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Theory of conducting polymers with weak electron-electron interactions

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We show that the properties of many conducting polymers can be determined from the study of a simple, continuum, one-dimensional model with a limited number of relevant interaction parameters. Over most of the range of validity of the model, low-order perturbation theory in the electron-electron interactions is reliable. Properties of the ground state and low-lying excitations (especially solitons and polarons) can thus be determined perturbatively. The results are compared successfully with experiments in polyacetylene and other polymers.

I. INTRODUCTION

For the past few years, there has been enormous research interest in the properties of conducting polymers, especially polyacetylene [$(\mathrm{CH})_x$]. Two simple noninteracting models, the Su-Schrieffer-Heeger[1] (SSH) and Takayama—Lin-Liu—Maki[2] (TLM) models, have been widely used in the study of these quasi-one-dimensional materials. However, it has been realized for some time that electron-electron (e-e) interactions may play an important role in the electronic structure of these materials. To study the effects of these interactions, slightly more complex models have been investigated in which the simplest short-ranged e-e interactions (i.e., extended Hubbard interactions) are included. The properties of the model have been studied using perturbation theory,[3,4] the Hartree-Fock approximation,[3,5] and Monte Carlo calculations[6–8] among other methods.[9–12] Comparison of these results with experiment has led to conflicting claims about the importance and strengths of these interactions.

We feel that to study the effects of e-e interactions on the properties of conducting polymers, it is necessary to examine thoroughly the validity and correct interpretation of the simple models themselves. In the following discussion, the term "simple model" is used to refer to any one-dimensional model Hamiltonian with a single electronic (π) band with *at most* short-range electron-electron interactions. We will show that such an examination yields a partial resolution of the controversy. In this paper, we present a general model for the e-e interactions in terms of which we discuss the following questions: (i) To what extent can conducting polymers, which are quite complicated materials, actually be described by a simple model Hamiltonian? (ii) What are the effects of e-e interactions on the properties of these polymers and what are the interaction strengths indicated by the experimental data?

The paper is arranged as follows. In Sec. II, we discuss the relation between the physics of real conducting polymers and the simple models. Two conditions *for the validity of the simple models* are obtained there. In Sec. III, we derive expressions for a large range of properties of conducting polymers obtained by the perturbative solution of a model Hamiltonian which incorporate the most general form of (short-range) e-e interactions. Conditions for the validity of perturbation theory are also derived. In Sec. IV, our results are compared to the experimental data with emphasis on those quantities which would be zero in the absence of e-e interactions. Finally, in Sec. V, we discuss the validity of both the model and the perturbative solution in light of the results of Sec. IV, and the relation of the present work to other approaches.

Our results as they apply to $(\mathrm{CH})_x$ can be summarized as follows. (1) The simple models are only semiquantitatively reliable. Corrections to physical quantities due to interactions which are missing from the model are expected to make on the order of 20% corrections to observable quantities such as the soliton creation energy. (2) To comparable accuracy ($\sim 30\%$) the properties of the model can be computed using low-order perturbation theory in the e-e interactions. Thus, the major effect of interactions is to lift some of the degeneracies that are present in the noninteracting model and to make small quantitative corrections to other quantities. (3) Crude estimates of the values of the various interaction parameters can be obtained by comparing the theory with experiment.

II. PHYSICAL INTERPRETATION OF THE SIMPLE MODEL

The many degrees of freedom (e.g., σ bands, π bands, lattice vibrations, etc.) and the complicated interactions in the real conducting polymers, coupled with the importance of fluctuations and nonlinear phenomena characteristic of one-dimensional systems, make a complete theoretical description impractical. However, in many cases it is possible to construct a simple effective model (as in Landau theory of a normal Fermi liquid) if one is only interested in the low-energy long-wavelength excitations of the system. This is a consequence of the fact that in many conducting polymers, the characteristic correlation length ξ_0 is much larger than the lattice constant a, so the low-energy excitations of the systems are relatively insensitive to details of the underlying lattice structures. ($\xi_0/a = W/\Delta_0$ is large since the π-band width, $2W$, is large compared to the band gap, $2\Delta_0$.) One can treat these systems in the continuum approximation obtained by expanding all interactions about the Fermi surface. Therefore, it is possible to derive the properties of the system accurately from an effective Hamiltonian which describes a field theory with a finite cutoff. There are only a few relevant interactions in the continuum limit and the general forms of these interactions can be determined easily. However, the effective interaction strengths in the model are extremely difficult to derive from first principles and must generally be deduced from experiment. Despite appearance, the interactions are not truly bare microscopic interactions.

Since any simple model is only an approximate representation of the real material, it is important from the outset to examine the conditions for the validity of these models. As we pointed out in Ref. 4, the simple models only give a satisfactory description of the electronic structure of the real materials near the Fermi energy[13] (see Fig. 1). Those properties of the models which depend only on states near the Fermi surface are independent of the details of the model and hence we will refer to them as "universal." Those which depend on the states near the band edges are model dependent, hence "nonuniversal." Since the simple models are incorrect near the band edges, only the universal terms are meaningful. (See Ref. 4 for a more complete discussion.) We thus obtain two important criteria for the validity of the simple models. First, the band gap $2\Delta_0$, which sets the scale of interesting energies, must be small compared to the π-band width $2W$; equivalently, the characteristic correlation length ξ_0 must be large compared to the lattice constant a

$$\frac{\Delta_0}{W} \cong \frac{a}{\xi_0} \ll 1 . \tag{1}$$

Second, the characteristic magnitude of the e-e interactions $\bar{U}$ must be small compared to the valence band width

$$\frac{\bar{U}}{W} \ll 1 . \tag{2}$$

This second condition emerges from detailed analysis of the structure of high-order perturbation theory (see discussion in Refs. 4 and 14). It can be understood on the basis of a simple intuitive argument. An interaction with strength $\bar{U}$ will strongly mix the states with energy

$$|E - E_f| \leq \bar{U} , \tag{3}$$

where E_f is the Fermi energy. Clearly, only if condition (2) is satisfied, will the results be independent of the band structure near the band edges. Therefore, conditions (1) and (2) are necessary for the validity of the simple models.

Since most conducting polymers have a small band gap compared to π-band width, condition (1) is always satisfied. However, condition (2) indicates that the simple models are only valid when e-e interactions are weak ($\bar{U}/W \ll 1$). Detailed comparison with experiment of results obtained from the simple models, even from the exact solution of the models, is extremely difficult to justify when Coulomb interactions are not weak. We conclude that model calculations are only valid to lowest order in $\bar{U}/W$. *At best,* the results are qualitatively correct outside this regime, but even that is not guaranteed. For instance, we showed in Ref. 4 that in the presence of strong e-e interactions, charge-conjugation symmetry (which is a feature of the simple models), is strongly broken.

The successes of the simple noninteracting models in explaining many experimental observations suggest that the e-e interactions in these materials are indeed weak. For instance, the dimerization in $(\mathrm{CH})_x$, was found[15] to have the magnitude predicted[1] on the basis of the noninteracting SSH model, and an analysis[16] of the Raman spectrum has shown that the Peierls relation between the gap and the electron-phonon coupling constant is well obeyed (see discussion below). Another piece of evidence which strongly supports both the claims that the properties of conducting polymers are insensitive to the band structure far from the Fermi surface, and simultaneously that the interactions are weak, comes from a comparison of the optical absorption spectra of different materials. In Fig. 2, we have plotted the optical absorption coefficient $\alpha(\omega)$, normalized to its peak value $\alpha(\omega_p)$ versus frequency ω in units of the peak frequency ω_p for several conducting polymers: *trans*- and *cis*-$(\mathrm{CH})_x$, polythiophene, polypyrrole, and polydiacetylene. The curves in Fig. 2(a) display a remarkable similarity among the four different conducting polymers. They all lie within about 30% of an average curve. For comparison, note the fact that samples of thermally and electrochemically isomerized *trans*-$(\mathrm{CH})_x$ differ by about 20% [see Fig. 2(b)]. In view of the enormous differences in the structures of these materials, the observed similarity in $\alpha(\omega)$ is remarkable.

If the interactions were weak, this similarity could be readily understood, since the simple models would be accurate and to zeroth order, a single parameter, namely, the gap Δ_0, determines the entire spectrum. The rescaled optical absorption would thus lie on a universal curve [see Eq. (12)]. The striking universality demonstrated in the $\alpha(\omega)$'s thus strongly suggests that in most conducting polymers, conditions (1) and (2) are fairly well satisfied. However, the fact that the optical data of polydiacetylene does not lie on this curve [see Fig. 2(c)], suggests that the

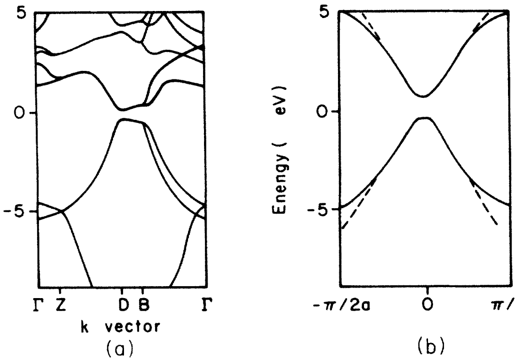

FIG. 1. (a) Calculated band structure of *trans*-$(\mathrm{CH})_x$ from Ref. 13. (b) Band structure of lattice (Solid line) and continuum (dashed line) models of *trans*-$(\mathrm{CH})_x$.

interactions in this material may be quite different than in the others; presumably they are much stronger than in $(\mathrm{CH})_x$ as has been claimed in chemistry literature.[17] We will show that the long-range nature of Coulomb interactions may contribute to this difference.

The model we have studied is a massive field theory which includes (almost) all possible interactions in the continuum limit,

$$H=\sum_s \int dx\,\{\psi_s^\dagger(x)[-i\partial_x\sigma_3+\Delta(x)\sigma_1]\psi_s(x)+g_{\parallel}\psi_{1s}^\dagger\psi_{2s}^\dagger\psi_{1s}\psi_{2s}+g_{1\perp}\psi_{1s}^\dagger\psi_{2\bar{s}}^\dagger\psi_{1\bar{s}}\psi_{2s}+g_{2\perp}\psi_{1s}^\dagger\psi_{2\bar{s}}^\dagger\psi_{2\bar{s}}\psi_{1s}$$
$$+\tfrac{1}{2}g_{3\perp}(\psi_{1s}^\dagger\psi_{1\bar{s}}^\dagger\psi_{2\bar{s}}\psi_{2s}+\psi_{2s}^\dagger\psi_{2\bar{s}}^\dagger\psi_{1\bar{s}}\psi_{1s})+\tfrac{1}{2}g_{4\perp}(\psi_{1s}^\dagger\psi_{1\bar{s}}\psi_{1\bar{s}}\psi_{1s}+\psi_{2s}^\dagger\psi_{2\bar{s}}^\dagger\psi_{2\bar{s}}\psi_{2s})\}$$
$$+\int dx\left[\frac{[\Delta(x)-\Delta_{\mathrm{int}}]^2\omega_Q^2}{2g_0^2}+\frac{\dot{\Delta}^2(x)}{2g_0^2}\right]. \tag{4}$$

Here $\psi_s^\dagger(x)=(\psi_{1s}^\dagger,\psi_{2s}^\dagger)$ is a two-component spinor with components $\psi_{1s}^\dagger(x)$ which creates a right-moving electron of spin s at position x, and $\psi_{2s}^\dagger(x)$ which creates a left-moving electron. $\Delta(x)$ is proportional to the local lattice dimerization, and g_0/ω_Q is the electron-phonon coupling constant. Δ_{int} is the term which breaks the symmetry between the two senses of dimerization [hence $\Delta_{\mathrm{int}}=0$ in *trans*-$(\mathrm{CH})_x$, but $\Delta_{\mathrm{int}}\neq 0$ for other polymers]. The g_i's are the five independent e-e interaction constants in the usual "g-ology" picture.[18] In Eq. (4), we have chosen the units such that $\hbar v_f=Wa=1$, where v_f is Fermi velocity. In these units, the g_i's are dimensionless. We have ignored those terms which are higher than quadratic order in the Bose field $\Delta(x)$ by invoking the small magnitude of the lattice distortion.

The momentum dependence of g's can only be neglected for short-range interactions; for $1/r$ interactions the forward-scattering terms g_2 and g_4 would be infinite. Long-range interactions are also intrinsically three dimensional. Since the actual Coulomb interaction is long range, we should briefly discuss the justification for the use of a short-range one-dimensional model. We are always interested in $2k_F$-type response functions. The forward-scattering lines g_2 and g_4 are thus almost always integrated over k and ω. At frequencies greater than the gap and less than the plasma frequency ω_p the Coulomb interactions are fully screened by the electrons on other chains. Thus, following Ref. 19, we find that whenever the forward-scattering term occurs on an internal leg of a diagram, it is equivalent to a short-range interaction

$$g_{2,4}=g_{2,4}^{(0)}+\frac{e^2}{\epsilon_0 bW}\ln\left[\frac{W}{\hbar\omega_p}\right]. \tag{5}$$

Where $g_{2,4}^{(0)}$ is determined by short-range consideration, e.g., U and V; b is the intra-chain lattice constant; and ϵ_0 is the static dielectric constant; $\omega_p^2=4\pi ne^2/m_e$, where n is the π-electron density. For $(\mathrm{CH})_x$, where $n=10^{22}$ cm^{-3}, $\hbar\omega_p\sim 3.5$ eV so the Coulomb interaction is effectively screened. On the other hand, in polydiacetylene, where $n=10^{21}$ cm^{-3}, $\hbar\omega_p\sim 1.1$ eV so the forward scattering is largely unscreened. This suggests that the e-e interactions are much stronger in polydiacetylene which explains the observed difference in the behavior of polydiacetylene in the optical absorption data [Fig. 2(c)].

Hamiltonian (4) is a (1 + 1)-dimensional field theory which is convenient for analytic analysis. Moreover, this model contains many other widely studied models as spe-

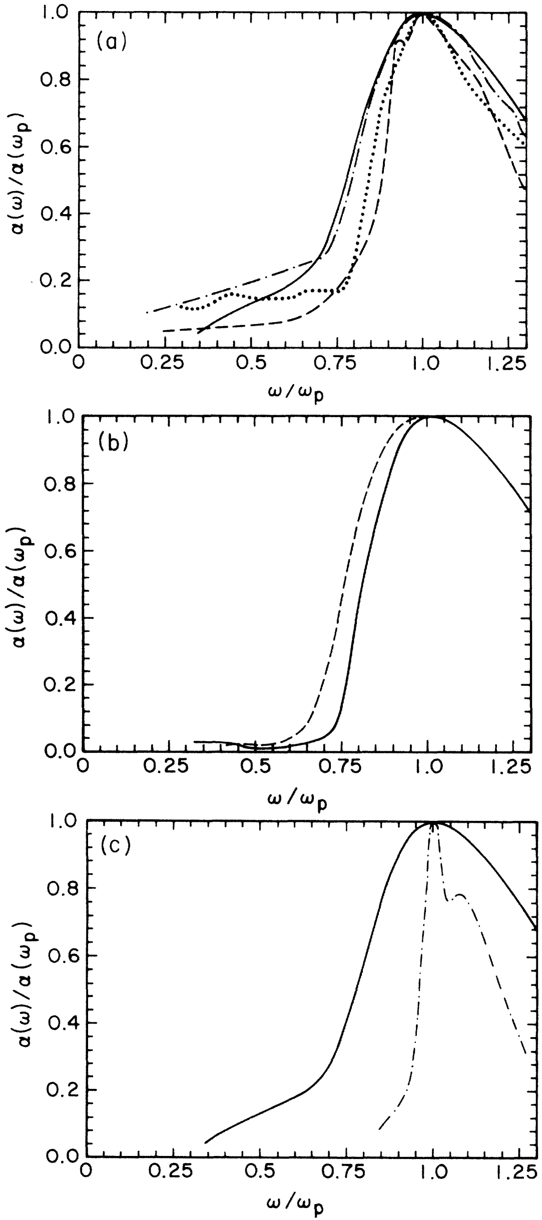

FIG. 2. (a) Rescaled absorption coefficients for various conducting polymers. (Solid line) *trans*-$(\mathrm{CH})_x$; (dashed line) *cis*-(CH); (dashed-dotted line) polythiophene; (dotted line) polypyrrole. (b) Rescaled optical absorption coefficients for thermally (solid line) and electrochemically (dashed line) isomerized *trans*-$(\mathrm{CH})_x$. (c) Rescaled optical absorption coefficients for *trans*-$(\mathrm{CH})_x$ (solid line) and polydiacetylene (broken line).

cial cases. For $g_{i\perp}=0$, the model is equivalent to the massive Thirring Model. [This equivalence was exploited in Ref. 14 to identify the universal terms in the theory, and hence to justify condition (2)]. For $g_{\parallel}=-4V_{\parallel}/W$, $g_{1\perp}=-g_{3\perp}=(U-2V_{\perp})/W$, $g_{2\perp}=g_{4\perp}=(U+2V_{\perp})/W$, the model is the continuum limit of the SSH-extend Hubbard model with $H_{\text{int}}=U/2\sum_{n,s}[\rho_{ns}\rho_{n\bar{s}}]+\sum_{ns}[V_{\parallel}\rho_{ns}\rho_{n+1,s}+V_{\perp}\rho_{ns}\rho_{n+1,\bar{s}}]$. This latter model has been intensely studied by Monte Carlo[6–8] thus providing us with an additional check of our perturbative results.

The model in Eq. (4) is not well-defined unless a regularization or cutoff scheme is specified. The results are generally dependent on the cutoff scheme, but the universal terms are scheme independent. Unfortunately, our model has six unknown parameters. Our strategy is to calculate various properties of the model, and then determine these parameters roughly by fitting the results with experiment data. The resulting values for the g's should be interpreted as being characteristic, but not taken too seriously in detail.

Since the simple model in Eq. (4) is only valid when interactions are weak, the model can be solved by straightforward (though tedious) perturbation theory. The condition for the validity of low-order perturbation theory is

$$\frac{\bar{U}}{2\pi W}\ln\left[\frac{2W}{\Delta_0}\right]\ll 1\ . \tag{6}$$

The logarithmic dependence on the cutoff is the expected ultraviolet behavior of Fermions in $1+1$ dimension. Note that the presence of the factor $(2\pi)^{-1}$ in Eq. (6) which occurs explicitly in each order of perturbation theory, helps explain the fact that Monte Carlo calculations differ substantially from perturbation results only when $\bar{U}$ is larger than W (see Fig. 3). For most conducting polymers $\ln(2W/\Delta_0)\sim 2$, so conditions (2) and (6) are roughly equivalent. Therefore, for most conducting polymers, low-order perturbation calculations are accurate so long as the simple models are valid.

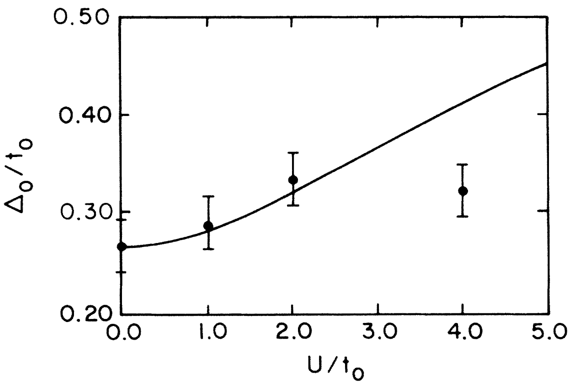

FIG. 3. Lattice order parameter Δ_0 as function of on-site Hubbard interaction U. Solid line is the second-order perturbation theory results from Ref. 3; the full circles are the Monte Carlo results from Ref. 6.

III. PERTURBATIVE RESULTS

We have evaluated the perturbative effects of the interactions on the various quantities of physical importance. Here we report some of our results.

A. Perfectly dimerized lattice

For a perfect dimerized chain, we have calculated the effects of electron-electron interactions on the physical gap, the magnitude of the dimerization, the phonon spectrum, and the optical absorption coefficient by using standard Green's function methods.

(i) The physical gap. Up to two-loop order the physical gap is found to be

$$\Delta=\Delta_0\left\{1-\frac{g'}{2\pi}\ln\left[\frac{2W}{\Delta_0}\right]+\left[\frac{g'}{2\pi}\right]^2\ln^2\left[\frac{2W}{\Delta_0}\right]\right.$$
$$+\left[\frac{g''}{2\pi}\right]^2\left[\ln^2\left[\frac{2W}{\Delta_0}\right]+\ln(2)\ln\left[\frac{2W}{\Delta_0}\right]\right.$$
$$\left.\left.+0.2370+O\left[\frac{\Delta_0}{2W}\right]\right]+O(g^3)\right\}\ , \tag{7}$$

where

$$g'\equiv g_{1\perp}+g_{3\perp}+g_{\parallel}\ , \tag{8}$$

$$(g'')^2=g_{1\perp}g_{2\perp}-g_{1\perp}g_{3\perp}-g_{2\perp}g_{3\perp}-\tfrac{1}{2}g_{\parallel}^2\ . \tag{9}$$

This result explicitly shows that the nth-order term in the perturbation series has the form

$$(g/2\pi)^n[A_n\ln^n(2W/\Delta_0)+B_n\ln^{n-1}(2W/\Delta_0)+\cdots]\ .$$

The leading coefficient A_n is independent of the cutoff scheme while other terms are scheme dependent. This is not an artifact of perturbation theory; the same scheme dependence appears in exact solutions of this sort of model as discussed in detail in Ref. 14. In most polymers, $\ln(2W/\Delta_0)\cong 2-3$, so the next-to-leading terms are not completely negligible compared to the leading terms. Typically, much of this scheme dependence can be absorbed into a scheme-dependent redefinition of the coupling constants. Thus, it is important to remember that even the magnitudes of the interactions are somewhat cutoff scheme dependent. To first order in g, the entire effects of the e-e interactions on the one-particle Green's function are contained in the renormalization of the gap; in higher order there are further vertex effects. Note that in the Hubbard model, the first effect occurs to order U^2. Hubbard interactions thus increase the gap for fixed dimerization, regardless of the sign of U.

(ii) The magnitude of the dimerization Δ_0 is found by solving the self-consistency equation, $dE_T/d\Delta_0=0$, which expresses the fact that the ground-state value of Δ_0 is that which minimizes the total energy per unit length E_T. From the Hellmann-Feynman theorem it follows that the self-consistency relation can be expressed as

$$\begin{aligned}\Delta_0 &= \Delta_{\text{int}} - \frac{g_0^2}{\omega_Q^2}\sum_s \langle \psi_s^\dagger \sigma_x \psi_s \rangle_{\Delta_0} \\ &= \Delta_{\text{int}} + \frac{2g_0^2\Delta}{\omega_Q^2\pi}\ln\left[\frac{2W}{\Delta}\right][1+O(g^2)] , \end{aligned} \tag{10a}$$

where $\langle\ \rangle_{\Delta_0}$ means ground-state expectation value with fixed Δ_0, and, in the second line, the only effect of e-e interactions to the first order in g is to replace Δ_0 by Δ in the usual Peierls relation. For the case of *trans*-(CH)$_x$, where $\Delta_{\text{int}}=0$, Eq. (10a) can be inverted to obtain an expression for Δ as a function of g_0

$$\Delta = 2W\exp\left[-\frac{1}{2\lambda}\left[1+\frac{g'}{4\pi\lambda}+O(g^2)\right]\right] , \tag{10b}$$

where $\lambda \equiv g_0^2/\pi\omega_Q^2$ is the dimensionless electron-phonon coupling, and g' is defined in Eq. (8). Note that the dependence of Δ on λ is fundamentally altered if g' is not small.

(iii) The optical phonon spectrum which we have computed to the first order in the e-e interaction is

$$\omega^2(k) = \omega_0^2\left[\frac{(1+\eta^2)^{1/2}}{\eta}\sinh^{-1}\eta - \frac{g'}{2\pi}\ln\left[\frac{2W}{\Delta_0}\right] + \frac{g_{\parallel}}{2\pi}\frac{(\sinh^{-1}\eta)^2}{4\eta^2(1+\eta^2)}\right] , \tag{11}$$

where $\omega_0^2 \equiv 2\lambda\omega_Q^2$, and $\eta \equiv v_f k/2\Delta$ with Δ the physical gap [see Eq. (6)].

The first term in Eq. (11) is exactly the result of Nakahara and Maki[20] except that bare gap Δ_0 is replaced by the physical gap Δ. In addition, the e-e interaction gives an extra contribution to the phonon spectrum [the last two terms in Eq. (11)].

(iv) The optical absorption, to first order is

$$\alpha(\omega) \propto \begin{cases} \dfrac{1}{z^2(z^2-1)^{1/2}} + \dfrac{g_{\parallel}}{2\pi}\dfrac{\cosh^{-1}(z)}{z(z^2-1)}, & \text{if } z \geq 1 \\ 0, \ \text{if } z < 1 \end{cases} \tag{12}$$

where $z \equiv \hbar\omega/2\Delta$. Here again, the first term in Eq. (12) has the same form as the noninteracting result except Δ_0 is replaced by Δ. Obviously, this term, properly rescaled, is the same for all materials. However, the second term is proportional to $g_{\parallel}$. In different materials, with different values of $g_{\parallel}$, the magnitude of this term will not be the same. The presence of the second term in Eq. (12) makes the rescaled optical absorption curves of the different conducting polymers differ from the universal curve slightly. As stated previously, the similarity in the observed optical absorption among the various polymers strongly indicates the interactions in these materials are "weak." Note Eq. (12) is valid only for weak e-e couplings. If the e-e couplings are strong, then all g's would enter into the expression for the optical absorption and one should expect even greater dissimilarity between the different materials.

B. Properties of the soliton

In *trans*-(CH)$_x$, the twofold degenerate ground state permits the existence of domain wall or soliton excitations. These are characterized by a a region of width ξ over which the lattice order parameter $\Delta(x)$ changes sign. The soliton can exist in three charge states, $Q=+e$, 0, or $-e$, and has the reversed charge-spin relations from the constituent electrons; it is spinless when charged and has spin $\frac{1}{2}$ when neutral. In Ref. 2 it was shown that for the continuum model without e-e interactions, the soliton shape which minimizes its creation energy is

$$\Delta(x) = \Delta_0\tanh\left[\frac{x}{\xi}\right] . \tag{13}$$

The soliton creation energy as a function of its width was also calculated there, and found to take its minimal value of $E_s = 2\Delta_0/\pi$ when $\xi=\xi_0$, regardless of the charge state of the soliton. We have calculated to first order the effects of interactions on the soliton creation energy, width, and in the case of the neutral soliton, the spin density. In these calculations, we have assumed soliton shape as in Eq. (13). This approximation is examined in Appendix A.

(i) The soliton creation energy as a function of its width can be expressed in terms of two dimensionless functions $f_j(\xi/\xi_0)$:

$$E_s = \frac{2\Delta}{\pi}\left[f_0\left[\frac{\xi}{\xi_0}\right] \pm V_1 f_1\left[\frac{\xi}{\xi_0}\right] + O(g^2)\right] , \tag{14}$$

where $V_1 = \pi/48\ (g_{1\perp}+g_{2\perp}-g_{3\perp}+g_{4\perp})$, and the + and − refer, respectively, to the charged and neutral soliton. Note that charge-conjugation symmetry implies the exact result that E_s is independent of the sign of the charge. The functions f_j can be computed to arbitrary accuracy. $f_0(\nu)$ is calculated in Ref. 2 (see Fig. 1 in Ref. 2); and

$$f_1(\nu) = \frac{3}{\sqrt{\pi}\nu}\frac{\Gamma^2(\nu+\frac{1}{2})\Gamma(2\nu)}{\Gamma^2(\nu)\Gamma(2\nu+\frac{1}{2})} ,$$

where $\nu \equiv \xi/\xi_0$. However, in the perturbative regime they can be expanded to low order in $\chi \equiv (\xi-\xi_0)/\xi_0 = \nu - 1$: $f_0 = 1+\frac{1}{2}\kappa\chi^2+O(\chi^3)$, where $\kappa \approx 0.25$; $f_1 = 1-\frac{1}{3}\chi + O(\chi^2)$. The equilibrium width for a charged (ξ_+) or neutral (ξ_-) soliton is obtained by minimizing E_s with respect to ξ:

$$\xi_\pm = \xi_0\left[1 \pm \frac{V_1}{3\kappa}\right] . \tag{15}$$

In this limit,

$$E_{s+}(\xi^+) - E_{s0}(\xi^-) = \frac{4\Delta_0}{\pi}V_1 . \tag{16}$$

In Fig. 4, we plot the soliton creation energy as a function of its width for different values of V_1. The curves are quite flat near the equilibrium width. This is due to the softness of the soliton shape mode.

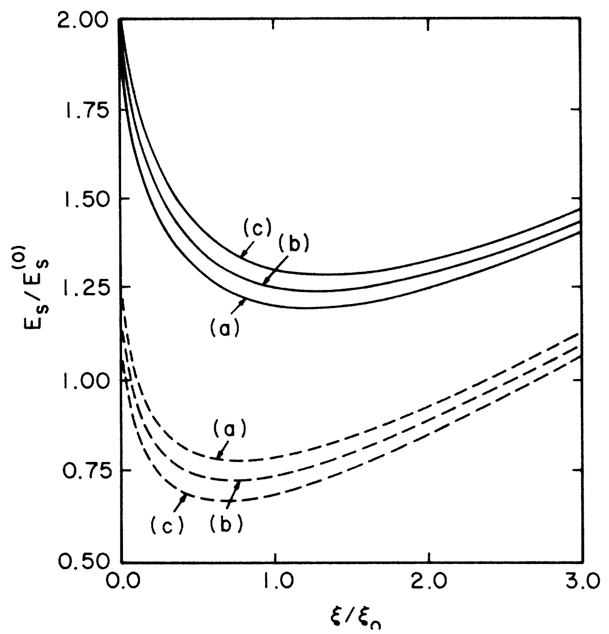

FIG. 4. Charged (solid line) and neutral (dashed line) soliton creation energy as function of its width. (a) $V_1=0.21$; (b) $V_1=0.26$; (c) $V_1=0.31$.

(ii) The spin density of the neutral soliton is the difference between spin-up and spin-down densities,

$$s(x)=\langle\rho_\uparrow(x)\rangle-\langle\rho_\downarrow(x)\rangle$$
$$=\frac{1}{\xi_0}\operatorname{sech}^2\left[\frac{x}{\xi_0}\right][(1+V_4)\cos^2(k_fx)-V_4\sin^2(k_fx)]+\tilde{S}(x)\ , \qquad (17)$$

where $V_4=1/4\pi(g_{1\perp}+g_{2\perp}-g_{3\perp}+g_{4\perp})\ln(2W/\Delta)$ and $\tilde{s}(x)$ is a complicated function which has the property that it yields zero when averaged over even numbered sites ($k_fx=\pi n$) or odd numbered sites ($k_fx=\pi n+\pi/2$) (see Appendix B). It is easy to check that Eq. (17) satisfies the sum rule $\int s(x)dx=1$ (particle conservation). Thus, the major effect of e-e interactions is to increase the spin density on the even sites, and induce a compensating negative spin density on odd sites.

Besides the soliton, other excitations such as polarons and bipolarons had been investigated by several authors using noninteracting models.[21,22] The polaron or bipolaron is a bound pair of solitons where the order parameter takes the form

$$\Delta(x)\equiv\Delta_p(x)$$
$$=\Delta_0\left\{1-(\xi_0/\xi)\left[\tanh\left[\frac{x+x_0}{\xi}\right]-\tanh\left[\frac{x-x_0}{\xi}\right]\right]\right\}, \qquad (18)$$

where the width ξ is determined by

$$\xi_0/\xi=\tanh\left[\frac{2x_0}{\xi}\right]. \qquad (19)$$

As in the soliton case, we have calculated the polaron (bipolaron) creation energy as a function of its width ξ by assuming Eq. (18) (see Appendix A for derivation):

$$E_p=(n_+-n_-+2)\epsilon+\frac{4}{\pi}\Delta_0\xi_0/\xi-\frac{4\epsilon}{\pi}\tan^{-1}\left[\frac{\xi_0}{\xi}\frac{\Delta_0}{\epsilon}\right]+\frac{8}{\pi}\Delta_{\rm int}\frac{\Delta_0}{\Delta_0-\Delta_{\rm int}}\ln\left[\frac{2W}{\Delta_0}\right][\tanh^{-1}(\xi_0/\xi)-\xi_0/\xi]$$
$$+\frac{\Delta_0}{12}(g_{1\perp}+g_{2\perp}-g_{3\perp}+g_{4\perp})(f_{+\uparrow}+f_{-\uparrow}-1)(f_{+\downarrow}+f_{-\downarrow}-1)\xi_0/\xi$$
$$-\frac{\Delta_0}{2}\{g_{\|}[(f_{+\uparrow}+f_{-\uparrow}-1)^2+(f_{+\downarrow}+f_{-\downarrow}-1)^2]+\tfrac{1}{2}(g_{1\perp}-g_{2\perp}-g_{3\perp}-g_{4\perp})(f_{+\uparrow}+f_{-\uparrow}-1)(f_{+\downarrow}+f_{-\downarrow}-1)\}$$
$$\times\left[\frac{\epsilon\xi}{\Delta_0\xi_0}\right]^2[\tanh^{-1}(\xi_0/\xi)-\xi_0/\xi]\ , \qquad (20)$$

where $\epsilon=\Delta_0[1-(\xi_0/\xi)^2]^{1/2}$ and $\pm\epsilon$ are the energies of two mid-gap states; and f_{+s} (f_{-s}) is the occupancy number of electrons with spin s in state ϕ_+ (ϕ_-) and $n_\pm=\sum_s f_{\pm s}$.

Define $\epsilon\equiv\Delta_0\cos\theta$; $\xi_0/\xi\equiv\sin\theta$ ($0\le\theta\le\pi/2$):

$$N\equiv n_+-n_-+2;\quad F_s\equiv(f_{+s}+f_{-s}-1)$$
$$\Gamma\equiv\frac{2\Delta_{\rm int}}{\Delta_0-\Delta_{\rm int}}\ln(2W/\Delta_0)=\frac{\Delta_{\rm int}}{\Delta_0}\pi\left[\frac{\omega_0^2}{g_0^2}\right]. \qquad (21)$$

Equation (20) becomes

$$E_p/\Delta_0=N\cos\theta+\frac{4}{\pi}(\sin\theta-\theta\cos\theta)+\frac{4}{\pi}\Gamma(\tanh^{-1}(\sin\theta)-\sin\theta)$$
$$+\tfrac{1}{4}(g_{1\perp}+g_{2\perp}-g_{3\perp}+g_{4\perp})F_\uparrow F_\downarrow\sin\theta-\tfrac{1}{2}[g_{\|}(F_\uparrow^2+F_\downarrow^2)+\tfrac{1}{2}(g_{1\perp}-g_{2\perp}-g_{3\perp}-g_{4\perp})F_\uparrow F_\downarrow]\cot^2\theta[\tanh^{-1}(\sin\theta)-\sin\theta]. \qquad (22)$$

The width is determined by minimizing Eq. (22):

$$
\begin{aligned}
0=\frac{1}{\Delta_0}\frac{d}{d\theta}E_p={}&-N\sin\theta+\frac{4}{\pi}\theta\sin\theta+\Gamma\sin\theta\tan\theta\\
&-\tfrac{1}{12}(g_{1\perp}+g_{2\perp}-g_{3\perp}+g_{4\perp})F_\uparrow F_\downarrow\cos\theta\\
&-\tfrac{1}{2}[g_{\|}(F_\uparrow^2+F_\downarrow^2)+\tfrac{1}{2}(g_{1\perp}-g_{2\perp}-g_{3\perp}-g_{4\perp})F_\uparrow F_\downarrow]\left[\cos\theta-\frac{2\cos\theta}{\sin^3\theta}[\tanh^{-1}(\sin\theta)-\sin\theta]\right] .
\end{aligned}
\tag{23}
$$

From Eqs. (22) and (23), one can readily get the polaron (bipolaron) creation energy and its equilibrium width as functions of the e-e interaction coupling constants and the intrinsic gap Δ_{int}.

In the weak-interaction limit, θ will differ from its noninteracting value θ_0 by a small amount, δ. That is, $\theta=\theta_0+\delta$ with

$$\theta_0+\Gamma\tan\theta_0=\frac{\pi}{4}N . \tag{24}$$

To the first order in e-e interactions, one can solve Eq. (23) by expanding to linear terms in δ. This gives

$$
\begin{aligned}
\delta=\frac{1}{A}\{&F_\uparrow F_\downarrow(g_{1\perp}+g_{2\perp}-g_{3\perp}+g_{4\perp})B\\
&+[(F_\uparrow^2+F_\downarrow^2)g_{\|}+\tfrac{1}{2}(g_{1\perp}-g_{2\perp}-g_{3\perp}-g_{4\perp})F_\uparrow F_\downarrow]C\} ,
\end{aligned}
\tag{25}
$$

where

$$
\begin{aligned}
A={}&-N\cos\theta_0+\frac{4}{\pi}(\theta_0\cos\theta_0+\sin\theta_0)\\
&+\frac{4}{\pi}\Gamma\sin\theta_0\left[1+\frac{1}{\cos^2\theta_0}\right] ,
\end{aligned}
\tag{26}
$$

$$B=-\tfrac{1}{12}\cos\theta_0 \tag{27}$$

$$C=\tfrac{1}{2}\cos\theta_0\left[1+\frac{2}{\sin^2\theta_0}-\frac{2}{\sin^3\theta_0}\tanh^{-1}(\sin\theta_0)\right] . \tag{28}$$

When $\Delta_{\text{int}}=0$ [e.g., in *trans*-(CH)$_x$], only the polaron is stable. For the polaron configuration, $N=1$; $F_\uparrow=1$; $F_\downarrow=0$; $\theta_0=\pi/4$. Then we get

$$\delta=g_{\|}(\pi/4)[\tfrac{5}{2}-2\sqrt{2}\ln(1+\sqrt{2})] , \tag{29}$$

$$\theta=(\pi/4)\{1+g_{\|}[\tfrac{5}{2}-2\sqrt{2}\ln(1+\sqrt{2})]\} , \tag{30}$$

$$E_p=\frac{2\sqrt{2}}{\pi}\Delta_0\left[1-\frac{\pi g_{\|}}{8}[\sqrt{2}\ln(1+\sqrt{2})-1]\right] , \tag{31}$$

$$\xi=\sqrt{2}\xi_0\{1+(\pi/4)g_{\|}[2\ln(1+\sqrt{2})-5/2\sqrt{2}]\} , \tag{32}$$

$$
\begin{aligned}
2\chi_0={}&\sqrt{2}\ln(1+\sqrt{2})\\
&\times\xi_0\left[1-\frac{\pi g_{\|}[2-\ln(1+\sqrt{2})][2\sqrt{2}\ln(1+\sqrt{2})-\frac{5}{2}]}{4\sqrt{2}\ln(1+\sqrt{2})}\right].
\end{aligned}
\tag{33}
$$

IV. COMPARISON WITH EXPERIMENT

In this section, we compare some of our results with experiment in order to estimate the magnitudes of the various e-e interaction coupling constants. Since none of the spectroscopic features are sharp, none of the parameters, not even the gap parameter Δ, can be determined precisely from experiment. Moreover, the simple models are accurate descriptions of the properties of real materials only to leading order in Δ/W and $g/2\pi$, thus one should interpret the values of the parameters we derive by comparing with experiment as being only semiquantitatively meaningful.

Since the most extensive experimental studies of any conducting polymer have been of *trans*-(CH)$_x$, we have only analyzed the (CH)$_x$ data, although our results could apply to other materials as well.

(i) The ratio of average spin density on the even and odd sites for a neutral soliton. In the noninteracting model, the spin density on odd sites vanishes, so the ratio of average spin density on odd and even sites (ρ_-/ρ_+) is zero; in the presence of e-e interactions[23(a)] there is negative spin density on the odd sites which leads to a finite ρ_-/ρ_+. According to Eq. (16), this ratio is $-V_4/(1+V_4)$. The ratio has been measured recently by Thomann *et al.*[23(b)] to be $\rho_-/\rho_+=-\frac{1}{3}$ in (CH)$_x$. From this we deduce that $V_4=\frac{1}{2}$, which in turn implies that the dimensionless combination, $(g/2\pi)\ln(2W/\Delta_0)$ which enters perturbation theory is small, $(g/2\pi)\ln(2W/\Delta)\approx\frac{1}{4}$; the e-e interactions are indeed moderately weak. If we relate this to the extended Hubbard model, the result implies $U\approx 3\sim 4$ eV. Note that in the context of this model, the ratio only depends upon the on-site interaction U, not upon the nearest-neighbor interaction V. The physics behind this is simple; since the electronic density vanishes on odd sites in the zeroth order, the nearest-neighbor e-e interaction can have no effect on the spin density in first-order perturbation theory.

The spin density is an equilibrium quantity so that the measured value is quite reliable and the physical interpretation is clear. Also the theoretical result yields a value which is moderately insensitive to the magnitude of parameter Δ_0 (which is not precisely known). We therefore regard the spin-density measurement as the most unambiguous measurement of the strength of the e-e interaction in (CH)$_x$.

(ii) The photoinduced optical absorption. In the photoinduced optical absorption measurement, two peaks at $\hbar\omega_L=0.45$ eV and $\hbar\omega_H=1.40$ eV had been observed.[24]

We believe that these peaks are due to electronic transitions which involve charged and neutral solitons. To be precise, the low-energy peak corresponds to the process $S^- \rightarrow S^0 + e^-$; (or equivalently, $S^+ \rightarrow S^0 + e^+$) and we interpret the high-energy peak as the process $S^0 \rightarrow S^+ + e^-$ (or $S^0 \rightarrow S^- + e^+$) (see Ref. 25).

To calculate the peak positions, several subtleties should be taken into account. (a) the electron final state is properly a packet state with energy E_e instead of any particular one-electron eigenstate. (b) The Coulomb correlation, (ΔE_{Se}), between the extra electron and the soliton in the final state has to be considered. (c) For the high energy peak, the long-range Coulomb interaction cannot be neglected since the final state consists of two far-separated oppositely charged particles (the electron and soliton). This contributes an extra term $E_c > 0$ (the magnitude of E_c should be of order $\sim e^2/\epsilon_0 \xi_0 \sim 0.5$ eV) to the high-energy peak position. Combining these results, we obtain the following relations for the observed peak positions:

$$\begin{aligned} \hbar\omega_L &= E_e - (E_{S^+} - E_{S^0}) + \Delta E_{S^0 e^-} , \\ \hbar\omega_H &= E_e + (E_{S^+} - E_{S^0}) + \Delta E_{S^+ e^-} + E_c . \end{aligned} \tag{34}$$

Let us discuss the terms in this expression that we have not evaluated previously in Sec. III. The optical absorption coefficient is proportional to the current. In our model, the current operator is σ_z, so the wave-packet state is computed as

$$| \psi_p \rangle = N \sum_{k \in \mathrm{CB}} | k \rangle \langle k | \sigma_z | \phi_0 \rangle \equiv \sum_k B_k | k \rangle , \tag{35}$$

where the sum is over all states in the conduction band, and $| \phi_0 \rangle$ is the mid-gap state. In the first-order perturbation theory, we can approximately take the states in Eq. (22) as those in the noninteracting model. It is easy to show

$$B_k = \pi \left[\frac{\xi_0}{2L} \right]^{1/2} \operatorname{sech} \left[\frac{\xi_0 k \pi}{2} \right] . \tag{36}$$

The expectation value of the Hamiltonian in the wave-packet state can be readily evaluated, to yield

$$E_e = 1.1\Delta_0 - \tfrac{1}{3}\Delta_0 \frac{g'}{2\pi} \ln \left[\frac{2W}{\Delta_0} \right] \tag{37}$$

and

$$\begin{aligned} \Delta E_{Se^-} = \frac{\Delta_0}{12} [g_{\parallel} \mp \tfrac{1}{6} (g_{1\perp} + g_{2\perp} - g_{3\perp} + g_{4\perp}) \\ \mp (-g_{1\perp} + g_{2\perp} + g_{3\perp} + g_{4\perp})] , \end{aligned} \tag{38}$$

where $-$ $(+)$ refer to charged (neutral) soliton. $E_{S^+} - E_{S^0}$ is evaluated in Sec. III, Eq. (16).

Obviously, there are too many parameters in Eq. (34) for a meaningful fit to the experiment. In order to estimate the characteristic magnitudes of the e-e coupling constants, we imagine that the g's can be parametrized in terms of the interaction of extended Hubbard model (i.e., U and V) with $V_{\parallel} = V_{\perp}$. Using the value of U estimated from spin density experiment ($U = 4$ eV), we find from Eq. (16) that the creation energy splitting $E_{S^+} - E_{S^-} = 0.25$ eV (see Fig. 4). Taking this value and the experimental values for $\hbar\omega_L$ and $\hbar\omega_H$, we get $V \approx -U/2 \approx -2$ eV; and $E_c \sim 0.3$ eV. Again, the magnitudes of the e-e interactions are within the perturbative regime.

At first glance, the negative V obtained above looks quite strange. However, it is all natural in the g-ology picture. In fact, the noninteracting model describes a quasiparticle system. Some of the effects of the Coulomb correlation have already been taken into account in an average sense. A negative V does not necessarily really mean attractive interactions between electrons. It only tells us that in such half-filled systems, electrons prefer to avoid each other. The effect of a negative V is similar to the effect of a positive U; it is also a consequence of e-e repulsion.

We repeat that the above estimates are fairly crude. Several sources which contribute to the uncertainty in the above analysis are (a) All five coupling constants g_i should be fit independently. In principle, they cannot be represented simply by a U and a V. (b) The experiments do not measure soliton creation energy very precisely. For instance, the low-energy peak in the photoinduced optical absorption experiment has a half-width about 0.3 eV. (c) The corrections due to interactions far from the Fermi surface, which may be as large as 20–30 %, are of course not correctly included in any simple models. Nonetheless, it is gratifying to obtain results which are consistent with the spin-density measurements.

V. DISCUSSION AND CONCLUSION

The effects of electron-electron interactions on the properties of conducting polymers have been studied by a variety of approaches and utilizing a number of different models. We here comment briefly on what our results imply concerning the proper interpretation of these other results, and conversely what these results imply concerning the validity of our approach.

(1) *Models.* Most[6–9] of the numerical approaches involve the solution of a finite chain problem and take as their starting point the extended SSH Hubbard model. This model has only interaction parameters, U and V. There is no compelling reason we know of to expect this *model* to be quantitatively reliable, since even in the weak coupling limit there are five independent coupling constants g_i [see subsection (3) below]. The model, indeed any simple one-band model, is even less reliable in the strong coupling limit, $\overline{U}/W > 1$, since the full-band structure, which is tremendously oversimplified in the model, plays a role in the determining of the low-energy properties of the material (see Refs. 4 and 14). Numerical studies have also been performed for the *PPP* model[10] with long-range $1/r$ interactions. While this model may, in fact, be correct for an isolated polymer chain, when the chain is embedded in a solid, or even in a solution, three-dimensional screening effects are always relevant. For most purposes, this implies that the effective interactions can be taken to be short ranged (see Ref. 19).

(2) *Accuracy of perturbation theory.* The numerical

solutions of the extended SSH Hubbard model are extremely useful for understanding the qualitative effects of interactions, and, for our purposes, can be used as important bench marks for testing the accuracy of perturbation theory. We have extensively compared perturbative results with numerical results for the Hubbard model as shown in Fig. 3. From this comparison we conclude that perturbation theory is quite reliable out to $U/2t_0 \lesssim 1$. For $U/2t_0 > 2$, perturbation theory breaks down rather catastrophically. (Note, for $U/2t_0 > 2$, strong-coupling perturbation theory in powers of t_0/U becomes quite accurate.)

(3) *Renormalized perturbation theory.* We have recently received a report by Horvitz and Solyom[26] (HS) which contains an elegant application of renormalization-group techniques to essentially the same model as we have analyzed. In fact, HS have summed up the leading logarithmic contribution $[\sim \ln(2W/\Delta_0)]$ to all orders in g. The results agree with ours in the weak-coupling regime, $(g/2)\ln(2W/\Delta_0) \ll 1$. The approach is not, however, easily generalized to permit the study of the effects of interactions on properties of solitons. Moreover, as noted by HS, since $\ln(2W/\Delta_0)$ is of order 2, it is not clear that the interactions are fully renormalized.

(4) *Comparison with experiment.* We have deduced the value of two combinations of coupling constants from a fit to experiment. To facilitate comparison with other theoretical work, we have quoted the results in terms of equivalent values of U and V. Care must be taken in interpreting this equivalence; given the values of the physical observables such as the gap and the soliton creation energies, the deduced values of the bare interactions that appear in the Hamiltonian depend somewhat on the nature of the ultraviolet cutoff of the one-electron spectrum, especially if U/W is not small (see Ref. 14). Thus, even if the physical interactions were exactly modeled by a single Hubbard U, we should expect the value of U deduced from continuum model calculations to differ from the discrete model value by order $\delta U \sim U[U/(2t_0)]$. This is consistent with the fact that our estimates of U, and those of other workers, mostly fall in the range $U \sim (4\pm1)$ eV.

We conclude that simple models are only valid when $\Delta_0/W \ll 1$ and $\bar{U}/W \ll 1$. When $\bar{U}/2\pi W \ln(2W/\Delta_0) \ll 1$, perturbation calculations are accurate. For most conducting polymers, $\ln(2W/\Delta_0) \sim 2$, so perturbation theory is typically valid as long as the simple models themselves are valid. Experimental evidence suggests that in *trans*-(CH)$_x$, $U \approx 3 \sim 4$ eV. In the cases where $\bar{U}/W > 1$ the simple models break down and a more realistic model is required.

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APPENDIX A: SOLITON AND POLARON CREATION ENERGY

Here we give the derivations of Eqs. (14) and (20). The creation energy of a defect as a functional of the lattice configuration is defined as

$$\begin{aligned} E_{\text{creat}} &= E_{\text{total}}[\Delta] - E_{\text{total}}(\Delta_0) \\ &\equiv E^{(0)} + \Delta E^{(1)} + \Delta E^{(2)} , \end{aligned} \tag{A1}$$

where $E^{(0)}$ is the creation energy in the noninteracting model and was calculated in Ref. 2 for "soliton" and Ref. 22 for "polaron" configurations. $\Delta E^{(1)}$ is the correction due to the change in the self-consistent determined electron-phonon coupling constant (ω_0^2/g_0^2); $\Delta E^{(2)}$ is the correction due to e-e interactions. To the first order in the e-e interaction

$$\Delta E^{(2)} = \langle H_{e\text{-}e} \rangle_\Delta - \langle H_{e\text{-}e} \rangle_{\Delta_0} , \tag{A2}$$

where $H_{e\text{-}e}$ is the e-e interaction Hamiltonian [see Eq. (4)]; and $\langle\ \rangle_\Delta$ is the ground-state expectation value as a functional of the order parameter $\Delta(x)$.

Since the ground state is a product state, so

$$\begin{aligned} \langle H_{e\text{-}e} \rangle = \sum_s \int dx [& g_{\parallel} \langle \psi_{1s}^\dagger \psi_{2s}^\dagger \psi_{1s} \psi_{2s} \rangle + g_{1\perp} \langle \psi_{1s}^\dagger \psi_{2\bar{s}} \psi_{1\bar{s}} \psi_{2s} \rangle + g_{2\perp} \langle \psi_{1s}^\dagger \psi_{2\bar{s}}^\dagger \psi_{2\bar{s}} \psi_{1s} \rangle \\ & + \tfrac{1}{2} g_{3\perp} (\langle \psi_{1s}^\dagger \psi_{1\bar{s}}^\dagger \psi_{2\bar{s}} \psi_{2s} \rangle + \langle \psi_{2s}^\dagger \psi_{2\bar{s}}^\dagger \psi_{1\bar{s}} \psi_{2s} \rangle) + \tfrac{1}{2} g_{4\perp} (\langle \psi_{1s}^\dagger \psi_{1\bar{s}}^\dagger \psi_{1\bar{s}} \psi_{1s} \rangle + \langle \psi_{2s}^\dagger \psi_{2\bar{s}}^\dagger \psi_{2\bar{s}} \psi_{2s} \rangle)] \\ = \sum_s \int dx \{ & g_{\parallel} (\langle \psi_{1s}^\dagger \psi_{2s} \rangle \langle \psi_{2s}^\dagger \psi_{1s} \rangle - \langle \psi_{1s}^\dagger \psi_{1s} \rangle \langle \psi_{2s}^\dagger \psi_{2s} \rangle) + g_{1\perp} \langle \psi_{1s}^\dagger \psi_{2s} \rangle \langle \psi_{2\bar{s}}^\dagger \psi_{1\bar{s}} \rangle + g_{2\perp} \langle \psi_{1s}^\dagger \psi_{1s} \rangle \langle \psi_{2\bar{s}}^\dagger \psi_{2\bar{s}} \rangle \\ & + \tfrac{1}{2} g_{3\perp} [\langle \psi_{1s}^\dagger \psi_{2s} \rangle \langle \psi_{1\bar{s}}^\dagger \psi_{2\bar{s}} \rangle + \langle \psi_{2s}^\dagger \psi_{1s} \rangle \langle \psi_{2\bar{s}}^\dagger \psi_{1\bar{s}} \rangle] \\ & + \tfrac{1}{2} g_{4\perp} [\langle \psi_{1s}^\dagger \psi_{1s} \rangle \langle \psi_{1\bar{s}}^\dagger \psi_{2\bar{s}} \rangle + \langle \psi_{2s}^\dagger \psi_{2s} \rangle \langle \psi_{2\bar{s}}^\dagger \psi_{2\bar{s}} \rangle] \} . \end{aligned} \tag{A3}$$

The expectation values in Eq. (A3) are readily determined. In the soliton case, there is one mid-gap state $|\psi_0\rangle$ and $\Delta_{\text{int}} = 0$. Then

$$\begin{aligned} \langle \psi_{1s}^\dagger(x) \psi_{1s}(x) \rangle_\Delta &= (f_s - \tfrac{1}{2}) |\phi_0|^2 \\ &= \langle \psi_{2s}^\dagger(x) \psi_{2s}(x) \rangle , \end{aligned} \tag{A4}$$

$$\langle \psi_{1s}^\dagger(x) \psi_{2s}(x) \rangle_\Delta = -\frac{\omega_Q^2}{4g_0^2} \Delta(x) - i (f_s - \tfrac{1}{2}) |\phi_0|^2 , \tag{A5}$$

where

$$\psi_0 = \begin{bmatrix} 1 \\ -i \end{bmatrix} \phi_0$$

is the mid-gap wave function and f_s is the number of electrons of spin s in the mid-gap state. Similarly, in the perfect dimerized system, we have

$$\langle \psi_{1s}^\dagger(x)\psi_{1s}(x)\rangle_{\Delta_0}=\langle \psi_{2s}^\dagger(x)\psi_{2s}(x)\rangle_{\Delta_0}=0 \,, \tag{A6}$$

$$\langle \psi_{1s}^\dagger(x)\psi_{2s}(x)\rangle_{\Delta_0}=-\frac{\omega_Q^2}{4g_0^2}\Delta_0=-\frac{\Delta_0}{\pi}\ln\left(\frac{2W}{\Delta_0}\right) . \tag{A7}$$

By using Eqs. (A4)—(A7), we get

$$\Delta E^{(2)}=(2f_\uparrow-1)(2f_\downarrow-1)(g_{1\perp}+g_{2\perp}-g_{3\perp}+g_{4\perp})I_+ \\ -g'I_0 \,, \tag{A8}$$

where

$$I_+\equiv\tfrac{1}{2}\int dx\,|\phi_0|^4 \,, \tag{A9}$$

$$I_0\equiv 2\int dx\left(\frac{\omega_Q^2}{4g_0^2}\right)^2[\Delta^2(x)-\Delta_0^2] \,. \tag{A10}$$

In principle, the lattice configuration $\Delta(x)$ should be computed self-consistently to find that lattice configuration which minimizes the defect creation energy. This is generally quite difficult. However, $\Delta E^{(2)}$ is insensitive to the exact form of $\Delta(x)$, since it only depends on integrals of this quantity. Moreover, as long as the e-e interactions are weak, the defect shape will not be very different than in the absence of interaction. Therefore, as a quite good approximation, we assume that the soliton has the same shape as in the absence of interactions

$$\Delta(x)=\Delta_0\tanh(x/\xi) \tag{A11}$$

so that only its width is a function of the interactions. This ansatz is exact to first order in the e-e interactions (see discussion below). We have also tried other forms of $\Delta(x)$, and found that the corrections to $\Delta E^{(2)}$ were smaller than corrections due to interactions which are missing from the simple model.

Under the above ansatz [Eq. (A12)], ϕ_0 can be computed exactly.

$$\phi_0(x)=\left(\frac{1}{2\sqrt{\pi}\xi}\frac{\Gamma(\nu+\frac{1}{2})}{\Gamma(\nu)}\right)^{1/2}\operatorname{sech}^\nu(x/\xi) \,, \tag{A12}$$

where

$$\nu\equiv\xi/\xi_0=1+\chi \,, \tag{A13}$$

$$\chi=(\xi-\xi_0)/\xi_0 \,. \tag{A14}$$

Using Eqs. (A11) and (A12), we get

$$\Delta E^{(2)}=\frac{2\Delta_0}{\pi}\Bigg[(2f_\uparrow-1)(2f_\downarrow-1) \\ \times\frac{\pi}{48}(g_{1\perp}+g_{2\perp}-g_{3\perp}+g_{4\perp})\frac{3}{\sqrt{\pi\nu}} \\ \times\frac{\Gamma^2(\nu+\frac{1}{2})\Gamma(2\nu)}{\Gamma^2(\nu)\Gamma(2\nu+\frac{1}{2})}-\frac{g'}{2\pi}\ln^2\left(\frac{2W}{\Delta_0}\right)\nu\Bigg] . \tag{A15}$$

The self-consistency equations require

$$\frac{\omega_Q^2}{g_0^2}\left(\frac{\omega_Q^2}{g_0^2}\right)_0-\frac{1}{\Delta_0}\frac{d}{d\Delta_0}\langle H_{e\text{-}e}\rangle \\ =\left(\frac{\omega_Q^2}{g_0^2}\right)_0\left[1-\frac{g'}{2\pi}\ln\left(\frac{2W}{\Delta_0}\right)\right] \\ =\frac{\Delta}{\Delta_0}\left(\frac{\omega_Q^2}{g_0^2}\right)_0 , \tag{A16}$$

where $(\omega_Q^2/g_0^2)_0$ is the electron-phonon coupling in the absence of e-e interactions; and Δ is the physical gap in Eq. (7). Equation (A16) indicates that the first-order effect of e-e interactions is to renormalize the bare gap to the physical gap. This explicitly shows that the ansatz [Eq. (A11)] is exact in the first-order perturbation theory and

$$\Delta E^{(1)}=\left[\left(\frac{\omega_Q^2}{2g_0^2}\right)-\left(\frac{\omega_Q^2}{2g_0^2}\right)_0\right]\int[\Delta^2(x)-\Delta_0^2]dx \\ =\frac{2\Delta_0}{\pi}\left(\frac{g'}{2\pi}\right)\ln^2\left(\frac{2W}{\Delta_0}\right) . \tag{A17}$$

$E^{(0)}=(2\Delta_0/\pi)f_0(\nu)$ is calculated in Ref. 2. Put all terms together, we finally get

$$E_s=\frac{2\Delta_0}{\pi}\left[f_0(\nu)\pm\frac{\pi}{48}(g_{1\perp}+g_{2\perp}-g_{3\perp}+g_{4\perp})f_1(\nu)\right] . \tag{A18}$$

This is Eq. (14).

Similar calculations have been carried out for the polaron and bipolaron configurations. Here we just briefly mention a few new features. We refer to a polaronlike configuration when the lattice has the form

$$\Delta_p(x)=\Delta_0\left\{1-\xi_0/\xi\left[\tanh\left(\frac{x+x_0}{\xi}\right)\right.\right. \\ \left.\left.-\tanh\left(\frac{x-x_0}{\xi}\right)\right]\right\} , \tag{A19}$$

where

$$\xi_0/\xi=\tanh\left(\frac{2x_0}{\xi}\right) . \tag{A20}$$

There are two mid-gap states (antibounding and bounding states).

$$\psi_+=\frac{1}{4\sqrt{\xi}}\begin{bmatrix}(1-i)\operatorname{sech}\left(\dfrac{x+x_0}{\xi}\right)+(1+i)\operatorname{sech}\left(\dfrac{x-x_0}{\xi}\right)\\ (1+i)\operatorname{sech}\left(\dfrac{x+x_0}{\xi}\right)+(1-i)\operatorname{sech}\left(\dfrac{x-x_0}{\xi}\right)\end{bmatrix} , \tag{A21}$$

$$\psi_-=\sigma_y\psi_+ \,.$$

Let

$$S_{\pm} \equiv \operatorname{sech}\left[\frac{x \pm x_0}{\xi}\right] . \tag{A22}$$

Then

$$\langle \psi_{1s}^{\dagger} \psi_{1s} \rangle = \langle \psi_{2s}^{\dagger} \psi_{2s} \rangle = (f_{+\uparrow} + f_{-s} - 1)\frac{1}{8\xi}(S_+^2 + S_-^2) , \tag{A23}$$

$$\langle \psi_{1s}^{\dagger} \psi_{2s} \rangle = -\frac{\omega_Q^2}{4g_0^2}\Delta_p(x) + i(f_{+s} + f_{-s} - 1)\frac{1}{8\xi}(S_+^2 - S_-^2) . \tag{A24}$$

The self-consistency equations are now given by $(\Delta_{\text{int}} \neq 0)$

$$\frac{\omega_Q^2}{g_0^2} = \frac{2}{\pi}\frac{\Delta}{\Delta_0 - \Delta_{\text{int}}}\ln\left[\frac{2W}{\Delta_0}\right] . \tag{A25}$$

By using Eqs. (A19)—(A25) one readily gets Eq. (20).

APPENDIX B: NEUTRAL SOLITON SPIN DENSITY

In deriving Eq. (17) we use standard perturbation theory. The nonperturbated wave functions are

$$\psi_k(x) = \frac{1}{2\sqrt{L}E_k}\begin{Bmatrix} k + i\Delta_0\tanh(x/\xi_0) + E_k \\ -i[k + i\Delta_0\tanh(x/\xi_0) - E_k] \end{Bmatrix} e^{ikx} \tag{B1}$$

and the mid-gap state

$$\psi_0(x) = \frac{1}{2\sqrt{\xi_0}}\begin{bmatrix} 1 \\ -i \end{bmatrix}\operatorname{sech}(x/\xi_0) . \tag{B2}$$

Define spin density operator

$$\hat{S}(x) = \hat{p}_{\uparrow}(x) - \hat{p}_{\downarrow}(x) , \tag{B3}$$

where

$$\begin{aligned}\hat{p}_s(x) &\equiv (\psi_{1s}^{\dagger} e^{-ik_F x} - i e^{ik_F x}\psi_2^{\dagger})(\psi_{1s} e^{ik_F x} + i e^{-ik_F x}\psi_{2s}) \\ &= \psi_{1s}^{\dagger}\psi_{1s} + \psi_{2s}^{\dagger}\psi_{2s} - i[\psi_{2s}^{\dagger}\psi_{1s} e^{2ik_F x} - \psi_{1s}^{\dagger}\psi_{2s} e^{-2ik_F x}]\end{aligned} \tag{B4}$$

is the density of electron of spin *s*. (Note the phase factor in the definition of this operator.) Standard perturbation theory yields

$$S(x) = \langle 0 | \hat{S}(x) | 0 \rangle + \sum_{n \neq 0}\left[\frac{\langle n | H_{e\text{-}e} | 0 \rangle}{E_0 - E_n}\langle 0 | \hat{S}(x) | n \rangle + \text{H.c.}\right] , \tag{B5}$$

where $|0\rangle(|n\rangle)$ is the ground state (*n*th exciting state) in the noninteracting model.

Using formula (B1)—(B6), one can readily get $s(x)$ by carrying out several complicated integrals. The result is

$$S(x) = \frac{1}{\xi_0}\operatorname{sech}^2\left[\frac{x}{\xi_0}\right][(1+V_4)\cos^2(k_F x) - V_4\sin^2(k_F x)] + \tilde{S}(x) , \tag{B6}$$

where

$$\begin{aligned}\tilde{S}(x) \equiv \frac{1}{\pi\xi_0}\Bigg\{ & g_{1\perp}\ln\left[\frac{2W}{\Delta_0}\right]\cos^2(k_F x)\operatorname{sech}(x/\xi_0)[1 - \ln(2\cosh(x/\xi_0)] \\ & + (g_{2\perp} + g_{4\perp})\left[\frac{W}{\Delta_0}\right]\sin(2k_F x)\operatorname{sech}\left[\frac{x}{\xi_0}\right]\left[\frac{x}{\xi_0} - \sinh(x/\xi_0)\ln(1 + e^{-2|x|/\xi_0})\right] \\ & + g_{3\perp}\ln\left[\frac{2W}{\Delta_0}\right]\operatorname{sech}(x/\xi_0)\cos^2(k_F x)\left[\frac{1}{4} - \frac{2}{\pi}\operatorname{sech}(x/\xi_0)\frac{e^{-|x|/\xi_0}}{(1 + e^{-2|x|/\xi_0})^{1/2}}\right]\Bigg\} .\end{aligned} \tag{B7}$$

This is Eq. (17).

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