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Abstract

We study disordered Peierls systems described by the fluctuating gap model. We show that the typical electron states with energies lying deep inside the pseudogap are localized near large disorder fluctuations (instantons), which have the form of a soliton–antisoliton pair. Using the "saddle-point" method we obtain the average density of states and the average optical absorption coefficient at small energy. © 1997 Elsevier Science B.V.

Disorder in quasi-one-dimensional conductors strongly affects the electron states, reducing the tendency of these materials to develop $2k_F$-instabilities, such as the Peierls instability [1]. Existing Peierls materials, like the conjugated polymer transpolyacetylene, are known to suffer from various kinds of disorder: conformational defects, cross-links, impurities, etc. (see for a review Ref. [2]). While in a perfect Peierls chain the single-electron spectrum has a gap, with a value related to the amplitude of the periodic chain distortion, in a disordered chain the gap is filled. At weak disorder, the density of disorder-induced states that occur inside the gap is small, leading to a pseudogap, while at large disorder the gap disappears entirely, and in the middle of the band the density may even diverge [3].

In this Letter, we find the typical form of the disorder-induced electron states lying close to the center of the pseudogap. In addition to giving new insight into these disordered systems, this result is useful, as it allows for a relatively easy calculation of disorder averages. As examples, we will explicitly calculate the average density of states and the average absorption coefficient at small energies.

It is crucial for our approach, that a large disorder fluctuation is required to create an electron state close to the center of the pseudogap, implying that the probability for such a state to occur is small at weak disorder. The main contribution to the density of states at small energy then comes from the disorder realizations close to one most probable fluctuation. The form of this fluctuation can be found consistently with the form of the wave function of the electron state induced inside the pseudogap. This wave function turns out to be localized in the vicinity of the disorder fluctuation. A similar situation is encountered when calculating the density of states of electrons moving in a random potential at large negative energies [4,5]. These states were found to be localized in regions where the dis-

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order potential has the form of a deep well.

The approximate calculation of disorder averages, valid when the dominant contribution comes from a small part of all possible disorder realizations, is closely related to the semiclassical approximation in quantum mechanics and field theory. In the path integral version of this approximation, the paths giving the largest contribution to the Green function lie close to the "saddle point" of the Euclidean action, called the instanton [6].

To describe the disordered Peierls chain we use the fluctuating gap model (FGM) [7]. This has previously been considered in the context of the thermodynamical properties of quasi-one-dimensional organic compounds (NMP-TCNQ, TTF-TCNQ) [3], and has been applied to the study of the effect of disorder on the Peierls transition [8], as well as the effect of quantum lattice fluctuations on the optical spectrum of Peierls materials [9–11]. In this model the electron motion is described by the one-dimensional Dirac equation,

$$\hbar\psi = \left(\sigma_3 \frac{v_F}{i} \frac{d}{dx} + \sigma_1 \Delta(x)\right)\psi(x) = \varepsilon\psi(x), \quad (1)$$

where σ_1 and σ_3 are the Pauli matrices, and

$$\psi(x) = \begin{pmatrix} \psi_R(x) \\ \psi_L(x) \end{pmatrix}$$

is the wave function of the single-electron state close to the Fermi energy $\varepsilon_F = 0$. The first term in the Hamiltonian $\hat{h}$ describes the free motion of the electrons and the two amplitudes $\psi_R(x)$ and $\psi_L(x)$ correspond to particles moving, respectively, to the right and to the left with the Fermi velocity v_F. The second term in the Hamiltonian describes the backward scattering of electrons from the lattice distortion wave, whose amplitude is proportional to $\Delta(x)$. Disorder is modelled by assuming $\Delta(x)$ to fluctuate randomly along the chain around some average value Δ_0,

$$\Delta(x) = \Delta_0 + \eta(x), \quad (2)$$

where $\eta(x)$ is the fluctuating part with a Gaussian correlator,

$$\langle\eta(x)\eta(y)\rangle = A\delta(x - y). \quad (3)$$

In the absence of disorder ($\Delta(x) = \Delta_0$), the electron spectrum has a gap between the energies $\varepsilon = -\Delta_0$

and $\varepsilon = +\Delta_0$. At nonzero disorder the average density of states lying close to the middle of the pseudogap ($|\varepsilon| \ll \Delta_0$) was found in Ref. [3] by means of the "phase formalism" [12],

$$\langle\rho(\varepsilon)\rangle \propto |\varepsilon|^{2/g-1}, \quad (4)$$

where $g = A/v_F\Delta_0$. We note that due to the charge conjugation symmetry (particle–hole symmetry) of the Dirac Hamiltonian $\hat{h}$, the density of states is a symmetric function of the energy $\langle\rho(-\varepsilon)\rangle = \langle\rho(\varepsilon)\rangle$, and in what follows we will assume ε to be positive.

From Eq. (4) it is clear that at weak disorder ($g \ll 1$) the density of states close to the middle of the pseudogap is strongly suppressed. As we mentioned above, the explanation for this is that a large fluctuation of $\Delta(x)$ is required in order to create an electron state with energy $\varepsilon \ll \Delta_0$. This motivates us to apply the "saddle-point" approach to study the typical electron states and to calculate disorder averages. The "saddle-point"disorder fluctuation (or instanton) $\bar{\eta}(x)$ is the least suppressed one among the required large fluctuations. It can be found by minimizing

$$\mathcal{A}[\eta(x)] = \frac{1}{2A}\int dx\,\eta^2(x) - \mu(\varepsilon_+[\eta(x)] - \varepsilon). \quad (5)$$

The first term in this equation describes the suppression of the probability of the fluctuation with the correlator, Eq. (3) (the weight $p[\eta(x)]$ of the disorder configuration is $\exp[-(1/2A)\int dx\,\eta^2(x)]$), while the second term stems from the condition that the energy $\varepsilon_+[\eta(x)]$ of the lowest positive energy single-electron state for the disorder realization $\eta(x)$ equals ε. The factor μ is a Lagrange multiplier. The minimization of $\mathcal{A}[\eta(x)]$ gives

$$\bar{\eta}(x) = \mu A\psi_+^\dagger(x)\sigma_1\psi_+(x), \quad (6)$$

where $\psi_+(x)$ is the wave function of the state with energy $\varepsilon_+[\bar{\eta}(x)]$.

It may be shown by inspection that the solution of Eq. (6) is a soliton–antisoliton pair configuration,

$$\bar{\eta}(x) = -v_F K\{\tanh[K(x - x_0 + \tfrac{1}{2}R)] \\ - \tanh[K(x - x_0 - \tfrac{1}{2}R)]\}, \quad (7)$$

where x_0 describes the position of the disorder fluctuation in the chain, R is the distance between the soliton and the antisoliton, and K is determined by

$$v_F K = \Delta_0 \tanh(KR). \qquad (8)$$

The instanton is shown in Fig. 1 by plotting $\Delta(x) = \Delta_0 + \bar{\eta}(x)$. The spectrum of electron states that occur for this $\Delta(x)$ has previously been considered [13,14] in relation with polarons in the Su–Schrieffer–Heeger model of conjugated polymers [15,16], and is depicted in Fig. 2. It consists of a valence band (with highest energy $-\Delta_0$), a conduction band (with lowest energy Δ_0), and two localized intragap states with energies $\pm\varepsilon_+(R)$, where

$$\varepsilon_+(R) = \frac{\Delta_0}{\cosh(KR)}. \qquad (9)$$

Thus, the soliton–antisoliton separation R is fixed by the condition $\varepsilon_+(R) = \varepsilon$. The two intragap states are the bonding and antibonding superpositions of the midgap states localized near the soliton and antisoliton,

$$\psi_{\pm R}(x) = \psi_{\pm L}^*(x)$$
$$= \sqrt{\frac{K}{8}} \left(\frac{e^{i\pi/4}}{\cosh[K(x - x_0 - \frac{1}{2}R)]} \right.$$
$$\left. \pm \frac{e^{-i\pi/4}}{\cosh[K(x - x_0 + \frac{1}{2}R)]} \right) \qquad (10)$$

$(\psi_{\pm}^{\dagger}(x)\psi_{\pm}(x)$ is schematically plotted in Fig. 1). The energy splitting 2ε decreases exponentially with the soliton–antisoliton separation, so that for $\varepsilon \ll \Delta_0$,

$$R \approx \xi_0 \ln \frac{2\Delta_0}{\varepsilon}, \qquad (11)$$

where $\xi_0 = v_F/\Delta_0$ is the correlation length. The suppression factor, Eq. (5),

$$\mathcal{A}[\bar{\eta}(x)] \approx \frac{1}{2A}(2\Delta_0)^2 R \approx \frac{2}{g}\ln\frac{2\Delta_0}{\varepsilon}, \qquad (12)$$

also depends logarithmically on energy, so that the weight of the saddle-point configuration is

$$p[\bar{\eta}(x)] \propto \varepsilon^{2/g}. \qquad (13)$$

This result already gives a good estimate for the shape of the density of states inside the pseudogap at $g \ll 1$ (cf. Eq. (4)).

A more detailed calculation requires performing the Gaussian integration over the disorder realizations
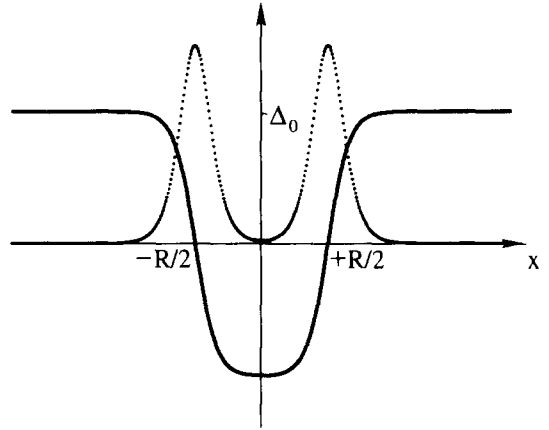

Fig. 1. The form of $\Delta(x) = \Delta_0 + \bar{\eta}(x)$ for the instanton disorder fluctuation (thick line) and the electron density $|\psi_+(x)|^2 = |\psi_-(x)|^2$ for the corresponding intragap states (dotted line).
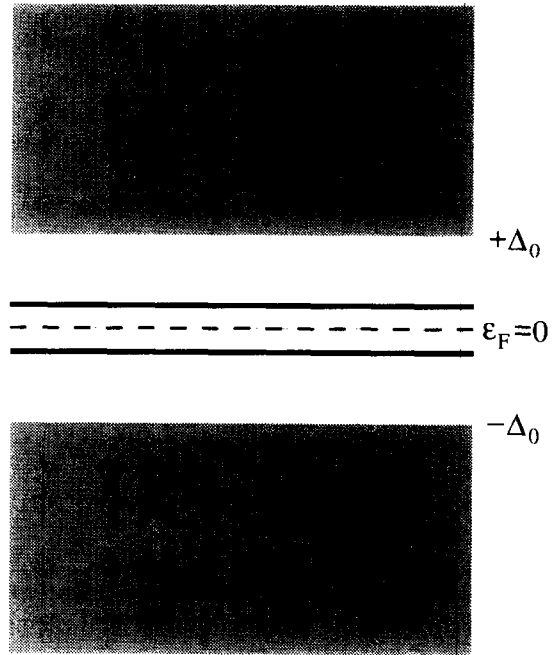

Fig. 2. The spectrum of electron states for the instanton configuration $\Delta(x)$ plotted in Fig. 1.

close to the "saddle-point" configuration, Eq. (7). We then find the following expression for the average density of electron states per unit length,

$$\langle \rho(\varepsilon) \rangle = \frac{e}{\pi g v_F} \left(\frac{e\varepsilon}{2\Delta_0} \right)^{2/g-1}. \qquad (14)$$

For $g \ll 1$, this agrees with Eq. (36) of Ref. [3], confirming the validity of the "saddle-point" approximation at small energies and weak disorder. The easiest way to get the result Eq. (14) is to use the correspondence between the averaging over disorder realizations $\eta(x)$ and the quantum-mechanical averaging over the ground state for a certain double-well potential. The details of this calculation will be reported elsewhere.

Having obtained the form of the most probable disorder-induced electron states, we can now also calculate in a relatively straightforward way the optical absorption coefficient for a half-filled chain at photon energy $\omega \ll 2\Delta_0$, and $g \ll 1$. Again, only a large disorder fluctuation can make the energy difference between the empty and filled electron levels small. With the highest probability the photon absorption will induce a transition from the highest occupied to the lowest unoccupied electron state. Due to the particle-hole symmetry, the energy of the lowest unoccupied state at half-filling should equal $+\frac{1}{2}\omega$, while the energy of the highest doubly occupied state should equal $-\frac{1}{2}\omega$. Hence, the "saddle-point" disorder configuration, whose probability largely determines the absorption rate, is given by Eqs. (7)–(9) with $\varepsilon_+(R) = \frac{1}{2}\omega$.

Thus, in the "saddle-point" approximation, the absorption coefficient is the product of the averaged density of states (which is essentially the probability to find the necessary disorder fluctuation) and the strength of the optical transition between the two intragap levels,

$$\langle \alpha(\omega) \rangle = \left\langle C\omega \sum_f |\langle f|\hat{d}|0\rangle|^2 \delta(E_f - E_0 - \omega) \right\rangle$$
$$\approx \frac{1}{2}C\omega |\langle +|\hat{d}|-\rangle|^2 \langle \rho(\varepsilon = \frac{1}{2}\omega) \rangle. \quad (15)$$

Here $\hat{d}$ is the electric dipole operator, $|\pm\rangle$ denote the wave functions of the intragap states (with energies $\pm\frac{1}{2}\omega$) and C is an ω-independent coefficient (for small ω, we can neglect the weak ω-dependence of the real part of the dielectric constant).

The wave functions of the intragap states $|\pm\rangle$ are the bonding and antibonding superpositions of the wave functions of the midgap states localized near the soliton and the antisoliton (see Eq. (10)), from which the transition dipole matrix element is obtained as

$$\langle +|\hat{d}|-\rangle = \frac{1}{2}qR. \quad (16)$$

Here q denotes the electron charge and R is the soliton–antisoliton separation. Thus, for the asymptotic behavior of the averaged absorption coefficient at low photon energy, we obtain

$$\langle \alpha(\omega) \rangle \propto \omega^{2/g} \left(\ln \frac{4\Delta_0}{\omega} \right)^2. \quad (17)$$

At this point we want to comment on the calculations of the optical conductivity in Refs. [9,11], in which the factorization approximation, $\langle GG \rangle = \langle G \rangle \langle G \rangle$, was used to evaluate the disorder average of the product of two Green functions. From above, it is clear that this approximation is not valid at low photon energies, as it results in the optical conductivity (as well as the absorption coefficient) being proportional to the second power of the weight, Eq. (13), rather than the first (cf. Eq. (15)). Of course, at weak disorder the absorption at photon energies $\omega \ll 2\Delta_0$ is small anyhow, but the factorization approximation makes it even much smaller.

We would also like to point out that the small difference between the energies of the bonding and antibonding states is potentially dangerous for the saddle-point calculation of both the average optical absorption coefficient and the density of states. The problem arises in the calculation of the contribution of the disorder realizations close to the "saddle-point" fluctuation,

$$\eta(x) = \bar{\eta}(x) + \delta\eta(x).$$

The perturbation $\delta\hat{h} = \sigma_1 \delta\eta(x)$ can, in principle, strongly mix the bonding and antibonding states, because of the small energy denominator 2ε appearing in the perturbation series. Such a mixing would affect the values of both the energy splitting between the two states and the dipole matrix element. To see if that is the case, we considered the effective perturbation Hamiltonian, acting on the subspace of the two bonding and antibonding states, which includes the virtual excitations to all other (high-energy) electron states. We found that the off-diagonal matrix elements of this Hamiltonian are $O(\varepsilon)$, which cancels ε in the denominator and makes the mixing of the two states small. This result is a direct consequence of the charge conjugation symmetry of the Dirac Hamiltonian, Eq. (1). Thus, despite the small energy splitting, the saddle-point method is applicable.

We conclude that in the FGM the most probable form of the wave function of the electron state lying deep within the pseudogap contains two peaks. The "saddle-point" disorder fluctuation, which induces such a state, has the form of a soliton–antisoliton pair and the peaks of the wave function are localized near the two kinks of this fluctuation (see Fig. 1). Away from the kinks, the electron wave function, Eq. (10), falls off exponentially on a length scale ξ_0. This observation is consistent with the fact, that the localization length at zero energy,

$$l_{\text{loc}}(\varepsilon = 0) = \frac{\xi_0}{1 - \frac{1}{2}g},$$

calculated using the Thouless formula [17], at weak disorder equals the correlation length ξ_0. As we demonstrated, the instanton approach allows for a relatively easy calculation of the small-energy density of states and absorption coefficient.

Our results (Eqs. (14) and Eq. (17)) are valid if the density of the disorder-induced states is small, which is the case when $|\varepsilon| \ll \Delta_0$ and $g \ll 1$. It is useful, however, to comment briefly on the effects of a large disorder. For $g \sim 1$ the typical size of the disorder fluctuation $\eta(x)$ on the scale of the correlation length ξ_0 becomes comparable to Δ_0, so that disorder fluctuations inducing the electron states with small energy are no longer suppressed, and for $g > 2$ the density of states even diverges at $\varepsilon = 0$ [3]. This is essentially the singularity found long ago by Dyson [18] for a gapless system, because at strong disorder there is no principal difference between the electron states in Peierls insulators and conducting ($\Delta_0 = 0$) chains. In the latter case the localization length of the electron states diverges as $\varepsilon \to 0$ and the wave functions have an irregular structure, these being large in many separated chain regions [19]. Surprisingly, the "saddle-point" method gives the correct exponent $(2/g - 1)$ (cf. Eq. (14)) for the energy dependence of the average density of states for all values of g. This suggests, that even for large g the typical form of the wave function may be close to the one given by Eq. (10) in the regions where the wave function is large, and that multi-instanton disorder configurations (a gas of the soliton–antisoliton pairs) may become important at strong disorder.

References

[1] R.E. Peierls, Quantum Theory of Solids (Clarendon, Oxford, 1955), p. 108.

[2] H. Kies (ed.), Conjugated Conducting Polymers (Springer, Berlin, 1992).

[3] A.A. Ovchinnikov, N.S. Erikhman, Zh. Eksp. Theor. Fiz. 73 (1977) 650 [Sov. Phys. JETP 46 (1977) 340].

[4] B. Halperin, M. Lax, Phys. Rev. 148 (1966) 722.

[5] J. Zittartz, J.S. Langer, Phys. Rev. 148 (1966) 34.

[6] S. Coleman, Aspects of Symmetry (Cambridge University Press, Cambridge, 1988).

[7] L.V. Keldysh, Zh. Eksp. Theor. Fiz. 45 (1963) 364 [Sov. Phys. JETP 18 (1964) 253].

[8] B.C. Xu, S.E. Trulinger, Phys. Rev. Lett. 57 (1986) 3113.

[9] K. Kim, R.H. McKenzie, J.H. Wilkins, Phys. Rev. Lett. 71 (1993) 4015.

[10] R. Hayn, J. Mertsching, Phys. Rev. B 54 (1996) R5199.

[11] B. Starke, J. Mertsching, Synth. Met. 76 (1996) 217.

[12] I.M. Lifshits, S.A. Gredeskul, L.A. Pastur, Introduction to the Theory of Disordered Systems (Wiley Interscience, New York, 1988).

[13] S.A. Brazovskiï, N. Kirova, Sov. Phys. JETP Lett. 33 (1981) 4.

[14] D.K. Campbell, A.R. Bishop, Phys. Rev. B 24 (1981) 4859.

[15] A.J. Heeger, S. Kivelson, J.R. Schrieffer, W.P. Su, Rev. Mod. Phys. 60 (1988) 781.

[16] H. Takayama, Y.R. Lin-Liu, K. Maki, Phys. Rev. 21 (1980) 2388.

[17] D.J. Thouless, J. Phys. C: Solid State Phys. 5 (1972) 77.

[18] F.J. Dyson, Phys. Rev. 92 (1953) 1331.

[19] T.P. Eggarter, R. Riedinger, Phys. Rev. B 18 (1978) 569, and references therein.