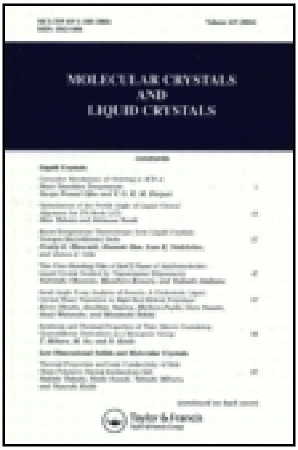

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# Effect of Electron-Electron Interactions in Conducting Polymers

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# EFFECT OF ELECTRON-ELECTRON INTERACTIONS IN CONDUCTING POLYMERS

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Abstract We argue that because of the large correlation length in most conducting polymers, their electronic properties can be understood semi-quantitatively in terms of a simple effective (coarse grained) model. This description is valid only so long as the effective electron-electron interactions are "weak." The effect of these interactions have been evaluated perturbatively, and values of the interaction strengths are found which are consistent with recent experiments in polyacetylene, and which are indeed "weak."

## I. PLAN OF ATTACK

The purpose of this paper is to determine the extent to which it is possible to obtain a quantitative understanding of the "interesting" properties of conducting polymers by studying the behavior of some simple model Hamiltonians. In Section II we seek a precise formulation of this goal as a series of concrete questions, and for each question we describe the strategy we will adopt to answer it. In the remainder of the paper we give a brief (and incomplete) report of the progress that we have made in following this program. In III we discuss the two classes of "simple models" of conducting polymers that we have studied. For the purposes of this paper, a "simple model" is a one-dimensional Hamiltonian (representing a single polymer chain) with one electronic ($\pi$) orbital and a single lattice degree of freedom per site. Electron-phonon and electron-electron interactions are both included in these models, although in this paper we will always assume that the ionic mass is sufficiently large that the adiabatic approximation is valid, and that the lattice can be treated semi-classically. Representative results of a perturbative solution of these models are also presented. In IV we consider what the effect of terms which are omitted from the simple models we have considered so far would be on the properties of conducting polymers. In this way, we can get a handle on how reliable the simple models are. Throughout the paper, we have briefly alluded to some of the best experimental evidence that supports the validity of our approach, and that allows us to obtain estimates of the values of some of the parameters that enter the theory. This part of the discussion focuses primarily on polyacetylene, since it is the most studied of the conducting polymers, but the results are also directly applicable to other materials, such as polythiophene, polydiacetylene, and polypyreole. Finally, in V our most important conclusions are listed.

## II. QUESTIONS

### A.) Can the properties of conducting polymers be represented by a "simple model"?

The answer to this question, on the face of it, is obviously no. The actual materials all have many more degrees of freedom (i.e. $\sigma$-bands, other $\pi$-bands, other lattice modes, etc.) and more complicated interactions than any of the simple models. However, one can hope, as is the case in many other physical systems such as normal Fermi liquids or systems near a critical point, that the low energy long wave length excitations of the system are well approximated by a simple effective (coarse grained) theory. In other words, we expect to be able to obtain an accurate description of the properties of these materials in the continuum limit, where the lattice constant is small compared to all other characteristic lengths. To derive the effective theory from a microscopic Hamiltonian is prohibitively complicated. Even the form of the interactions in effective Hamiltonian need not be the same as those in the microscopic Hamiltonian. Fortunately, the form of the most important interactions in the effective theory is easily determined since in the continuum limit there are only a few "relevant" interactions. However, the magnitude of these interactions is not known a-priori, nor, given the complexity of the connection, is there any reason to imagine that they are at all comparable in magnitude to the analagous atomic scale interactions which occur in the microscopic Hamiltonian. We are thus forced to treat the effective interactions as parameters to be determined empirically by comparison with experiment. Finally, since in real conducting polymers, the continuum approximation is not exact, one could include other "irrelevant" interactions to the effective Hamiltonian. However, there is an infinite number of such interactions possible, so that if they have important effects on the interesting properties of a conducting polymer, it is unlikely that any relatively simple model will give a satisfactory description of that polymer.

To make these considerations more concrete, consider the band structures of polyacetylene shown in Fig. 1. In Fig. 1a, an approximate all-electron band structure of dimerized trans-polyacetylene (from Ref. 1) is shown. It is obviously far more complicated than the band structure (shown in Fig. 1b) of the two most successful simple models (see Eqs. 3), the continuum model of Takayama, Lin Liu, and Maki[2], and the lattice model of Su, Schrieffer, and Heeger[3] (SSH). However, the one feature that all three band structures have in common is the dispersion relation in the vicinity of the Fermi surface. Those properties of the models which depend only on the states near the Fermi surface are thus independent of the details of the model, and hence we will refer to them as being "universal." Those features which depend on the details of the band structure near the band edges are model dependent, hence non-universal. Since the band structure of all simple models is incorrect far from the Fermi surface, only the universal properties of any simple model calculation can be expected to have bearing on the properties of the real materials. This immediately yields two important criteria for the validity of any simple model calculation: 1) That the band gap, $2\Delta$, which sets the scale of interesting energies, must be small compared with the band width W, or that the electronic correlation length $\xi = \Delta/\hbar V_F$ ($V_F$ is the Fermi velocity) be large compared with a lattice constant, a,

$$\Delta/W \cong (a/\xi) << 1 \qquad (1a)$$

and 2) that the characteristic magnitude of the electron-electron interactions, U, be small compared with the band width,

$$(U/W) << 1. \qquad (1b)$$

This second condition emerges explicitly from a detailed analysis of the structure of high order perturbation theory (see Ref. 4). In addition, the necessity of condition (1b) can be understood on the basis of a simple intuitive argument: An interaction of magnitude U strongly admixes states within an energy U of the Fermi surface. Clearly, the effect of this will only be independent of the band structure near the band edges if condition (1b) is satisfied. We repeat that conditions 1a) and b) are conditions for the validity of the simple models themselves; to the extent that they are not satisfied in the actual materials, no simple model calculation can be compared to experiment with any confidence.

B) What is the effective model that best describes the low energy properties of conducting polymers?

To some extent, this question is ill-posed since, by the very fact that the properties that we are interested in are universal features of a wide class of models, we recognize that the question does not have a unique answer. We will thus discuss two sorts of model: a lattice model which has a natural ultraviolet cutoff built in (the lattice constant "a"), and a continuum model into which we must put an artificial cutoff at large excitation energy, which we identify with the band width W. The advantage of the lattice model is that it conforms closely to our intuitive notion of the microscopic structure of a conducting polymer. However, the continuum model is in a sense preferable since it allows us to catalogue directly those interactions that are relevant, and it is closer in spirit to our overall approximation in that it has no pretense of being a fully microscopic model.

C. What are the effects of electron-electron interactions on the properties of the model?

To answer this question we must first identify three regimes of interaction strength:

1) Perturbative regime

$$(U/2\pi W)\ \ln\ (W/\Delta) << 1 \tag{2a}$$

In this regime the effects are "small," except where these interactions lift a degeneracy in the non-interacting model. Results in this regime have been computed in perturbation theory in Refs. 5 and 6.

2) Non-perturbative regime

$$\ln^{-1}(W/\Delta) \lesssim (U/2\pi W) << 1 \tag{2b}$$

In this regime the effects of interactions may be large but they can still be treated analytically by summing the leading terms in perturbation theory, which can be done using the renormalization group.[7]

3) Non-universal regime

$$(U/W) \gtrsim 1 \tag{2c}$$

Here no reliable analytic solutions exist. At the same time, the simple model ceases to be reliable because condition (1b) is violated.

D. How can we verify the validity of the coarse grained theory?

We consider three ways to answer this question. Firstly, the predictions of simple model calculations can be compared to experiment. This has been done for the non-interacting (SSH) model with remarkable qualitative and even quantitative[9] success. This is suggestive evidence that the effect of electron-electron interactions is small (condition 2a). However, once electron-electron interactions are included in the model, there are then a sufficient number of interactions whose magnitude must be determined empirically, that a naive quantitative fit to experiment is at best a consistency check. Secondly, the extent to which the results are actually independent of the details of the band structure (universality) can be checked directly by comparing the qualitative features of the excitation spectra of different conducting polymers, each of which have quite different band structures far from the Fermi surface. This has been done in Ref. 6. The remarkable qualitative similarities between different polymers is strong evidence that conditions 1a and b are satisfied. Thirdly, we can study slightly more general models than those discussed in Section III so that we can identify possible qualitative effects of non-universal terms in the model on the physical properties of the system. By placing experimental bounds on the magnitude of these non-universal effects, we can test the validity of our approach. Since in the continuum limit, the system possesses charge conjugation symmetry, we have chosen in Section IV to discuss the effect of terms which break this symmetry. We shall see that this permits a very sensitive test of conditions 1 a) and b).

E. What are the effects of electron-electron interactions on the properties of polyacetylene?

Space does not permit the answer to this question even to be sketched here. It is deferred to Ref. 6.

## III. SIMPLE MODELS AND PERTURBATIVE RESULTS

There are two classes of simple model Hamiltonians that have been used to study conducting polymers:

A. The discrete models (SSH-extended Hubbard π-band only models)

$$\begin{aligned} H_\alpha = & - \sum_{ns} [t_o + (-1)^n \tfrac{1}{2} \Delta_n][c^+_{ns} c_{n+1s} + \text{h.c.}] \\ & + \sum_{\substack{nn' \\ ss'}} U_{ss'}(n,n')[c^+_{ns} c_{ns} - \tfrac{1}{2}][c^+_{n's'} c_{n's'} - \tfrac{1}{2}] \qquad (3a) \\ & + \sum_n \frac{1}{4\, g_o t_o} (\Delta_n - \Delta_{int})^2 \end{aligned}$$

where $c^+_{ns}$ creates an electron of spin s on site n, $2t_o = W$ is the valence band width, $\Delta_n$ is proportional to the magnitude of the lattice dimerization between site n and site n+1, $g_o$ is the dimensionless electron-phonon coupling constant, U is the matrix of electron-electron interactions, and $\Delta_{int}$ is the term which breaks the symmetry between the two different senses of dimerization. (Hence $\Delta_{int} = 0$ in trans-polyacetylene but $\Delta_{int} \neq 0$ in all other polymers) This model includes nearest neighbor hopping only (the first term in Eq. (3a)) and interactions between site charge densities (the second term). In general $U_{ss'}(n,n')$ depends on the pattern of lattice distortion, so we have not assumed that it is translationally invariant. Finally, there are other terms that should, in principle, appear in Eq. (3a), among them a second neighbor hopping term, and interactions involving bond charge density. The effect of including such terms will be considered in Section IV.

### B. Continuum models (Massive field theory with (almost) all possible relevant interactions included.)

$$\begin{aligned} H_c = & \sum_c \int dx\, \psi_s^+(x) \{ i\partial_x \sigma_z + \Delta(x)\sigma_x \} \psi_s(x) \\ & + \sum_{\substack{ab \\ cd}} \sum_{ss'} \int dx\, g_{ss'}^{(abcd)} \psi_{sa}^+ \psi_{s'b}^+ \psi_{s'c}\psi_{sd} \\ & + \int dx \frac{(\Delta(x)-\Delta_{int})^2}{2g_o} \end{aligned} \tag{3b}$$

where $\psi_s^+(x)$ is a two component spinor with components $\psi_{s1}^+(x)$ which creates a right moving electron of spin s at position x, and $\psi_{s-1}^+(x)$ which creates a left moving electron, $\Delta(x)$ as before is proportional to the local lattice dimerization, and $g_o$ is the electron-phonon interaction. We have chosen units such that $\hbar V_F=1$ ($2t_o a=1$) where $V_F$ is the Fermi velocity, so $\Delta(x)$ is an inverse correlation length. $g_{ss'}^{(abcd)}$ is a matrix of electron-electron interactions which, as in the usual "g-ology" picture[8], consists of 5 distinct relevant constants, $g_{\parallel}$, the interaction between electrons with the same spin, and 4 interactions between electrons of opposite spin which are traditionally called $g_{1\perp}$, $g_{2\perp}$, $g_{3\perp}$, and $g_{4\perp}$. Unfortunately with $g_o$ this leaves us with 6 unknown interaction strengths to be determined empirically. One could reduce this number to 4 by assuming that the interaction is spin independent and by ignoring $g_{4\perp}$(which is the least important interaction) but this approximation is not well justified. (See Ref.8) (In low order perturbation theory the number of independent parameters is somewhat smaller.) In any case, we are left with a rather larger number of free parameters than we would like. Moreover, the Hamiltonian in Eq. (2) is not really the most general continuum model we could write down; higher than quadratic order terms in the Bose field $\Delta(x)$ could be added to the last line of Eq. (2). We invoke the small magnitude of the lattice distortion to justify ignoring these terms.

One further observation is that this class of models contains as special cases many other widely studied models: For $g_{\perp} = 0$ the model is equivalent to the exactly soluable Massive Thirring Model, which was exploited in Ref. 4 to identify the universal terms in the theory (i.e. to justify condition 1b) and the range over which perturbation theory is valid (condition 2a). For $g_{11}= 0$ and $g_1 = g_2 = -g_3 = g_4 = U/2t_o$ the model is the continuum limit of the SSH-Hubbard model.

### C. Some Perturbative Results:

If the interactions are weak, the properties of the simple models can be determined straightforwardly by doing perturbative theory in the interaction strength. Since in the conducting polymers that have been studied to date, $\ln(\Delta/W) \approx 2$, the range of validity of perturbation theory (condition 2a) is a substantial fraction of the range of validity of the simple models themselves (conditions 1 a and b). Thus, in most cases, the perturbative results will not be significantly less reliable than the (more complicated) results obtained by summing up the leading order terms to all orders in perturbation theory. It is straightforward (though tedious) to evaluate the perturbative effects of the interactions on the various quantities of physical importance, such as the magnitude of the dimerization or of the optical gap, as discussed in Refs. 4, 5, and 6. We have space here only to discuss the effects of electron-electron interactions on the soliton creation energy in polyacetylene (see Refs. 5 and 6 for a derivation).

$$E_s = E_s^{(o)}(\ell) \pm \frac{V_o}{3}\left(\frac{a}{\ell}\right) - \left(\frac{V_1}{W}\right)\frac{\Delta_o}{16\, g_o} + \mathcal{O}\left[\left(\frac{V}{2\pi W}\right)^2 \Delta_o \,\ln\left(\frac{W}{\Delta_o}\right)\right] \qquad (4)$$

where $E^{(o)}(\ell)$ is the soliton creation energy as a function of its width, $\ell$, in the absence of electron-electron interactions, $V_o$ and $V_1$ are the particular combinations of interactions $(V_o/W)=\frac{1}{2}(g_{2\perp}+g_{4\perp})$ and $(V_1/W) = -g_{1\parallel} + g_{1\perp} + g_{2\perp}$, and the ± **takes** on the value "+" for a charged soliton $S^{\pm}$ (regardless of the sign of the charge) and "-" for a neutral soliton $S^{o}$. Note that the soliton width is that value of $\ell$ which minimizes the soliton creation energy. Thus, in the absence of interactions, $\ell = \xi$ regardless of the charge state of the soliton, while for positive $V_o$ the neutral soliton tends to be somewhat narrower than the charged soliton,

$$\ell_o < \xi < \ell_\pm \ .$$

Since the splitting between a charged and neutral soliton is zero in the absence of electron-electron interactions, this splitting is an excellent probe of the magnitude of the interactions. In particular, if we treat the lattice purely classically, then the difference $\Delta E$ between the ionization energy of a neutral soliton and the electron affinity of a positively charged soliton is

$$\Delta E = \frac{2V_o}{3}\left\{\frac{a}{\ell_o} + \frac{a}{\ell_\pm}\right\} \ . \qquad (5)$$

The photo-induced optical absorption measurements of Ref. 10 can be interpreted as a measure of $\Delta E \approx 0.9$ eV, or in other words $V_o \approx 4$ eV. Thus, the characteristic combination which enters perturbation theory, $(V_o/2\pi W)\ln(W/\Delta_o) \sim \frac{1}{4}$. This is small enough so that we can argue that perturbation theory is sensible, although large enough that we do not expect it to be enormously accurate.

## IV. CORRECTIONS TO THE SIMPLE MODELS (BREAKDOWN OF CHARGE CONJUGATION SYMMETRY)

We have argued on general grounds that the simple models cannot accurately describe the properties of conducting polymers when conditions 1a or b are not satisfied. In this section we demonstrate this by an explicit example. Both the model Hamiltonians are charge conjugation symmetric. One consequence of this symmetry, is that the creation energy of a charged soliton (or polaron, or bipolaron) is independent of the sign of its charge. The actual band structure of a conducting polymer is certainly not charge conjugation symmetric (see Fig. 1a). In this section we consider the effect of including a term in our model which breaks the symmetry. Specifically, we calculate the difference $E_{s^+} - E_{s^-}$ between the creation energy of a positively and negatively charged soliton. We will see that this splitting is substantial if either of conditions 1a or b is violated. Thus, the fact that there are strong experimental bounds on this energy is strong evidence that conditions 1a and b are satisfied.

To begin with, we show that the simple models are charge conjugation symmetric by explicitly constructing an anti-unitary operator, A, which has the properties that it leaves the energy of a state unchanged

$$A^+HA = H \tag{6a}$$

but changes the sign of the charge density, $\hat{\rho}(n) \equiv \sum_s [c^+_{ns}c_{ns} - \tfrac{1}{2}]$,

$$A^+\hat{\rho}(x)\, A = -\, \hat{\rho}(x)\ . \tag{6b}$$

It is easy to verify that a version of this operator for the discrete model in (Eq. 3a) is

$$A = KS \tag{7a}$$

where S is the unitary operator

$$S \equiv \exp[i \sum_{ns} (-1)^n\, c^+_{ns}c_{ns}] \tag{7b}$$

and K is the complex conjugation operator. An analagous operator can be constructed for the continuum model.

The band structure of polyacetylene shown in Fig. 1a is manifestly not charge conjugation symmetric; the valence band is nearly twice as wide as the conduction band. Only near the Fermi surface is the band structure approximately symmetric. To model this band structure more accurately, let us consider the effect of adding a small second neighbor coupling

$$H_2 = - \sum_{ns} t_2[c^+_{ns}c_{n+2s} + \text{h.c.}] \tag{8}$$

to the discrete model. From the relative widths of the conduction and valence bands in Fig. 1a, we can estimate that $t_o \approx 2$ eV and the second neighbor hopping matrix element $t_2 \approx 0.25$ eV. $H_2$ is small, but it maximally breaks charge conjugation symmetry,

$$A^+ H_2 A = - H_2 \ .$$

Thus, for example, $H_2$ will produce a splitting between the creation energy for a positively and negatively charged soliton. We can easily calculate this splitting to lowest order in $t_2$ and to second order in the magnitude of the interaction U,

$$E_{s^-} - E_{s^+} \approx t_2 \left\{ \frac{8}{3}\left(\frac{\Delta_o}{2t_o}\right)^2 + X\left(\frac{U}{2t_o}\right)^2 + \dots\right\} \tag{9}$$

where X is a number of order 1 which depends on the exact form of the electron-electron interactions $U_{ss'}(n,n')$. For Hubbard interactions, $(U_{ss'}(n,n') = \frac{1}{2} U \delta_{n,n'})$ $X \approx 0.8$. Note that it is explicitly evident from Eq. (9) that only when conditions 1a and 1b are satisfied is this splitting very small. Conversely, since this splitting can be seen experimentally[10] to be less than 0.1 eV, we can place a bound of sorts on U, $(U/2t_o) < \frac{1}{2}$ .

## V. CONCLUSIONS

We end by listing our most important conclusions.

A) The simple model Hamiltonians are valid descriptions of conducting polymers only if the details of the model are unimportant (universality). This is true so long as all the interactions are weak, which for the continuum model implies

$$g_o << 1$$

which is equivalent to condition (1a) and

$$(g_i/2\pi) << 1$$

which is condition (1b).

B) So long as there is a finite Peierls gap, there is a substantial range of electron-electron interaction strengths, $g_i$, over which perturbation theory is useful:

$$(g_i/2\pi) \ \ln\ (W/\Delta_o) << 1 \ .$$

C) Our best guess of the magnitude of the interaction strengths in polyacetylene are

$$(\Delta_o/W) \approx 1/7 \qquad (\text{or } g_o \approx 0.4)$$

and

$$\frac{g_i}{2\pi} \ln\left(\frac{W}{\Delta_o}\right) \sim \frac{1}{4} \ .$$

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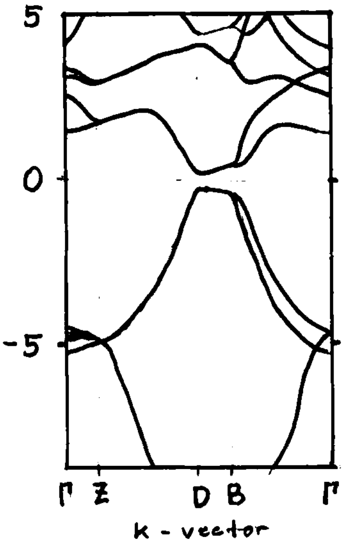

Fig. 1a - Band structure of trans-(CH)$_x$ from Ref. 1.

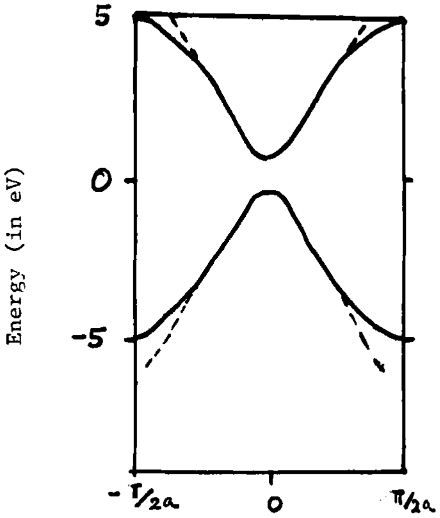

Fig. 1b - Band structure of lattice (solid line) and continuum (dashed line) of trans-(CH)$_x$.