

KINKS IN DISORDERED CONJUGATED POLYMERS

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Abstract: The influence of disorder on the structure of kinks in conjugated polymers is studied. Towards this end the quasi-classical Green's function equations are solved on the imaginary frequency axis and analytically continued to real frequencies via a Padé method. A substantial broadening of the kink on increasing disorder strength is found.

I. Introduction

One of the unsolved problems in the area of conjugated polymers is the detailed nature of the metal-insulator transition as found experimentally upon doping. Several attempts have been made which take into account the formation of nonlinear excitations such as kinks and polarons as more and more charges are introduced into the system. In most cases, however, a detailed microscopic description of the interaction of these excitations with the dopants has not been used. Only a qualitative change such as gap decreasing due to disorder or band broadening due to doping has been considered. (For a short review see Ref.1) Here we want to study in detail the change of electronic and lattice structure of kinks as the impurity concentration is increased. The interaction of a single kink with a single impurity within the t-matrix formalism has been studied before [2]. The generalization to the case of many impurities appears to be difficult. In our approach here we include the influence of disorder via a uniform background which is obtained through averaging over an impurity distribution. We expect to obtain thus some of the important aspects of the many impurity situation. On a general scale our approach might be viewed as an example how nonlinear structures are modified under the influence of external randomness starting from a microscopic description of the physical situation.

This paper is organized as follows: in the next Chapter we describe the microscopic model and give a short derivation of the coupled system of equations which we have to solve. Symmetries and asymptotics which are imposed for physical reasons will be discussed. In a following section we describe the numerical procedure which we have used in order to obtain a selfconsistent solution. Some remarks on the problem of a numerical analytic continuation are given. Finally we discuss the results for a kink in detail and close with some prospects on the polaron.

II. Model

As in most cases the relevant physics of an electronic system such as a conjugated polymer is governed by the states around the Fermi energy. Since this is clearly an approximation to the real situation one can nevertheless describe the universal features of a whole class of materials. In the case of conjugated polymers this approach leads to the widely used Su-Schrieffer-Heeger model [3] where only an effective coupling of one-dimensional electrons to the lattice is taken into account. The continuum description [4] within this model is a second step with respect to the universal features of these materials, the final Hamiltonian reads

$$H = \sum_s \int dx \psi_s^\dagger(x) \{-i \sigma_3 \partial_x + \Delta(x) \sigma_1\} \psi_s(x) + 1/2\lambda \int dx \Delta^2(x) \quad (1)$$

with the 2-spinor $\psi(x)$ describing left- and right-moving electrons, $\Delta(x)$ is the lattice order parameter (dimerization), and all quantities have been scaled such that the electron-phonon coupling constant λ appears in front of the lattice elastic energy. In this formalism the influence of bond impurities are represented by an additional term

$$H_{\text{imp}} = \sum_s \int dx \psi_s^\dagger(x) \sum_a U \sigma_1 \delta(x-x_a) \psi_s(x) \quad (2)$$

with U the strength and x_a the random position of the impurities. The order parameter has to be determined selfconsistently as the minimum of the total energy.

Our approach to solve this problem uses the conventional Green's function technique in the quasiclassical approximation. The derivation of the corresponding equations of motion has been given elsewhere [5], here we indicate the essential steps only. Starting from the Dyson equation for the matrix Green's function G the corresponding equation for the impurity averaged function $g = \langle G \rangle$ with a selfenergy Σ can be derived. With the usual left-right trick this inhomogeneous equation is transformed into a homogeneous one with an additional normalization condition.

Using the Born approximation (weak scattering limit) for the selfenergy the final system of equations reads

$$\partial_x b_1(x, \omega) = 2i \Delta(x) b_4(x, \omega) - 2i/\tau b_4(x, \omega) b_5(x, \omega) \quad (3a)$$

$$\partial_x b_4(x, \omega) = 2\omega b_5(x, \omega) - 2i \Delta(x) b_1(x, \omega) + 2i/\tau b_1(x, \omega) b_5(x, \omega) \quad (3b)$$

$$\partial_x b_5(x, \omega) = -2\omega b_4(x, \omega) \quad (3c)$$

$$1 = b_1^2(x, \omega) + b_4^2(x, \omega) + b_5^2(x, \omega) \quad (3d)$$

$$\Delta(x) = -i\pi \lambda \sum_s \int_s d\omega / 2\pi \exp(i\omega\epsilon) b_5(x, \omega) \quad (3e)$$

$$N(x, \omega) = \text{Im } 2i b_1(x, \omega) \quad (3f)$$

with b_n the components of the Green's function g , (3d) the normalization condition, (3e) the selfconsistency equation, and (3f) the electronic density of states. $1/\tau = c U^2$ describes the influence of the impurities with c concentration. In the absence of impurities ($\tau = \infty$) one can give analytical expressions [6] for the homogeneous ground state ($\Delta = \text{const.}$) as well as kink and polaron excitations with a spatially structured $\Delta(x)$.

One observes that in these solutions square root singularities around the gap determine the interesting functions. This suggests to go over to imaginary frequencies for a numerical solution. Decomposing the Green's function into imaginary and real part $b_n = R_n + iI_n$ and using fundamental symmetries of the spectral function we arrive at $I_5 = I_1 = R_4 = 0$ along the imaginary frequency axis so that we have only three coupled differential equations instead of six.

In addition we have $\Delta(x) = s \Delta(-x)$, $R_1(x) = R_1(-x)$, $I_4(x) = -s I_4(-x)$, $R_5(x) = s R_5(-x)$ with $s = +1$ for the ground state (and the polaron) and $s = -1$ for the kink. Also the relations $R_1(iv) = R_1(-iv)$, $I_4(iv) = -I_4(-iv)$, and $R_5(iv) = R_5(-iv)$ along the imaginary frequency axis can be derived. As boundary conditions we have $R_5(x=0) = 0$ from symmetry and $I_4^{\text{kink}}(x_{\text{max}}) = I_4^{\text{hom}}(x_{\text{max}})$ since far from the center of the kink the structure has relaxed to the homogeneous case.

II. Numerical Procedure

For a numerical treatment we confine ourselves to a finite system in both space x and frequency ν which leads to a fixed frequency cut-off ν_{max} . The scaling property of the equations (3) $\nu' = \nu/\Delta_0$, $x' = x\Delta_0$ together with $\Delta(x) = \Delta_0 f(x)$ combined with the asymptotic behavior $f(x \rightarrow \infty) = 1$ leads in the selfconsistency equation (3e) to an effective coupling constant $\lambda(\eta)$, $\eta = 1/\tau\Delta_0$,

$$\lambda(\eta) = [2 \int_0^{\nu'_{\text{cut}}} d\nu' b_5^{\text{hom}}(i\nu'; \eta)]^{-1} \quad (4)$$

if one wants to preserve the property that the scaled quantity Δ is indeed the correct asymptotic value for x going to infinity. In consequence the physical space which we can cover by this procedure is enhanced by a factor $1/\Delta_0(\eta) > 1$.

The coupled equations (3) are now solved by an iteration method: for a given function $f(x)$ the differential equations (3a-c) are solved by a relaxation procedure. From the new Green's function a new order parameter $f(x)$ is calculated and put back into (3a-c) until convergence is reached. For the determination of the density of states the Green's function b_1 has to be continued to real frequencies. It turned out that for the ground state as well as for the kink this can be achieved with sufficient accuracy through a Padé approximation (using the Thacher-Tuckey algorithm [7]). Unfortunately in order to solve the selfconsistency equation for the polaron this continuation has to be performed at every step of the iteration.

We have tested our method with the case of a homogeneous order parameter where the exact solution can be given analytically [5]. These results will be given elsewhere [8], the overall agreement is very good including the numerical analytic continuation.

IV. Dirty Kink

In Fig.1 we show the results for the spatial structure of the kink order parameter $f(x)$ for different values of disorder strength η . A substantial broadening can be observed as the impurity concentration is increased.

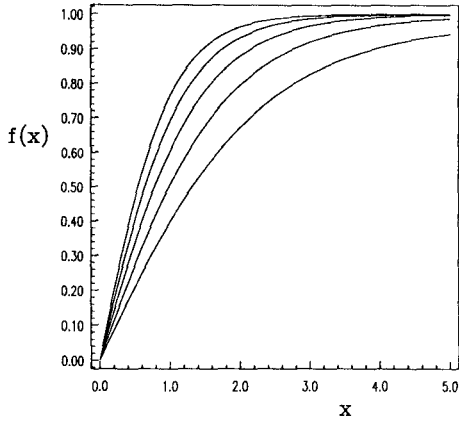


Fig.1: Spatial structure of the kink order parameter $f(x)=\Delta(x)/\Delta_0$ for different impurity concentrations: $\eta=0.0$ (upper curve), $\eta=0.8$ (lower curve), in steps of 0.2.

This broadening can be quantified by analyzing the behavior at the origin. Assuming a linear dependence $f(x)\sim x/\zeta$ (which is motivated by the exact result for the clean case) we can calculate the width ζ as function of impurity concentration. Keeping in mind

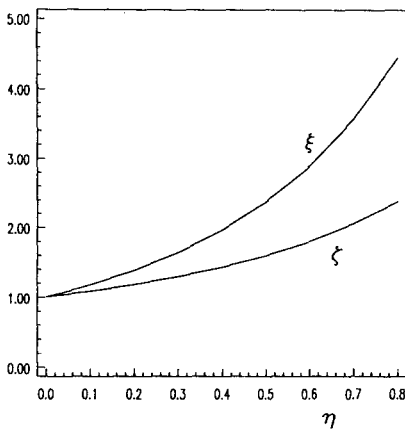


Fig.2: Kink width as function of impurity concentration (see text).

that we have used scaled variables the physical width ξ is given by $\xi = \zeta / \Delta_0(\eta)$. Both quantities are displayed in Fig.2. One can see that as η approaches the critical value $\eta=1$ the width of the kink appears to diverge. Unfortunately due to the finite length used in the solution of (3) a detailed investigation of the critical region is beyond the present approach.

This can also be seen clearly in Fig.3 where we show the asymptotic value $R_1(x_{\max})$ as function of impurity concentration. As stated in the previous section this should approach the value of zero corresponding to the homogeneous solution. Only up to $\eta < 0.4$ we are able to reproduce this boundary value with sufficient accuracy.

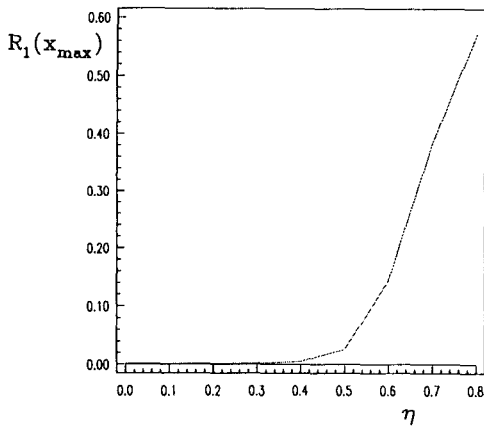


Fig.3: Asymptotic value $R_1(x_{\max})$ of the kink as function of impurity concentration.

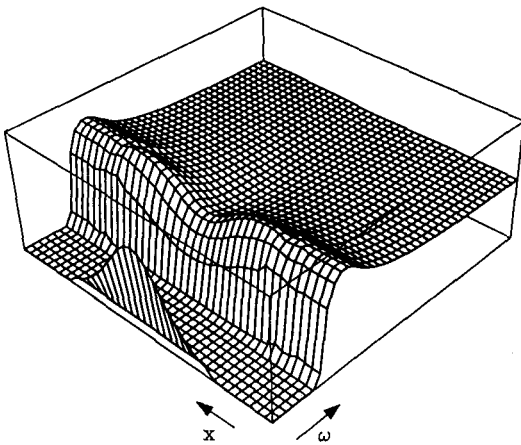


Fig.4: Electronic density of states for a kink as function of energy ω and spatial coordinate x ($x=0$ being the center of the kink) for impurity parameter $\eta=0.1$.

In Fig.4 we finally display the electronic density of states obtained from the Green's function via a numerical analytical continuation. The pole structure due to the kink at zero frequency is well reproduced, in the Figure the calculated values have been scaled down by a factor 10^5 . This pole modifies the density of extended states beyond the gap for $|\omega| > \Delta_0$ as well. Far away from the kink ($|x| \gg 1$) the system relaxes into the ground state.

V. Summary

In conclusion we have shown how a nonlinear excitation such as the kink in conjugated polymers is influenced by the presence of randomly distributed impurities starting from a microscopic description of these impurities. We find that the spatial structure is substantially broadened, the electronic properties change drastically as the gap decreases upon doping.

It turns out to be more difficult to study the polaron with the method presented here since at each step of the iteration an analytic continuation is necessary. The reason for this is the more complicated pole structure of the polaron state. However, as far as the doping process in the whole class of conjugated polymers is concerned, the polaron is the more important object to study. We shall address this question in a future publication [8].

We close with a technical remark: we have studied various methods for the analytic continuation problem [9]. For the purpose of this paper the method described in Chap. 3 gave satisfactory results; the polaron problem, however, poses more serious constraints on the quality of the continuation procedure.

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