An exact solution of the Peierls model with an arbitrary number of electrons in the unit cell

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The electron spectrum and the static lattice deformations for an arbitrary number of electrons in a unit cell in the metallic phase are determined exactly in a self-consistent-field approximation for a one-dimensional Peierls system in the continuous model.

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1. The properties of the dielectric phase of quasi-one-dimensional systems depend essentially on the number of electrons ρ in the unit cell in the metallic phase. For materials in which the gap Δ in the electron spectrum is caused by static lattice deformations (polyacetylene, KSR family) the transition from the Peierls state at $\rho = 1$ to the Peierls-Fröhlich state $|\rho - 1| \ll 1$ is determined by a decreasing role of the transfer process. Theoretically, this transition was analyzed by using numerical methods,[1] in the linear-response approximation,[2] and on the basis of the phenomenological model.[3] An interest in the properties of the Peierls system with $(\rho - 1) \ll 1$ has arisen recently in connection with experiments involving polyacetylene alloying.

In this paper we shall give an exact solution of the Peierls problem, which is constrained only by the condition $|\rho - 1| \ll 1$, in view of linearization of the electron dispersion law and continuity of the model. We show that all the properties of the system are continuous in ρ, except for the point $\rho = 1$. The gap in the electron spectrum remains finite and its dependence on ρ represents an increase of the coupling constant λ as a result of transition through the region of concentrations $n = |\rho - 1|/a \sim \Delta / v_F$ (a is the lattice constant and v_F is the Fermi velocity) in view of inclusion of the transfer processes at $\rho \approx 1$. There are two symmetrical forbidden bands that combine at $\rho = 1$. The average allowed band of width $E_0(\rho) \to 0$ when $\rho \to 1$ and $E_0(\rho) \sim \epsilon_F$ when $|\rho - 1| \sim 1$ is either completely filled ($\rho > 1$) or is empty ($\rho < 1$). The long-wave part of the lattice-deformation potential $\phi(x) = \Delta(x)\sin(\pi/a)x$ at $n \ll \Delta / v_F$ has the form of a domain structure whose origin is explained in the conclusion of the paper by one of the authors[6] in view of the polaron effect[5] and the result of Ref. 2. At $n \gg \Delta / v_F$ $\Delta(x) \approx \Delta_0 \sin[(2p_F - \pi/a)(x - x_0)]$, which corresponds to the Fröhlich limit (x_0 is an arbitrary constant). At $\rho \to 1$ each domain wall carries a single-electron charge, in accordance with the results of Ref. 6. At $|\rho - 1| \sim 1$ the oscillations of the electron density are $v(x) \sim \Delta / \epsilon_F$. These results are in qualitative agreement with the results of the calculations,[1] but the model[3] is found to be inadequate for the Peierls system. We also determined the dependence of the ground-state energy $W(\rho)$ and the effective masses at the edges of the bands.

2. We write the wave functions of electrons $\psi_\mu(x)$ in the field of static deformations in the form

$$\psi_\mu(x) = U_\mu(x)\cos(\pi x/a) + iV_\mu(x)\sin(\pi x/a).$$

The case $\Delta(x) = \Delta_1 = \text{const}$ corresponds to doubling of the period $\rho = 1$. The energy functional of the system $W\{\Delta, U_\mu, V_\mu\}$ has the form[6] (henceforth, $v_F = 1$ and $f' = df/dx$):

$$W\{\Delta, U_\mu, V_\mu\} = \int dx \left\{ \frac{\Delta^2}{g^2} + \sum_{E_\mu < \zeta} \left[-i\left(U_\mu^* V_\mu' + V_\mu^* U_\mu'\right) + i\Delta\left(V_\mu^* U_\mu - U_\mu^* V_\mu\right)\right]\right\}, \tag{1}$$

where the energy levels E_μ and the chemical potential ζ are measured from the center of the metallic phase. The Dirac-type equations for U and V follow from Eq. (1)

$$U' - \Delta U = iEV; \quad V' + \Delta V = iEU \tag{2}$$

or

$$U'' + [E^2 - P(x)]U = 0; \quad V'' + [E^2 - Q(x)]V = 0; \quad P(x) = \Delta' + \Delta^2;$$
$$Q(x) = -\Delta' + \Delta^2 \tag{3}$$

and the self-consistency condition

$$\frac{\Delta}{g^2} = \frac{1}{2i}\sum_{E_\mu < \zeta}\left(U_\mu^* V_\mu - V_\mu^* U_\mu\right) = -\sum_{E_\mu < \zeta}\frac{1}{E_\mu}\left(\Delta + \frac{1}{2}\frac{d}{dx}\right)V_\mu^* V_\mu. \tag{4}$$

In contrast to Refs. 5–7, we must seek a periodic solution of Eqs. (1)–(4), rather than an isolated solution. The solution can be simplified by using the method of Fateev *et al.*,[8] according to which the extremum (1), which has only a translation degeneracy, satisfied the equations

$$\Delta''' - 6\Delta^2\Delta' + A\Delta' = 0; \quad P''' - 6PP' + AP' = 0; \quad Q''' - 6QQ' + AQ' = 0. \tag{5}$$

A is an arbitrary parameter that defines the solution. Selecting $A = \Delta_k^2(1 + k^{-2})$, we obtain

$$\Delta(x) = \Delta_k\,\mathrm{sn}(\xi, k); \quad \xi = x\Delta_k/k; \quad k = k(\rho). \tag{6}$$

We write $P(x) = \Delta_k^2 p(\xi)$ and $Q(x) = \Delta_k^2 q(\xi)$. The $\Delta(\xi)$, $p(\xi)$, and $q(\xi)$ functions have a period $4\mathbf{K}(k)$, where $\mathbf{K}(k)$ is a complete, first-order elliptic integral. According to Ref. 9, the spectrum (3), because of Eq. (5), has only one forbidden band $E^2 = \Delta_k^2\epsilon^2$; $\epsilon_-^2 < \epsilon^2 < \epsilon_+^2$. The solution of Eqs. (2) with potential (6), which reduces to the Lamé functions, can be determined by numerical quadrature. In the notations $U(x) = (\Delta_k/2kL)^{1/2}u(\xi)$; $V(x) = (\Delta_k/2kL)^{1/2}v(\xi)$ (L is the length of the system) we obtain the normalized solution

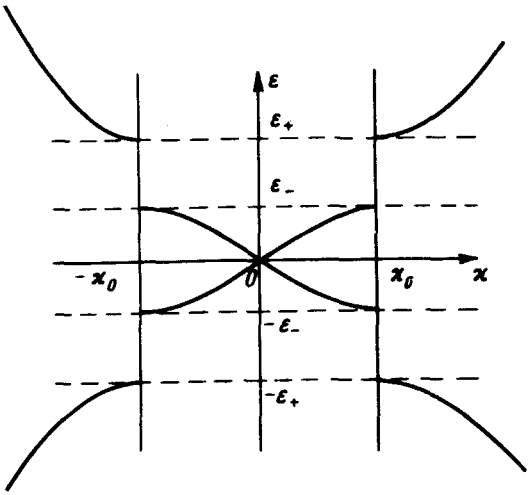

FIG. 1.

$$u(\xi) = [(p(\xi) + b)/(\bar{p} + b)]^{1/2} \exp\left\{ic \int_0^{\xi} \frac{d\eta}{p(\eta) + b}\right\} \tag{7}$$

in with $p(\xi)$ is replaced by $q(\xi)$ for $v(\xi)$. In the solution of Eq. (7)

$$b = b(\epsilon) = 2\epsilon^2 - 2^{-1}(1 + k^{-2}); \; c = c(\epsilon) = \pm\epsilon[(\epsilon^2 - \epsilon_+^2)(\epsilon^2 - \epsilon_-^2)]^{1/2},$$

$\epsilon_\pm = 2^{-1}(k^{-1} \pm 1)$ are the boundaries of the allowed bands, $-\epsilon_- < \epsilon < \epsilon_+$, and $|\epsilon| > \epsilon_+$ (Fig. 1)

$$\bar{p} = \overline{\delta^2}(k) = \frac{1}{4\mathbf{K}} \int_0^{4\mathbf{K}} \mathrm{sn}^2(\xi)\, d\xi = k^{-2}(1 - \mathbf{E}/\mathbf{K}),$$

where $\mathbf{E}(k)$ is a complete, second-order elliptic integral, $\overline{\delta^2(1)} = 1$, and $\overline{\delta^2(0)} = 1/2$.

The wave functions (7) are characterized by the wave vector $\kappa = \kappa(\epsilon)$, which determines the number of states in the thermodynamic limit

$$\sum_{\epsilon} = L \frac{\Delta_k}{k} 2 \int \frac{d\kappa}{2\pi}. \tag{8}$$

It follows from Eq. (7) that

$$\kappa(\epsilon) = (1/2\mathbf{K}\gamma^{1/2})[\mathbf{K} + (\gamma b - 1)\Pi(-\gamma, k)], \tag{9}$$

where $\gamma = \gamma(\epsilon) = \epsilon^2/(\epsilon^2 - \epsilon_+^2)(\epsilon^2 - \epsilon_-^2)$ and $\Pi(-\gamma, k)$ is a complete Schröder elliptic integral. The $\epsilon(\kappa)$ dependence is shown in Fig. 1. The extrema of the bands are

attained at

$$\kappa = \pm\kappa(k) = \pm(4k)^{-1} = \pm\frac{k}{\Delta_k}\left|\frac{\pi}{2a} - p_F\right|.$$

According to Eq. (8), the two branches of the central band contain $N = L/l$, $l = 4k\mathbf{K}/\Delta_k$ states each, where l is the period of the structure $\Delta(x)$. Thus, the parameters of the dielectric phase are related to the concentration of additional (or missing) electrons n for $\rho = 1$ by the relation

$$n = |\rho - 1|/a = \Delta_k/2k\mathbf{K}. \tag{10}$$

At $\rho < 1$ the central band must be empty and at $\rho > 1$ it must be filled. Because of symmetry, the total energy of the central band is equal to zero, i.e., the k and Δ_k parameters are independent of the sign of $\rho - 1$. Therefore, we shall examine below the case $\rho < 1$.

3. The self-consistent condition (4), after substituting (7) with allowance for (5), is satisfied identically in x, if the equation for the parameters is satisfied

$$\sum_{\epsilon_F k/\Delta_k < \epsilon < -\epsilon_+} \frac{-\epsilon}{b(\epsilon) + \overline{\delta^2}} = \frac{1}{g^2} = \frac{1}{\pi}\int_1^{\epsilon_F/\Delta_1} \frac{d\kappa}{(\epsilon^2 - 1)^{1/2}}, \tag{11}$$

where $2\Delta_1 = \epsilon_F \exp(-1/\lambda)$, $\lambda = g^2/\pi v_F$ is the gap in the Peierls state with $\rho = 1$, $(k = 1)$. It follows from Eq. (11) that with an accuracy of $\sim\Delta/\epsilon_F$ the gap $\Delta_k = \Delta_1 f(k)$ is evidently independent of the cutoff parameter ϵ_F and of λ.

Instead of calculating Eq. (11), it is more convenient to determine the additional energy $W(k,\Delta_k)$ with respect to the metallic phase with the same number of particles and to minimize it for the given n (10). The $k(n)$ dependence can be determined from the condition $(\partial W/\partial k)_n = 0$. Thus, we obtain

$$\Delta_k = k^{1/2}\Delta_1 = \frac{1}{2\mathbf{K}}\frac{\Delta_1}{n}; \quad k^{1/2}\mathbf{K} = \Delta_1/2n; \quad k = k(n)$$

$$L^{-1}W(n) = -\frac{2n^2}{\pi}\left[2\mathbf{K}(\mathbf{K} - \mathbf{E}) - \frac{1 + k^2}{2}\mathbf{K}^2 + \frac{\pi^2}{8}\right], \quad L^{-1}\frac{dW}{dn} = -\frac{4n}{\pi}$$

$$\times\left[\frac{1 - k^2}{2}\mathbf{K}^2 - \mathbf{E}\mathbf{K} + \frac{\pi^2}{8}\right],$$

In the limiting cases we have

$$n << \Delta_1, \quad k \approx 1, \ \Delta \approx \Delta_1; \quad W(n) = -\frac{1}{2\pi}\Delta_1^2 L + \frac{2}{\pi}\Delta_1 nL.$$

In the small-concentration limit the energy per particle $(2/\pi)\Delta_1$, as expected, coincides with the energy of the soliton.[6,7]

$$n >> \Delta_1,\ k \approx (\Delta_1/2\pi e n)^2,\ \Delta(n) \approx \Delta_1^2/2\pi e^2 n \approx \epsilon_F^2/n \exp(-2/\lambda).$$

We can see that, as a result of transition through the region $n \sim \Delta_1$, the coupling constant decreases by a factor of 2 and at $n \gg \Delta_1$ we have a pre-exponential dependence $\Delta(n) \sim n^{-1}$.

We note that the energy density $w(x)$, as in the case of an isolated soliton,[5,6] is rigorously homogeneous. After substitution,

$$w(x) = \frac{\Delta^2(x)}{g^2} + \sum_{E_\mu \leqslant -E_+} E_\mu (U_\mu^* U_\mu + V_\mu^* V_\mu) = \Delta^2(x) \left[\frac{1}{g^2} + \sum_{\epsilon_\mu \leqslant -\epsilon_+} \frac{\epsilon}{b(\epsilon) + \overline{\delta^2}} \right]$$

$$+ \frac{1}{L} \sum_{E_\mu \leqslant -E_+} E_\mu$$

the first term vanishes identically because of (11) and $w(x) = W/L$. The particle density $\nu(x)$ oscillates as follows:

$$\nu(x) - \overline{\nu} = \frac{2}{\pi} \frac{\Delta_k}{k} \int_{\epsilon_+}^{\infty} \frac{\delta^2(x) - \overline{\delta^2}}{b(\epsilon) + \overline{\delta^2}} d\epsilon$$

at $n \ll \Delta_1, (k \to 1), \nu(x) \approx (1/2)\Delta_1[\sin^2(\Delta_1 x/k) - 1]$, consistent with the charge distribution in the isolated solitons.[6] At

$$n \gg \Delta_1, (k \to 0), \nu(x) \approx [\Delta^2(n)/n] \cos\left[\left(4p_F - \frac{2\pi}{a}\right)x\right],$$

i.e., in the Fröhlich limit the oscillations have a period of the order of a and are small like $(\Delta/\epsilon_F)^2$.

The effective electron masses $M_\pm = m_\pm \Delta_k$ can be determined from Eq. (3) near the band edges by

$$\epsilon - \epsilon_\pm = \pm (|\kappa| - \kappa_0)^2 / 2k^2 m_\pm, \quad m_\pm = (1 \pm k\overline{\delta^2})^2 / 2(1 \pm k). \tag{12}$$

As $n \to 0$ we have $k \to 1$, $m_+ \to 1$, $m_- \to 2n^2/\Delta_1 E_0(n)$, where $E_0(n) = 8\Delta_1 \exp(-\Delta_1/n)$ is the width of the central band. At $n \gg \Delta_1$, $k \to 0$ and $m_\pm \to 1/2$, consistent with the Fröhlich limit.

The results of (7) and (12) allow us to determine the thresholds of optical absorption as a result of transitions between the edges of the different bands $\pm E_\pm$.

In conclusion, we note that the excited states of the examined system contain a gapless, optically active translation mode $\partial\Delta/\partial x_0$. We emphasize that the optical gap in the spectrum is finite and continuous in ρ except at the point $\rho = 1$, where it varies by a factor of 2. Metallization of the analyzed system, in contrast to the assumptions of Ref. 3, may occur due to Fröhlich conductivity.

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