Effect of interactions between electrons of like spin in conducting polymers

S. Kivelson
Department of Physics, State University of New York at Stony Brook, Stony Brook, New York 11794

H. B. Thacker
Fermi National Accelerator Laboratory, P.O. Box 500, Batavia, Illinois 60510

W.-K. Wu
Department of Physics, State University of New York at Stony Brook, Stony Brook, New York 11794
(Received 14 June 1984)

We consider the effects of repulsive electron-electron interactions between electrons of like spin in conducting polymers. Because the ratio $W/2m$ of the physical bandwidth W to the band gap $2m$ is large in these systems, they may be represented by a field-theory model with a cutoff. When only interactions between like spins are included, the resulting model is equivalent to the massive Thirring model which has been exactly solved by Bethe's ansatz. From the exact solution we are able to conclude that perturbation theory in the interaction strength g is quite accurate so long as $(g/\pi)\ln(W/2m) \ll 1$, while renormalization-group-improved perturbation theory is valid for $(g/\pi) \ll 1$. For $(g/\pi) \gtrsim 1$, results for the ground-state energy and mass gap are sensitive to the band structure far from the Fermi surface, and no simple field-theory model is adequate.

The simple model of polyacetylene proposed by Su, Schrieffer, and Heeger[1] (SSH) has had considerable success in explaining many of its experimentally observed properties. In order to understand this success and to develop a more quantitatively accurate model, it is important to investigate the effect of including electron-electron interactions, which are neglected in the SSH model. In particular we would like to begin to answer the following questions: Is it possible to construct a simple model of a conducting polymer that is quantitatively reliable? If so, what sort of electron-electron interactions must be included and how strong are they? And finally, can they be treated perturbatively or must they be introduced in some more fundamental fashion?

There is reason to hope that the answer to the first question is affirmative. The ratio $W/2m_0$ of the bandwidth W to the band gap $2m_0$ and hence the correlation length ξ, in units of the lattice constant, $\xi/a \approx W/2m_0$, is large. Thus the long-wavelength properties of the system may be relatively insensitive to microscopic details of the material. More precisely, it allows us to replace the lattice model with a continuum (field-theoretic) model with a finite cutoff (the bandwidth). Such a model was considered by Takayama, Lin Liu, and Maki[2] (TLM) for the noninteracting system, and they obtained results in good quantitative agreement with those obtained for the SSH model. More generally, in the large-ξ limit we expect the system to be well approximated by a continuum model with only a few relevant interactions whose strength is some complicated (and unknown) function of the parameters of the underlying lattice model. (Note, however, that since $\xi/a \sim 5$—10, it is not entirely clear that the "irrelevant" interactions are small enough to be ignored, even though they are higher order in a/ξ.)

Even if the low-energy physics of conducting polymers can be accurately modeled by a few effective interactions, the relative strengths of these interactions must be studied. A number of recent[3-10] papers have begun to address this second question. One strategy which can be adopted is to calculate various properties of an interesting model as a function of the strength of the interactions, and then, by comparing these properties with experiment, try to deduce the actual interaction strengths. For instance, in Refs. 3—7 the effect of adding to the SSH model an on-site (Hubbard) repulsion of magnitude U between electrons of opposite spin was considered. It was concluded in Ref. 5 that, to the extent that the interactions can be modeled by a single U, the size of U could be determined unambiguously to be less than $W/2$, while in Refs. 6 and 7 it was concluded that there was at present insufficient experimental evidence to bound U, but that it could be as large as $U \sim W$. A related issue is whether a noninteracting model is a valid zeroth-order approximation to the physics, i.e., whether the interactions can be treated perturbatively. Although in general perturbation theory is not even asymptotically convergent in a one-dimensional metal, it has been argued[11] that in a one-dimensional semiconductor, perturbation theory is valid as long as

$$(U/W)\ln(W/2m_0) \ll 1 . \tag{1}$$

In this paper we consider the effect of interactions between electrons of like spin on the ground-state properties of the continuum model of a conducting polymer. The advantage of considering only these interactions is that the model is then equivalent to the exactly solvable massive Thirring model.[12] Hence, we can examine both the physical consequences of these interactions and the validity of perturbation theory in a well controlled fashion. It is also interesting to study these interactions as represent-

ing the opposite extreme from the Hubbard model which forms the core of most previous studies. (The Hubbard model includes only interactions between electrons of unlike spin.) Because the interactions we consider are only between electrons of like spin, the electronic Hamiltonian can be expressed as the sum of two terms, one acting only on electrons with spin up, and the other on electrons with spin down. Thus we can ignore the electron spin in all of our calculations.

We are led to consider a model Hamiltonian similar to the TLM model with interactions

$$H_{\rm el}=\int dx\left[\psi^\dagger\left[-ihv_F\frac{\partial}{\partial x}\sigma_x+m_0(x)\sigma_x\right]\psi+2g_0\psi_1^\dagger\psi_2^\dagger\psi_2\psi_1\right], \tag{2}$$

where $\psi^\dagger(x)=(\psi_1^\dagger(x),\psi_2^\dagger(x))$ is a spinor field with two components corresponding to right- and left-moving electrons, respectively, σ_i are the Pauli matrices, v_F is the Fermi velocity (henceforth, we shall choose units such that $\hbar v_F=1$), and g_0 is the electron-electron interaction. Notice that our sign convention is such that $g_0>0$ corresponds to attractive interactions between electrons and $g_0<0$ to repulsive interactions. The scalar field $m_0(x)$ is proportional to the magnitude of the lattice (Peierls) distortion relative to an appropriately chosen undistorted lattice configuration; that is, $m_0(x)$ is the magnitude of the bond alternation in the polymer (see Refs. 1 and 2). $m_0(x)$ is properly a dynamical field, involving the motion of the ions, but following previous authors[1,2] we will invoke the large ionic mass to allow us to ignore fluctuations of the lattice. Thus the relevant lattice configurations are those which minimize the total adiabatic potential energy

$$E_T(\{m\})=2\langle H_{\rm el}\rangle+\int dx\,[m_0(x)-m_1]^2/2\lambda\,, \tag{3}$$

where $\langle H_{\rm el}\rangle$ is the ground-state expectation value of $H_{\rm el}$ as a functional of $m_0(x)$ (the factor of 2 is for spin), and the second term is the lattice elastic energy. m_1 is an asymmetry parameter which is zero in the case of *trans*-$(CH)_x$ where the two senses of bond alternation ($\pm m_0$) are equivalent, and nonzero in the case of most other conducting polymers, such as *cis*-$(CH)_x$ or polydiacetylene, where they are inequivalent. The ground-state configuration of the lattice is translationally invariant, $m_0(x)=m_0$ where m_0 is the magnitude of the lattice distortion which minimizes the total energy. It is also possible under appropriate circumstances to find nontranslationally invariant lattice configurations which are local minima of the adiabatic potential,[1,2] but we will not examine those cases here.

The model in Eq. (2) is ill defined until a regularization or cutoff procedure is specified. Note that we are here studying the effect of electron-electron interactions on static properties such as the ground-state energy and the relation between the dimerization (bare mass) and the physical mass gap. In field theory these are cutoff-dependent quantities, and thus different cutoff prescriptions can lead to different results. But since the band structure of an actual conducting polymer is much more complicated than that of Eq. (2), any term which ultimately depends on the cutoff procedure is suspect. In our discussion we will study this dependence in detail and thereby determine over what range of parameters a simple field-theory model can give reliable results.

In the Bethe-ansatz solution of the problem, the natural regularization procedure is a cutoff in the real part of the complex rapidity Λ. When $g_0=0$, this cutoff is related to the half bandwidth $W/2$ by

$$W/2=m_0\cosh\Lambda \tag{4}$$

since $W/2$ is the highest-energy single particle or hole excitation allowed in the model. We shall see that for small g_0, the most important features of the solution are independent of regularization scheme. To highlight those features, we will compare the Bethe-ansatz solution with the results of low-order perturbation theory.

The solution to the model is most conveniently expressed in terms of the parameter δ,

$$\delta=-1-\frac{\pi}{[2\cot^{-1}(\frac{1}{2}g_0)]}=-(g_0/\pi)+(g_0/\pi)^2+\cdots\,, \tag{5}$$

where δ is an analytic function of g_0 such that $\delta>0$ for repulsive and $\delta<0$ for attractive interactions between electrons. In terms of δ, the exact results[12] which will be used in our investigation can be summarized as follows:

(i) The single-fermion excitations have a dispersion relation

$$\epsilon=\pm(p^2+m^2)^{1/2}\,, \tag{6a}$$

where ϵ is the particle (or hole) energy, p is its momentum, and

$$m=m_0C_0(g_0)e^{-\delta\Lambda} \tag{6b}$$

per unit length.

(ii) The total ground-state electronic energy per unit length (with all negative energy states filled) is

$$\langle H_{\rm el}\rangle=-\frac{m_0^2}{4\pi}\left[\tfrac{1}{2}C_1(g_0)e^{2\Lambda}+\frac{1}{\delta}[C_2(g_0)-C_3(g_0)e^{-2\delta}]\right]. \tag{7}$$

In (6b) and (7), $C_i(g_0)$ are analytic functions which depend on g_0 only. The form of these functions depends on the particular prescription used to cut off the model (e.g., a continuum rapidity cutoff,[12] or a lattice cutoff via the Baxter *XYZ* spin chain[13]). For small g_0 they have the behavior

$$C_i(g_0)=1+O(g_0/\pi),\quad i=0,1,2,3 \tag{7'}$$

but the higher-order terms are prescription dependent. On the other hand, the cutoff dependence exhibited in (6b) and (7) is universal.

From the above results we see that the effect of repulsive electron-electron interactions are twofold: They

change (decrease) the magnitude of the dimerization m_0 which minimizes E_T in Eq. (3), and, for a fixed value of m_0, they decrease the magnitude of the physical band gap ($m < m_0$). Notice that both m and $\langle H_{el} \rangle$ are analytic functions of δ (and hence of g_0) for $|\delta| < \frac{1}{2}$ ($g_0 < 2$). Thus we can expand the exact expressions in a power series in g_0 and compare the result to the result of perturbation theory. To make this comparison more transparent we define the bandwidth, W, according to Eq. (4) and express the answer in terms of W rather than Λ. For large W/m_0 we can make use of the relation

$$\Lambda = \ln(W/m_0) - (m_0/W)^2 + O((m_0/W)^3) \tag{8}$$

and we will systematically ignore terms of order $(m_0)^3$ and higher. Thus, from Eq. (6b), (7), and (8), we find

$$m = m_0 C_0 \left\{ 1 + \frac{g_0}{\pi} \ln\left[\frac{W}{m_0}\right] + \left[\frac{g_0}{\pi}\right]^2 \left[\frac{1}{2} \ln^2\left[\frac{W}{m_0}\right] - \ln\left[\frac{W}{m_0}\right] \right] + O\left[\left[\frac{g_0}{\pi}\right]^3\right] + O\left[\left[\frac{m_0}{W}\right]^2\right] \right\}, \tag{9a}$$

$$\langle H_{el} \rangle = -\frac{W^2 C_1}{8\pi} + \frac{m_0^2 C_1}{8\pi} - \frac{m_0^2 (C_2 - C_3)}{4\pi\delta} - \frac{m_0^2}{2\pi} C_3 \left\{ \ln\left[\frac{W}{m_0}\right] + \frac{g_0}{\pi} \ln^2\left[\frac{W}{m_0}\right] + \frac{2}{3}\left[\frac{g_0}{\pi}\right]^2 \left[\ln^3\left[\frac{W}{m_0}\right] - \frac{3}{2}\ln^2\left[\frac{W}{m_0}\right] \right] \right\} + O\left[\left[\frac{g_0}{\pi}\right]^3\right] + O\left[\frac{m_0^4}{W^2}\right]. \tag{9b}$$

Notice that successive terms in the expansion are small as long as $|g_0/\pi| \ln(W/m_0) \ll 1$, as promised. For comparison, we calculate the same quantities in second-order perturbation theory with a momentum space cutoff $-W/2 < k \leq W/2$. The result is

$$m^{PT} = m_0 \left\{ 1 + \left[\frac{g_0}{\pi}\right] \ln\left[\frac{W}{m_0}\right] + \left[\frac{g_0}{\pi}\right]^2 \left[\frac{1}{2}\ln^2\left[\frac{W}{m_0}\right] - (\gamma + \ln 2 - 1)\ln\left[\frac{W}{m_0}\right] + \text{const} \right] + O(g_0^3) \right\}, \tag{10a}$$

$$\langle H_{el} \rangle^{PT} = -\frac{W^2}{8\pi}\left[1 - \left[\frac{g_0}{\pi}\right]\right] - \frac{m_0^2}{2\pi}\left\{ \left[\ln\left[\frac{W}{m_0}\right] + 1 \right] + \left[\frac{g_0}{\pi}\right] \ln^2\left[\frac{W}{m_0}\right] \right\} + O(g_0^2), \tag{10b}$$

where $\gamma = 0.577\ldots$ is Euler's constant. In these perturbative calculations, we have defined the momentum-space cutoff so that the first-order contribution to the physical mass is exactly the same in the two approaches. Note that in each order of perturbation theory, only the leading logarithm is independent of cutoff procedure.

In the language of perturbation theory we can understand this since all the intermediate states that contribute to the leading logarithm have small energies $\sim m_0$ and hence are insensitive to the cutoff procedure.[10] To the extent that these terms dominate, the results of the model calculations can be said to be realistic and can be compared quantitatively with experiments on conducting polymers. All the other terms involve intermediate states with energies of order W. These terms will, in general, be sensitive to the band structure near the band edge. To the extent that these terms are important, no simple model can be compared quantitatively with experiment; even a lattice model such as the SSH model is only marginally better. Quantitative information would then require a complete knowledge of the (rather complicated) band structure of the material.

We have thus found a partial answer to our original question. To determine where the simple models are reliable, we distinguish three ranges of interaction strengths.

(1) The perturbative regime $m_0/W \ll 1$ and $(g_0/\pi)\ln(W/m_0) \ll 1$. In this regime the simple models are reliable since the states near the Fermi surface dominate the physics. Moreover, the effects of electron-electron interactions can be reliably calculated using low-order perturbation theory.

(2) The scaling regime $m_0/W \ll 1$ and $g_0/\pi \ll 1$ (which includes the perturbative regime). In this regime the model is still reliable but finite-order perturbation theory is not necessarily useful. However, by proper resummation of perturbation theory (summing leading logarithms) using the renormalization group approach,[14,15] it is possible to reproduce all the *universal*

features of the exact solutions. The difference between exact and perturbative results, similar to the difference between exact results for models with different cutoffs, involves differences in the next to leading terms in $C_i(g_0)$. We stress that these differences are not problems associated with one or another calculational scheme; they are features which depend on the band structure far from the Fermi surface and hence are features which are not obtainable from any simple model. When expressed in terms of the bare parameters g_0 and m_0, there are necessarily *model-dependent* corrections to any physical quantity at least of order g_0 or of order $(m_0/W)^2$, which is therefore a fundamental limit on the accuracy of model calculations.

(3) Nonuniversal regime $m_0/W \sim 1$ or $g_0/\pi \gtrsim 1$. In this regime the simple models have little bearing on the ground-state properties of the real materials; to obtain reliable results it would be necessary to include the correct band structure within an energy interval of at least a few times the larger of m_0 or $g_0 W$ of the Fermi surface.

This still does not answer the question of what the actual physical interactions are in real conducting polymers. Of course, the massive Thirring model is almost certainly not the correct physical model in any regime. Nevertheless, the considerations we have applied here to the massive Thirring model can also be applied to models with more general interactions[15] characterized by a coupling strength g. If, as suggested in Ref. 5, typical values of the parameters in polyacetylene are $m_0/W \sim 0.15$ and $g/\pi \sim \frac{1}{3}$, then one may be able to compare the qualitative results of simple model calculations with experiment, but the models cannot be trusted quantitatively to better than approximately 30% accuracy. If the interaction strengths are much stronger than this, then the simple models cannot be trusted at all.

Some of this work was done at the Soliton Workshop in Trieste, Italy. We would like to thank Alan Luther and the International Center for Theoretical Physics for making this workshop possible.

[1]W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. **42**, 1698 (1979); Phys. Rev. B **22**, 2099 (1980).
[2]H. Takayama, Y. R. Lin-Liu, and K. Maki, Phys. Rev. B **21**, 2388 (1980).
[3]A. A. Ovchinikov, I. I. Ukraniinskii, and G. U. Krentsel, Usp. Fiz. Nauk **108**, 81 (1972) [Sov. Phys.—Usp. **15**, 575 (1973)]. K. R. Subbaswamy and M. Grabowski, Phys. Rev. B **24**, 2168 (1981).
[4]P. Horsch, Phys. Rev. B **24**, 7351 (1981).
[5]S. Kivelson and D. E. Heim, Phys. Rev. B **26**, 4278 (1982).
[6]J. E. Hirsch, Phys. Rev. Lett. **51**, 269 (1983); J. E. Hirsch and M. Grabowski, *ibid.* **52**, 1713 (1984); D. K. Campbell, T. A. DeGrand, and S. Mazumdar, *ibid.* **52**, 1717 (1984).
[7]S. Mazumdar and S. N. Dixit, Phys. Rev. Lett. **51**, 292 (1983).
[8]T. Nakano and H. Fukuyama, J. Phys. Soc. Jpn. **49**, 1679 (1980).
[9]Z. G. Zoos and S. Ramasesha, Phys. Rev. Lett. **51**, 2374 (1983).
[10]W. K. Wu and S. Kivelson (unpublished).
[11]D. Hone and S. Kivelson (unpublished).
[12]H. Bergknoff and H. B. Thacker, Phys. Rev. Lett. **42**, 135 (1979); Phys. Rev. D **19**, 3666 (1979); H. B. Thacker, Rev. Mod. Phys. **53**, 253 (1981).
[13]R. J. Baxter, Ann. Phys. (N.Y.) **70**, 323 (1972); A. Luther, Phys. Rev. B **14**, 2153 (1976).
[14]N. Andrei, K. Furuya, and J. H. Lowenstein, Rev. Mod. Phys. **55**, 331 (1983).
[15]J. Solyom, Adv. Phys. **28**, 201 (1979).