \qquad \varphi_0^+=1, \qquad \varphi_0^-\infty E \qquad (E\to 0),$$

$$\Lambda=\Lambda_2, \qquad \varphi_0^+=1, \qquad \varphi_0^-\infty E^{-1}.$$

It is clear therefore that at $E=0$ the wave function φ_n^- always has a pole on one sheet and a zero on the other. From the form of the matrix S_n it follows that the function φ_n^+ has no singularities at $E=0$. In addition, recognizing that $\Lambda=\exp(ipN)$, and taking (14) into account we obtain on the lower sheet

$$ip(E=0)=I_0-\ln 4. \qquad (23)$$

Similar reasoning holds also for $E=3^{1/2}T$. In this case

$$\Lambda_1=-\Pi(t_i/T), \qquad \Lambda_2=\Lambda_1^{-1}$$

and on the lower sheet

$$ip(E^2=3)=I_0-\ln 2+i\pi. \qquad (24)$$

3. We obtain now, in analogy with Ref. 8, an expression for the variation δp of the momentum when t_n is changed. We note that Eq. (2) is of the form

$$\hat{H}\psi=C_n\psi_{n+1}+C_n^T\psi_{n-1}+V_n\psi_n=E\psi_n,$$

where ψ_n is a four-component column, $V_n=$ const, and C_n^T is the transpose of a 4×4 matrix. Let ψ_n' be the solution of the equation

$$\hat{H}'\psi'=V_n\psi_n'+C_n'\psi_{n+1}'+C_{n-1}^{+'}\psi_{n-1}'=E\psi_n'.$$

Multiplying the first equation by ψ_n' and the second by ψ_n, we subtract and sum over n. Accurate to first-order terms, ψ_n' is the solution of the equation $H\psi_n'=E\psi_n'$. We choose for ψ_n' the value of ψ_n on the second sheet of the Γ surface. In allowed bands $\psi_n'=\psi_n^*$. We obtain the equation

$$C_{N-1}(\psi_N'\psi_{N-1}-\psi_N\psi_{N-1}')\,[\,(1-\Lambda^{-1}(\Lambda')^{-1}]$$

$$=\sum_{n=1}^{N-1}(\psi_{n+1}'\psi_n+\psi_n'\psi_{n+1})\delta C_n,$$

$$1-\Lambda^{-1}(\Lambda')^{-1}\approx -i\delta pN.$$

Expressing the components ψ_n in terms of φ_n^+ and φ_n^- we obtain ultimately

$$i\delta pN[\varphi_N^+\varphi_N^{-'}-\varphi_N^{'+}\varphi_N^-]=\sum_{n=0}^{N-1}\frac{\delta t_n}{t_n}\left[\frac{E(3T^2-E^2)}{T^3}\right.$$

$$\left.\times\varphi_{n+1}^{'+}\varphi_{n+1}^++\varphi_{n+1}^{'+}\varphi_{n+1}^-+\varphi_{n+1}^{'-}\varphi_{n+1}^+\right]. \qquad (25)$$

Using (17), we readily see that the right-hand side is a rational function of E, in the form

$$P_{q+5}(E)\,\Big/\prod_s (E-\gamma_s),$$

where $P_{q+5}(E)$ is a polynomial of degree $q+5$, and the left-hand side is

$$R^{1/2}(E)P_4(E)/\Pi(E-\gamma_s).$$

We verify with the aid of (18) that $P_4(E)=(E^2-T^2)(E^2-4T^2)$. The right-hand side of (25) also vanishes at $E=\pm T$, $\pm 2T$. Substituting the resultant expressions in (25) we get $i\delta p=P_{q+1}(E)/R^{1/2}(E)$, where $P_{q+1}(E)$ is a polynomial of degree $q+1$. From the fact that at $E^2=T^2$ we have $\Lambda^2=-1$ and $p=\pi/2N+2\pi m/N$ it follows that $i\delta p(E^2=T^2)=0$. Therefore, ultimately,

$$i\delta p=(E^2-T^2)P_{q-1}(E)/R^{1/2}(E), \qquad (26)$$

where the polynomial $P_{q-1}(E)$ of degree $q-1$ is linear in the variations δt_n.

That the statement $i\delta p(E^2=T^2)=0$ is correct can also be verified in the following manner. We note for this purpose that an equation similar to (25) can be obtained if (5a) is rewritten in the form

$$C_n\psi_{n+1}^++C_{n-1}\psi_{n-1}^++V_n\psi_n=E\psi_n,$$

$$C_n=t_n^{-1}, \qquad V_n=-(E^2-T^2)(E^2-4T^2)/2t_{n-1}^2,$$

$$E=-(E^2-T^2)/2.$$

After transformations similar to those used to derive (25) we get

$$C_{N-1}(\varphi_N^{'+}\varphi_{N-1}^+-\varphi_N^+\varphi_{N-1}^{'+})\,i\delta pN=\sum_{n=0}^{N-1}\delta C_n(\varphi_{n+1}^{'+}\varphi_n^+$$

$$+\varphi_n^{'+}\varphi_{n+1}^+)+\sum_{n=0}^{N-1}\delta V_n\varphi_n^{'+}\varphi_n^+.$$

Substituting at $E = \pm T$ the solution in the form (21b) and (19) we find that the right-hand side of the expression vanishes but the coefficient of δp in the left-hand side does not, hence $i\delta p \propto (E^2 - T^2)$.

From (25) at $E = 0$ or $E^2 = 3T^2$ it follows that on the lower sheet

$$i\delta p\,(E=0) = i\delta p\,(E^2 = 3T^2) = \delta I_0. \tag{27}$$

The same equations can be obtained by varying (23) and (24). The polynomial $P_{q-1}(E)$ in (26) is given by

$$P_{q-1}(E) = \sum_{j=0}^{q-1} l_j E^{q-1-j}, \quad j \text{ — are even.} \tag{28}$$

Expanding (26) as $E \to \infty$ on the upper sheet and comparing with (14) we obtain the connection between the coefficients l_i and the variations δI_i:

$$l_i = \sum_{j=0}^{i} \alpha_{ij}\delta I_j, \quad i, j \text{ — are even,} \quad \alpha_{jj} = -1. \tag{29}$$

We write down the first few coefficients:

$$l_0 = -\delta I_0, \quad l_2 = -\delta I_2 + \delta I_0(s/2 - 1),$$
$$l_4 = -\delta I_4 + (s/2 - 1)\delta I_2 + \delta I_0(r/4 - s^2/8 + s/2 - 1) \tag{30}$$

(here and below $T = 1$). It follows from (14) and (29) that not more than $(q + 1)/2$ of the differentials δI_k are linearly independent. In fact, since the δI_k are linear combinations of the l_i, which in turn are linear combinations of δi_j, $0 \leq j \leq q - 1$, it follows that δI_k are also linear in δI_j. It turns out that not all of these $(q + 1)/2$ differentials are linearly independent, in contrast to the case of Ref. 8. Substituting Eqs. (27)–(29) in (26), we obtain two linear equations that relate $(q + 1)/2$ differentials δI_k. Consequently, not more than $(q - 3)/2$ differentials δI_k are independent.

4. We turn now to Eq. (5a). The Wronskian of this equation is

$$W_n = (\varphi_{n+1}\psi_n - \varphi_n\psi_{n+1})/t_n, \tag{31}$$

where φ_n and ψ_n are two solutions of (5a). It is easily seen that W_n does not depend on n. We use here the basis $c_n(E)$, $s_n(E)$, where

$$c_0 = 1, \quad c_1 = 0; \quad s_0 = 0, \quad s_1 = 1. \tag{32}$$

We normalize the Bloch function $\psi_n^\pm$ to the condition $\psi_0 = 1$. Following the procedure of Ref. 12, we introduce the following notation:

$$\psi_n^\pm = \exp\sum_0^{n-1}\Delta_n, \quad \chi_n(E) = \exp\Delta_n. \tag{33}$$

From (5a) we get the equation

$$\exp(-\Delta_{n-1})/t_{n-1} + \exp(\Delta_n)/t_n$$
$$= -\tfrac{1}{2}(E^2 - 1)[1 - (E^2 - 4)/t_{n-1}^2]. \tag{34}$$

In the allowed bands we obtain from (34)

$$\chi = \operatorname{Re}\chi + i\operatorname{Im}\chi, \quad \psi^+ = \psi^{-*},$$
$$\chi = \chi^+ = \chi^{-*}, \quad \Delta_n = \operatorname{Re}\Delta_n + i\operatorname{Im}\Delta_n,$$
$$\exp(2\operatorname{Re}\Delta_n) = t_{n+1}\operatorname{Im}\chi_n/t_n\operatorname{Im}\chi_{n+1}. \tag{35}$$

From (35) it follows that (in allowed bands)

$$\psi_n^\pm = \left(\frac{t_n\operatorname{Im}\chi_0}{t_0\operatorname{Im}\chi_n}\right)^{1/2}\exp\left(i\sum_0^{n-1}\operatorname{Im}\Delta_n\right). \tag{36}$$

From the definition (31) of the Wronskian it follows that

$$W(\psi^+, \psi^-) = 2it_0^{-1}\operatorname{Im}\chi(n_0, E), \quad \psi^\pm = c + \chi(n_0, E)s. \tag{37}$$

The function $\chi(n, E)$ is expressed in terms of the translation-matrix coefficients:

$$\operatorname{Im}\chi(n, E) = \frac{1}{\alpha_{21}}[1 - (\operatorname{Sp}\hat{T}_1)^2/4]^{1/2}, \quad \hat{T}_1 = \begin{pmatrix} \alpha_{11} & \alpha_{12} \\ \alpha_{21} & \alpha_{22} \end{pmatrix}. \tag{38}$$

From (34) we readily obtain the asymptotic form of $\chi^\pm$ and W as $E \to \infty$ on the two sheets of the Riemann surface Γ:

$$\chi_n^+ \to E^4 t_n/2t_{n-1}^2, \quad \chi_n^- \to 2t_n/E^4, \quad W \to E^4/2t_{N-1}^2. \tag{39}$$

From (39) we easily obtain

$$2Wt_{N-1}^2 = R^{1/2}(E)\bigg/\prod_{j=1}^{(q-3)/2}(E^2 - \gamma_j(0)). \tag{40}$$

In the allowed bands it follows from (37) and (40) that

$$\operatorname{Im}\chi(0, E) = t_0 R^{1/2}(E)/4t_{N-1}^2\Pi(E^2 - \gamma_j(0)). \tag{41}$$

Comparing with Eqs. (35), which are valid inside the allowed bands, we obtain the formula

$$\chi_i^\pm(n, E) = t_n[R^{1/2} + (R + 16\Pi_n\Pi_{n+1}t_{n-1}^2)^{1/2}]/4t_{n-1}^2\Pi_n,$$
$$\Pi_n = \prod_{i=1}^{(q-3)/2}[E^2 - \gamma_i(n)]. \tag{42}$$

Using (42), we obtain from (36) for the function $\psi^\pm$

$$\psi_n^\pm = \frac{t_{n-1}}{t_{N-1}}\left(\frac{\Pi_n}{\Pi_0}\right)^{1/2}\exp\left(i\sum_0^{n-1}\operatorname{Im}\Delta_n\right). \tag{43}$$

From the fact that the quantity $\chi^\pm$ from (42) is algebraic on the Γ surface, it follows that the sum in the radicand should be a perfect square of some polynomial of degree $q + 1$:

$$R + 16\Pi_n\Pi_{n+1}t_{n-1} = \prod_{k=1}^{(q+1)/2}(E^2 - \alpha_k^2(n))^2. \tag{44}$$

From (44) follows a complete set of relations of the form

$$\gamma_i(n+1) = f_i(\gamma_1(n), \ldots, \gamma_{(q-3)/2}(n)),$$
$$t_{n-1} = t_{n-1}(\gamma_1(n), \ldots, \gamma_{(q-3)/2}(n)). \tag{45}$$

From (34) we get the asymptotic form of χ_n^+ as $E \to \infty$:

$$\chi_n^+ = \frac{E^4 t^n}{2t_{n-1}^2}\left(1 - \frac{5 + t_{n-1}}{E^2} + \frac{4 + t_{n-1}}{E^4} - \frac{4t_{n-2}^2}{E^8} + \ldots\right). \tag{46}$$

Comparing (46) with the (42), we can obtain the expressions usually called the trace identities:

$$5 + t_{n-1}^2 = \frac{1}{2}\sum_1^{q+1} E_i^2 - \sum\gamma_k(n), \tag{47}$$

$$4 + t_{n-1}^2 = -\frac{1}{8}\sum E_i^4 + \frac{1}{4}\sum_{i>j}E_i^2 E_j^2$$

$$-\frac{1}{2}\sum E_i{}^2 \sum \gamma_k + \sum \gamma_i{}^2 + \sum_{i>j} \gamma_i \gamma_j, \tag{48}$$

$$-\frac{1}{16}\sum E_i{}^6 + \frac{1}{16}\sum_{i\neq j} E_i{}^2 E_j{}^4$$

$$-\frac{1}{8}\sum E_i{}^4 \sum \gamma_i + \frac{1}{4}\sum_{i>j} E_i{}^2 E_j{}^4 \sum \gamma_k$$

$$-\frac{1}{2}\sum E_i{}^2 \sum \gamma_k{}^2 + \sum \gamma_k{}^3$$

$$-\frac{1}{2}\sum E_i{}^2 \sum_{k>m} \gamma_k \gamma_m + \sum_{k\neq m} \gamma_k \gamma_m{}^2 = 0. \tag{49}$$

5. We apply now the foregoing mathematical results to the problem of determining the ground state of the model. The system-energy functional is

$$W = \sum_{E<\mu} E + W_{ph}, \qquad W_{ph} = \varkappa \sum t_i{}^2, \tag{50}$$

where W_{ph} is the lattice deformation energy and μ is the chemical potential of the electrons. It is easily seen that apart from a constant the deformation energy can be represented in the form $W_{ph} = \varkappa I_2 N$. We consider first the case of homogeneous deformation $t_i = t = $ const. Solving Eq. (2), we obtain the spectrum of the system

$$E^2(p) = \frac{1}{2}(5+t^2) \pm \frac{1}{2}[(t^2+3)^2 + 16t\cos p]^{1/2}. \tag{51}$$

From (51) we obtain expressions for the variation of the momentum and its derivative

$$i\delta p = (E^2-1)(E^2-4+t^2)R^{-1/2}(E)t^{-1}\delta t, \tag{52}$$

$$idp/dE = 4[E^3 - \frac{1}{2}(5+t^2)E]R^{-1/2}(E). \tag{53}$$

Varying the functional (50) with respect to t, we obtain with the aid of (52) the self-consistency condition

$$\varkappa = \frac{i}{\pi}\int_{E<\mu} (E^2-1)(E^2-4+t^2)R^{-1/2}(E)t^{-2}\,dE. \tag{54}$$

In the ground state (Fig. 2), the spectrum has three forbidden and four allowed bands. The two lower allowed bands are completely occupied, and the two upper ones are empty, so that the number of electrons per benzene molecule is $\rho = 6$. The end points $\pm E_A$, $\pm E_B$, $\pm E_c$, $\pm E_D$ of the spectrum are determined from (51) at $p = 0$ and π. The occupation number ρ can be varied by doping.[5-7] Let us find the ground state for arbitrary ρ. We seek the solution in the form
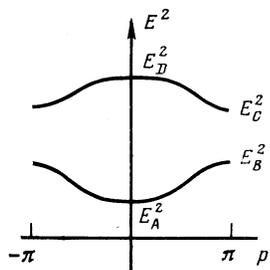

FIG. 2

of a finite-band potential that contains q forbidden bands of finite size in the spectrum. As already seen, the bands will be symmetric about the level $E = 0$. We note that since the level $E = 0$ is always in the forbidden band, q is odd. The extremum condition for the functional is

$$0 = \delta W = -\frac{2}{\pi}\int_{E<\mu} \delta p(E)\,dE + \varkappa \delta I_2. \tag{55}$$

For the variation δp we obtain, substituting (28) in (26) and using (27),

$$i\delta p = (E^2-1)R^{-1/2}(E)\left[l_0(E^{q-1} \right.$$
$$- (3^{(q-3)/2} + \frac{1}{3}R_0 + \frac{1}{6}R_3)E^2 + R_0)$$
$$\left. + \sum_{k=1}^{(q-5)/2} l_{2k}(E^{q-1-2k} - 3^{(q-3-2k)/2}E^2) \right], \tag{56}$$

$$R_0 = R^{1/2}(0), \qquad R_3 = R^{1/2}(3^{1/2}).$$

With the aid of the equations in (30) we obtain expressions for δI_2 in terms of l_0 and l_2:

$$\delta I_2 = -l_2 - l_0(s/2 - 1). \tag{57}$$

Substituting (56) and (57) in (55) and equating to zero the coefficients of the independent variations of l_j, we obtain the following self-consistency conditions:

$$\frac{2i}{\pi}\int_{E<\mu} R^{-1/2}(E^2-1)(E^2-3)E^{2k}\,dE = 0, \quad k=1,\dots,(q-7)/2, \tag{58}$$

$$\frac{2i}{\pi}\int_{E<\mu} R^{-1/2}(E^2-1)(E^{q-3} - 3^{(q-5)/2}E^2)\,dE = \varkappa, \tag{59}$$

$$\frac{2i}{\pi}\int_{E<\mu} \frac{(E^2-1)}{R^{1/2}}\left[E^{q-1} - \left(3^{(q-3)/2} + \frac{1}{3}R_0 + \frac{1}{6}R_3\right)\right.$$
$$\left. \times E^2 + R_0\right]dE = \left(\frac{s}{2} - 1\right)\varkappa. \tag{60}$$

It can be shown in analogy with Ref. 8 that Eqs. (48) have no solutions at $q > 11$.

The algebraic equations (58)–(60) are valid at $q > 3$. For the case $q = 3$ the conditions (27) give two equations for the two unknowns l_0 and l_2. The condition for their compatibility is

$$6 + R_3 + 2R_0 = 0. \tag{61}$$

The self-consistency condition for $q = 3$ is

$$\frac{2i}{\pi}\int_{E<\mu} (E^2-1)(E^2+R_0)R^{-1/2}\,dE = \left(\frac{s}{2} - 1 + R_0\right)\varkappa. \tag{62}$$

Equations (13) take for the case $q = 3$ the form

$$\frac{2}{\pi}\int_{E_A}^{E_B} dp = \frac{2}{\pi}\int_{E_C}^{E_D} dp = 2. \tag{63}$$

From (23), (24) and (61)–(63) we determine uniquely the spectrum of the system. It is easy to verify that all these equations are satisfied by the solution (51) that corresponds to the homogeneous state $t_i = t = $ const. For $\rho \neq 6$ we seek the solution of the system (58)–(60). From (47)–(49) we can find that

at $q = 5, 7$, and 9 there is no solution $t_i \neq$ const, consequently the only possibility is the case $q = 11$. Equations (58)–(60) take at $q = 11$ the form

$$\frac{2i}{\pi} \int_{E<\mu} R^{-1/2} (E^2-1)(E^2-3)E^2 \, dE$$

$$= \frac{2i}{\pi} \int_{E<\mu} R^{-1/2}(E^2-1)(E^2-3)E^4 \, dE = 0, \qquad (64)$$

$$\frac{2i}{\pi} \int_{E<\mu} R^{-1/2}(E^2-1)(E^2-3)E^6 \, dE = \varkappa, \qquad (65)$$

$$\frac{2i}{\pi} \int_{E<\mu} R^{-1/2}(E^2-1)(E^2-3)E^8$$

$$- \frac{2i}{\pi} \int_{E<\mu} R^{-1/2}\left[\left(\frac{1}{3}R_0 + \frac{1}{6}R_3\right)E^2 - R_0\right]dE$$

$$= \left(\frac{s}{2} - 4\right)\varkappa, \qquad (66)$$

where

$$R(E) = \prod_{k=1}^{12}(E^2 - E_k^2).$$

The derivative dp/dE is obtained from the system (12). To determine the 12 values of E_k we need 12 self-consistency conditions. Four of them are Eqs. (64)–(66). The remaining conditions are:

$$\frac{2}{\pi}\int_{E_1}^{E_2} dp = \frac{2}{\pi}\int_{E_3}^{E_4} dp = \frac{2}{\pi}\int_{E_5}^{E_6} dp = \frac{|\rho-6|}{3a},$$

$$\frac{2}{\pi}\int_{E_{11}}^{E_{12}} dp = \frac{|\rho-6|}{a}, \qquad (67)$$

$$\frac{2}{\pi}\int_{E_1}^{E_3} dp = \frac{2}{\pi}\int_{E_8}^{E_{12}} dp, \qquad (68)$$

where a is the period of the chain of benzene rings. Equation (68) is similar to (63) for the case $q = 3$. It follows from the fact that $\delta p = 0$ at $E = \pm T$ that $P(\pm)$ is a constant independent of t_i. Since in the homogeneous case when t_i is constant it follows from (51) that $p(\pm 1) = \pi/2$, we can state that the following equality always holds (on the lower sheet)

$$p(E^2 = 1) = \pi/2. \qquad (69)$$

We have thus obtained 12 equations for the determination of the end points of the spectra, see Eqs. (64)–(69), (23), and (24). Plots of $E(p)$ are shown in Fig. 3. The bands occupied in the ground states are those with energy $E \leqslant E_6$ at $\rho > 6$ and $E \leqslant -E_6$ at $\rho < 6$. It is impossible to obtain an explicit expression for the quantities $E_i(\varkappa, \rho)$ in the general case, except at $\rho = 6$. Assuming $T = 2.5$ eV and $2E_A \approx 3.5$ eV (the optical gap observed in polyphenylene), we find that $\varkappa \approx 0.4$ and $t = 0.5T$. When an even number of electrons or holes is added to a system with $\rho = 6$, self-trapped states are pro-
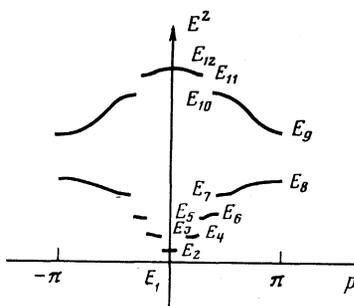

FIG. 3

duced, containing six particles (electrons or holes) each located at three different levels: $E_1 < |E| < E_2$, $E_3 < |E| < E_4$, $E_5 < |E| < E_6$.

Assuming that the produced self-trapped state is not deep and that the local electron levels are not very distant from the forbidden bands, we shall attempt to find the position of the local level E and the energy for a bipolaron, by linearizing Eq. (5a). We express (5a) as

$$c_n\psi_{n-1} + c_{n+1}\psi_{n+1} + v_n\psi_n = 0, \qquad (70)$$

$$c_n = t_{n-1}^{-1}, \qquad v_n = \tfrac{1}{2}(E^2-1)[1-(E^2-4)c_n^2].$$

We rewrite c_n, v_n, and ψ_n in the form

$$c_n = c_0 + \delta c_n, \qquad c_0 = t^{-1} = 2,$$

$$v_n = v(E_A, c_0) + \frac{\partial v}{\partial E}\delta E + \frac{\partial v}{\partial c_n}\delta c_n, \qquad (71)$$

$$\psi_{n\pm 1} = \psi_n \pm \psi_n' + \psi_n''/2.$$

Substituting the equations of (71) in (70) we get the equation

$$-\frac{\psi''}{2\cdot 3} + \frac{\delta c_n}{7.5}\psi = \delta E\psi. \qquad (72)$$

The energy of the system takes in the same approximation the form

$$W = \frac{1}{2}K\sum_n(\delta c_n)^2 + 2E_A + 2\delta E, \qquad (73)$$

where

$$K = \partial^2 W(c_i = c_0)/\partial c^2 = 0{,}013.$$

From the condition $\delta W/\delta(\delta c_n) = 0$ and (72), (73) we obtain a nonlinear Schrödinger equation

$$-\frac{\psi''}{2\cdot 3} - \frac{2}{K(7.5)^2}|\psi|^2\psi = \delta E\psi, \qquad (74)$$

from which it follows that the energy of the localized level $\delta E \approx 1$, i.e., our assumption that the local level is shallow turned out to be incorrect. We must thus expect in this case strong self-trapping of the electron and appearance of symmetrically arranged levels in the interior of the forbidden band $(-E_A < E < E_A)$.

6. We obtain now an explicit expression for the wavefunction component φ_n^+ and for the deformation t_n. The component φ_n^- is easily expressed in terms of φ_n^+ with the aid of Eq. (4):

$$\varphi_n^- = \frac{(E^2-1)(E^2-4)}{E(3-E^2)}\frac{\varphi_{n+1}^+}{t_n} - \frac{2\varphi_n^+}{E(3-E^2)}. \qquad (75)$$

At $E = 0$, $\pm 3^{1/2}$ the function φ_n^- has poles, but φ_n^+ does not. In addition, it was found in Sec. 4 that the function φ_n^+ has poles in $q - 3$ forbidden bands, one in each band, and zeros in the same bands. In the forbidden bands that contain the points $E = 0$, $\pm 3^{1/2}$ the function φ_n^+ has neither zeros nor poles. It can be assumed that in these bands the zeros and the poles of the function φ_n^+ coincide. The fact that the functions φ_n^+ have no singularities in certain bands imposes restrictions on the form of the spectrum [see Eqs. (23) and (24)]. At infinity, the function takes the form (17). Thus, the Bloch function $\varphi_n^+(P)$ is a meromorphic function of the point P on the surface Γ. A general expression for the function of the Baker-Akhiezer type was obtained in Ref. 13 and elsewhere.

We shall use below the results of Ref. 14. For convenience, we renumber here the energy levels as follows: $-E_{q+1} = e_1$, $-E_q = e_2$, ..., $E_{q+1} = e_{2q+2}$. Let the function φ_n^+ have poles at the points $\gamma_1, \gamma_2, ..., \gamma_q$; with $\gamma_{(q+1)/2} = 0$, $\gamma_i = -\gamma_{q+1-i}$, $\gamma_{i_0} = 3^{1/2}$ for a certain number i_0.

Let Ω_j be holomorphic differentials on Γ:

$$\Omega_j = \sum_{j=0}^{q-1} d_{ij} E^j R^{-1/2}(E)\, dE,$$

such that

$$2 \int_{e_{2j}}^{e_{2j+1}} \Omega_i = -\delta_{ij}.$$

The matrix B is defined by the equality

$$B_{ik} = \frac{1}{2} \int_{e_1}^{e_{2i}} \Omega_k,$$

It is known that it is symmetric and has a positive-definite imaginary part. Using Ref. 14, we obtain an expression for the wave function

$$\varphi_n^+(P) = r_n \exp\left(ni \int_{e_1}^{P} dp \right) \frac{\theta(A(P) + 4nU - z)}{\theta(A(P) - z)}, \quad (76)$$

where r_n is a constant,

$$A_k(P) = \int_{e_1}^{P} \Omega_k, \quad Z_k = \sum_{j=1}^{q} \int_{e_{2j}}^{\gamma_j} \Omega_k + \frac{k}{2},$$

$$U_k = \frac{1}{4\pi} \int_{e_1}^{e_{2k}} dp, \quad 0 < \ldots < U_k < U_{k+1} < \ldots < 1.$$

The theta-function in (76) is defined, as in Ref. 14, by

$$\theta(u_1, \ldots, u_q) = \sum_{k \in Z^q} \exp\{\pi i (Bk, k) + 2(k, u)\},$$

$$(k, u) = k_1 u_1 + \ldots + k_q u_q.$$

In the vicinity of an infinitely remote point on the upper sheet of Γ we have

$$\exp\left(i \int_{e_1}^{E} dp \right) = E^k e^{-I_0}[1 + O(E^{-2})].$$

Comparing the expansion of φ_n^+ in transforms of infinitely remote points $\pm z_0$

$$z_{0k} = \int_{e_1}^{\infty} \Omega_k$$

with the expansion (13), we get

$$\frac{e^{2I_0 n}}{(2T^3)^{2n} t_{n-2}^2 \ldots t_0^2 (t_{N-1})^2} = \frac{\theta(z_0 + 4nU - z)\, \theta(-z_0 - z)}{\theta(-z_0 + 4nU - z)\, \theta(z_0 - z)}.$$

We ultimately have for t_n

$$t_n^2 = \frac{e^{2I_0}\theta(z_0 + 4(n+1)U - z)\,\theta(-z_0 + 4(n+2)U - z)}{4\theta(z_0 + 4(n+2)U - z)\,\theta(-z_0 + 4(n+1)U - z)} \quad (77)$$

It follows from the Riemann bilinear relations[13] that

$$2z_0 = -U.$$

CONCLUSION

We have investigated here a realistic discrete model proposed for the description of the conducting polymer polyphenylene. It was shown that this model admits of an exact solution that yields the distribution of the deformation, the wave functions, and the spectrum of the electron state at an arbitrary electron density ρ per molecule. In the case of neutral occupation ($\rho = 6$) we obtained the explicit expression (5.1) for the dependence of the energy on the momentum. The spectrum of the system has four allowed and three forbidden bands. Corresponding to this case is a homogeneous deformation $t_n = \text{const}$. At an arbitrary occupation number $\rho \neq 6$, which corresponds to the doped state, we have shown that the system energy functional has a minimum in the class of finite-band potentials. The self-consistency conditions that determine the spectrum were written out and a general expression (77) was obtained for the deformation t_n. The spectrum of the electron states contains 12 allowed and 11 forbidden bands; the band edges are determined by the conditions (23), (24), and (64)–(69). At low density of the additional particles, $\rho - 6 \ll 1$, the system is a periodic series of self-trapped electron states, each of which contains six electrons or holes that occupy three different levels located in the interior of the central forbidden band.

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