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ELECTRON HOPPING CONDUCTION IN THE SOLITON MODEL OF POLYACETYLENE

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It is shown that at low temperatures a novel conduction mechanism, phonon assisted hopping between soliton bound states (intersoliton hopping), may be the dominant conduction process in lightly doped polyacetylene. The theory is developed from a more general phenomenological viewpoint than previously,¹ and the model independent aspects of the transport are stressed. It is found that the theory successfully accounts for experiments in polyacetylene which simultaneously show the hallmarks of solitons (e.g. no increase in the number of spins upon doping, a highly one-dimensional spin mobility, a qualitative dependence on cis to trans isomerization) and the characteristics of hopping transport (e.g. a strongly frequency and electric field dependent conductivity). It is further suggested that, since the theoretical considerations that lead to the conclusion that intersoliton hopping is important in polyacetylene are quite general, the same basic transport process may be important in many quasi-one dimensional semiconductors.

I. INTRODUCTION

In this paper we discuss the theory of intersoliton hopping (ISH) conduction in quasi-one-dimensional Peierls systems. The theory has been discussed¹ previously in considerable detail for an explicit microscopic model of trans-polyacetylene $(CH)_x$ which is a three dimensional generalization of the model of Su, Schrieffer and Heeger² (SSH). In the present paper we shall discuss the theory from a more general, hence phenomenological viewpoint. We

will focus our attention on the qualitative features of the theory with a view toward understanding:

- 1) What are the general, model independent features of ISH?
- 2) What are the basic assumptions that go into the theory and under what circumstances do we expect them to be valid?
- 3) What experimentally accessible features distinguish ISH from other hopping processes?

From the phenomenological viewpoint of this paper, the theory can potentially be applied to a wide class of quasi-one dimensional Peierls systems including materials other than $(\text{CH})_x$ with commensurability 2 and systems with other commensurabilities such as perhaps TTF-TCNQ under pressure. With some changes, the theory also can be adapted to apply to systems with slightly non-degenerate ground states, such as $\text{cis}-(\text{CH})_x$. Here, the hopping is between weakly bound soliton-antisoliton pairs (one dimensional large polarons). The discussion in this paper will be primarily directed at $\text{trans}-(\text{CH})_x$, but an attempt will be made to indicate any results that are peculiar to $(\text{CH})_x$ and to indicate how they would differ in other, related solids.

11. THE SOLITON MODEL

For the purpose of the present discussion, a few general features of the soliton model are important. At the conceptual core of this discussion lies the Born-Oppenheimer approximation which allows us to talk about the electronic states associated with some specified pattern of ion displacements. This approximation should be valid at least so long as the electronic energy gap, $2\Delta_0$, is much greater than the typical phonon frequency, $\hbar\omega_0$.

An n -fold commensurate electron-ion system has a strong Peierl's instability toward n -merization. There are n degenerate ground state lattice configurations associated with the different possible senses of this n -merization. The soliton is a domain wall between regions of two different ground state configurations. Associated with each soliton is a localized electronic state which lies in the band gap between the valence and conduction bands. For $n=2$, this bound state must lie at mid-gap so long as the model has electron-hole symmetry. For other commensurabilities, the bound state can lie anywhere, in the gap, depending on the shape of the soliton.⁴ The gap state can be unoccupied

or doubly occupied, in which case the soliton is spinless, or it can be singly occupied, in which case the soliton has spin $1/2$. For $n=2$, the singly occupied soliton is neutral, and in the other two cases it is charged. For other commensurabilities the charge relations are more complicated. Intersoliton hopping ISH involves an electron hopping from the gap state of one soliton to the gap state of another.

The large polarons found in systems with inequivalent ground states have³ similar gap state structure as solitons, except associated with the polaron are two bound states in the gap. None-the-less, under certain circumstances, interpolaron hopping may be quite similar to intersoliton hopping.⁵

Finally, we note that electron-electron interactions, and, for the most part, soliton-soliton interactions are ignored in the following discussion. The effects of these interactions are currently being investigated by the author.

III. WHY DO WE NEED INTERSOLITON HOPPING?

From the point of view of transport, one of the most important distinctions between solitons and more conventional charged excitations is their extremely one dimensional character.⁶ Although the mobility of an electron in a quasi-one dimensional metal may be quite anisotropic due to the narrowness of the transverse band, in an ideal array of infinite chains solitons are topologically confined to one chain. Thus, no transverse conduction can occur in an ideal soliton system. The extreme one dimensionality also implies that solitons are particularly strongly affected by disorder. This follows from the fact that solitons cannot avoid defects such as impurities or chain breaks. Any disorder will localize the solitons.

We are thus driven immediately to the expectation that soliton transport is a very inefficient process. This conclusion is strengthened by the observation that, although the solitons are light compared to the ions, they tend to be heavier than band electrons. (This is certainly true in $(\text{CH})_x$ where the soliton mass, $m_s \approx 6m_e$, while the band edge effective mass, $m^* = \Delta_0 (\hbar/2t_0a)^2 \approx (1/7)m_e$.) Thus, solitons tend to be rather deeply trapped by defects such as charged impurities.

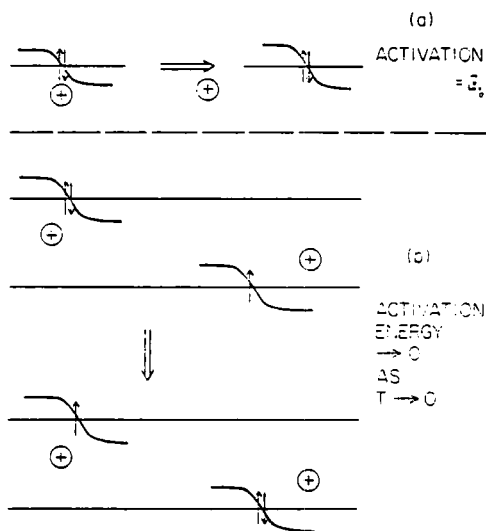
If solitons are present in a system due to a slight deviation from commensurability (as produced, for instance,

by lightly doping $(\text{CH})_x$, one expects them to be predominantly of one type with a localized gap state either doubly occupied or unoccupied (depending on the sign of the deviation). Such a system is expected to be quite insulating. However, the presence of a small concentration of solitons of a different charge (i.e., neutral solitons in $(\text{CH})_x$) might be expected to increase the conductivity in two possible ways. Firstly, two unlike charged solitons could bind to form a charged polaron. The polaron is not topologically confined to a single chain. Thus, three dimensional large polaron hopping might contribute to the conductivity. However, the generally large activation energy for polaron hopping makes it unlikely that this process will make a significant contribution to the conductivity.⁶ Secondly, the additional solitons act to "dope" the mid-gap band of localized electronic states. Thus intersoliton hopping becomes possible. Because the hopping can proceed along three dimensional pathways and, as we will see explicitly for the case of $(\text{CH})_x$, can have rather small activation energies, the hopping conductivity can be moderately large even for very low carrier concentrations.

IV. A BRIEF DESCRIPTION OF INTERSOLITON HOPPING IN $(\text{CH})_x$

To be concrete, let us first consider a simple phenomenological model of solitons in $(\text{CH})_x$. We imagine a perfectly crystalline array of $(\text{CH})_x$ chains. Distributed at random throughout the sample is a concentration per unit volume, c_{im} , of impurities or pinning centers of some sort. We also imagine a concentration per carbon atom y_n and y_{ch} of neutral and positively charged solitons respectively. Of course, if we associate the pinning centers with negatively charged acceptor impurities, charge neutrality requires that the numbers of pinning centers and of charged solitons be equal. However, it is convenient to consider c_{im} and y_{ch} as independent variables, both for conceptual clarity, and also so as to include the possibility of other types of pinning centers. For now, we will further assume that all the pinning centers are equivalent. For instance, the binding energy of a charged soliton to one of these centers, E_b , is assumed to be the same as to any other. Finally, we imagine that we can adequately describe a soliton by a single translational coordinate and by the occupancy of the midgap electronic state. To understand ISH, first picture a charged soliton bound to an impurity at the

origin. (See Fig. 1) If $kT \ll E_b$, little charge transport can be associated with soliton translation. Now expand the picture to include a neutral soliton a distance \bar{R} from the origin. Since there will in general be a non-zero overlap between the electronic states associated with the two solitons, it is possible for the electron to make a phonon assisted hop from one localized state to another. In the initial state (before the hop) there is a charged soliton at the pinning center at the origin while in the final state there is a neutral. Thus, we expect this process to be highly activated since the binding energy of a neutral soliton to an impurity is generally much less than that of a charged soliton. (To first order in the impurity potential, the binding energy of a neutral soliton is zero.) However, if there happens to be another impurity near \bar{R} , as shown in Fig. 1, the activation energy for hopping can be arbitrarily small.



Let us consider, schematically, the various factors which go into determining the primitive hopping rate between such a pair of solitons. First we picture freezing the solitons in some initial state with energy E_i , and we calculate the phonon assisted electronic transition rate from one soliton to the other, $\tilde{v}(\bar{R}; E_i - E_f)$, where E_f is the

energy of the final soliton state. $v(\vec{R}, E_i - E_f)$ can, in principle, be calculated from Fermi's Golden Rule. It is proportional to the square of the overlap, $S(\vec{R})$, between the electronic bound states on the two solitons and includes both transitions involving the emission or absorption of one phonon, as well as multi-phonon processes. A symmetry between absorption and emission processes is insured by the condition of detailed balance

$$\tilde{v}(\vec{R}, |\epsilon|) = e^{-|\epsilon|/kT} \tilde{v}(\vec{R}, -|\epsilon|) \quad (1a)$$

To simplify future discussion, it is convenient to rewrite \tilde{v} in terms of an effective electron-phonon coupling function, $g(\epsilon)$:

$$\tilde{v}(\vec{R}, \epsilon) = S^2(\vec{R}) g(|\epsilon|) \begin{cases} e^{-\epsilon/kT} & \text{for } \epsilon > 0 \\ 1 & \text{for } \epsilon < 0 \end{cases} \quad (1b)$$

In order to find the actual hopping rate $\tilde{v}(\vec{R})$ we must average \tilde{v} over initial and final soliton states

$$v(\vec{R}) = \int d\epsilon_i d\epsilon_f \frac{\rho(\epsilon_i, \epsilon_f) e^{-\epsilon_i/kT}}{Z(T)} \tilde{v}(\vec{R}, \epsilon_i - \epsilon_f) \quad (2)$$

where ρ is a joint density of initial and final soliton states normalized by a partition function, $Z(T)$

$$Z(T) = \int d\epsilon_i d\epsilon_f \rho(\epsilon_i, \epsilon_f) e^{-\epsilon_i/kT} \quad (3)$$

There are two potentially small factors which enter Eq. (2) for the hopping rate. The first is the probability that a neutral soliton is near an impurity (which enters implicitly through the factor $\rho(\epsilon_i, \epsilon_f)/Z(T)$ in Eq. (2)). If the interaction between the neutral and the impurity is ignored, this probability is just proportional to y_n . The second is the overlap factor, $S(\vec{R})$, between the electronic wave functions. This factor falls off exponentially with \vec{R} , and falls off less rapidly in the in chain (\parallel) direction than in the out of chain (\perp) direction. To model this \vec{R} dependence we adopt the ansatz

$$s(\vec{R}) = \exp[-\sqrt{(R_{\parallel}/\xi_{\parallel})^2 + (R_{\perp}/\xi_{\perp})^2}] \quad (4)$$

where ξ_{\parallel} and ξ_{\perp} are respectively the in-chain and out-of-chain wave function decay lengths ($\xi_{\parallel} > \xi_{\perp}$). This ansatz is appropriate for a continuous medium with an anisotropic effective mass.

The resulting expression for the transition rate can

be written

$$v(\vec{R}) = \gamma_n s^2(\vec{R}) \gamma(T) \quad (5)$$

where $\gamma(T)$ is a complicated thermal average of the electron-phonon coupling function $g(\epsilon)$. It depends only on the type of impurity centers involved but not on the distance between them nor on the concentration of solitons.

Once the primitive hop rate has been determined, it remains only to determine the nature of the conduction pathways. The first question we ask concerns the dimensionality of the conduction pathways. In Ref. 1 it is determined that so long as

$$c_{im} < \pi/3 (\xi_{\perp}/\xi_{||}) (1/b)^3 \quad (6)$$

it is more likely that an electron at an arbitrary impurity site will hop to an impurity site on a different chain than one on the same chain. Here b is the inter-chain lattice spacing. This result at first may seem surprising since the larger in-chain wave function decay length would seem to imply that intrachain hopping dominates interchain hopping. This would be true if the impurities were arranged on a super-lattice, with comparable spacings between near neighbor impurities on the same chain and on different chains. However, because the impurities are arranged at random, the typical separation between impurity sites on a given chain $\sim [c_{im} b^2]^{-1}$ while if we do not confine ourselves to a single chain, the spacing between impurities $\sim [c_{im}]^{-1/3}$. It is clear that at low impurity concentrations the phase space factors dominate and the conduction pathways are purely three dimensional. Thus, if we rescale lengths in the in- and out-of-chain directions, $R_{||} = R_{||}/\xi_{||}$, $\bar{R}_{\perp} = R_{\perp}/\xi_{\perp}$, the rescaled problem is equivalent to the much studied R-percolation problem.⁹ We can immediately deduce that the average DC conductivity

$$\sigma_{dc} = \frac{Ae^2}{KT} \Gamma(T) \left(\frac{\xi}{R_o^2} \right) e^{-2BR_o/\xi} \quad (7a)$$

where A and B are dimensionless numbers which can be determined^{1,9} with a fair degree of accuracy,

$$\xi = (\xi_{||}\xi_{\perp}^2)^{1/3} \quad (7b)$$

is the dimensionally averaged decay length,

$$R_o = (4\pi/3 c_{im})^{-1/3}$$

is the typical separation between impurities, and

$$\Gamma(t) = y_n \gamma(T) \frac{y_n y_{ch}}{(y_n + y_{ch})^2}. \quad (7c)$$

Here, the factor $y_n y_{ch} / (y_n + y_{ch})^2$ is needed to turn a quantum mechanical transition rate into a net transition rate.

Since the only anisotropy in the conductivity arises from the differences in length scales in the \parallel and \perp directions, it is easy to show that

$$(\sigma_{\parallel} / \sigma_{\perp}) = (\xi_{\parallel} / \xi_{\perp})^2. \quad (8)$$

At higher concentrations approaching the limit in eq. (6), the percolation pathway becomes more complicated. One simply deduced effect of higher impurity concentrations however, is to increase the conductivity anisotropy from its low concentration value.

Eq. (7) contains implicitly the assumptions that all impurity sites are equivalent; the only disorder included in the calculation is the random location of the impurity sites. This assumption reflects itself in the fact that v , and hence σ factors into a temperature dependent and a concentration dependent part. The temperature dependence of $\gamma(T)$ arises from the difference in energy between the initial and final soliton states and hence reflects the dynamical nature of the states between which the electron hops. In general, this temperature dependence can be quite complicated. However, since it is possible to find initial and final soliton states that are degenerate in energy, we expect that the apparent activation energy for hopping, $-kT^2 d \ln \sigma / dT$, tends to zero as $T \rightarrow 0$.

This behavior should be compared with the case of hopping between in-equivalent sites, which results in variable-range hopping (VRH). In that case, as the temperature is lowered, the typical hop length increases so as to reduce the typical activation energy. This also leads to a temperature dependent activation energy which vanishes as $T \rightarrow 0$. However, the physics is fundamentally different in the case of VRH. For ISH between equivalent sites, there is no change in the typical hopping distance as a function of the temperature. This difference is reflected in the fact that the conductivity does not factor in the case of VRH; the temperature and concentration dependences are intimately linked. In this sense, ISH is much more akin to small polaron hopping. Of course, in any real system, there will be some inequivalence between sites. Thus, at low enough temperatures we always expect to see VRH. For practical

purposes, however, the static disorder can be ignored so long as the dynamical disorder associated with the soliton motion is larger.

We conclude this section with a partial list of results from Ref. 1 for other transport coefficients. We want to stress that the results are quite generally applicable, with all the material dependent information contained in the decay length, ξ , and in the electron-phonon coupling function, $g(E)$ (and hence in such factors as $\gamma(T)$).

The thermopower is

$$S = \frac{k}{e} \left\{ \frac{\bar{\epsilon}(T)}{kT} + \ln\left(\frac{\gamma_n}{\gamma_{ch}}\right) + \sigma[\ln(T)] \right\} \quad (9)$$

where

$$\bar{\epsilon}(T) = \int dE_i \int dE_f E_i e^{-E_i/kT} \frac{\rho(E_i, E_f) \tilde{g}(E_i - E_f) / \gamma_n \gamma(T)}{Z(T)} \quad (10)$$

is the average energy transported per hop. The high frequency AC conductivity can also be found rather easily within the pair approximation:

$$\sigma_{ac}(\omega) = \frac{e^2}{\hbar} \frac{(c_{im})^2}{kT} \frac{\gamma_n \gamma_{ch}}{(\gamma_n + \gamma_{ch})^2} \frac{\xi_{||} \xi_{\perp}^2}{(384)} \times \hbar \omega [\ln(2\omega/\Gamma(T))]^4. \quad (11)$$

Since $\Gamma(T)$ contains the full temperature dependence of σ_{dc} , the resulting AC conductivity is strongly temperature dependent although less strongly temperature dependent than the DC conductivity.

Associated with the electron hopping is spin transport. Thus, we expect the out of chain component of the spin diffusion constant to be related to the conductivity by an Einstein relation

$$D_{\perp} = (1/e^2) (kT/c_{im}) \sigma_{\perp}$$

If, however, the neutral soliton is somewhat mobile, the conductivity need not be related to the in-chain component of the spin diffusion constant, at least a finite frequencies,

$$D_{||}(\omega) > (1/e^2) (kT/c_{im}) \sigma_{||}(\omega). \quad (12)$$

this curious decoupling of spin and charge would not be so striking for other commensurabilities, since the spin bearing soliton is also charged in those cases.

Finally, since the previous paper concerns, among other

things, photoconductivity, measurements, a few speculative thoughts on the photoconductivity might not be out of place. It has been noted by Su and Schrieffer³ that a photogenerated electron and hole rapidly become dressed to form a soliton antisoliton pair. It remains only to determine how the presence of these photogenerated solitons augments the conductivity. We suggest that the predominant effect could be due to the generation of neutral solitons (oppositely charged pairs remaining bound). These photogenerated solitons then act to further dope the soliton band according to Eqs. (7a) and (7c). The photoconductivity is thus predicted to scale roughly with the dark conductivity. Since the conduction process is still via hopping, transient photoconductivity experiments would be expected to show a highly dispersive character.¹² Moreover, due to the assumed equivalence of all sites, the dispersion should be roughly temperature independent, due to positional disorder alone. Although rigorous bounds can be placed on the extent of this dispersion,¹³ at low impurity concentrations these bounds are not severe. In broad outline, at least, these predictions seem to be in accordance with experiment in $(\text{CH})_x$. An important signature of this assumed mechanism of phototransport would be the presence of a photoinduced ESR signal which scales with the photoconductivity. Efforts to see such a signal are apparently under way.¹⁴

V. INTERSOLITON HOPPING IN $(\text{CH})_x$: MICROSCOPIC PARAMETERS

In Ref. 1, a slightly generalized version of the SSH model of $(\text{CH})_x$ was adopted in order to provide a microscopic basis for calculating the relevant properties of the parameters $\xi_{||}$, ξ_{\perp} , $\tilde{g}(E)$, and $\rho(E_i, E_f)$ defined in the previous section. It seems pointless to reproduce those calculations here. However, since the present paper appears in a section on $(\text{CH})_x$, it might be profitable to discuss briefly how these parameters are determined.

First, we consider the binding energy, E_b , of a charged soliton to a charged impurity. This energy depends on the nature of the dielectric screening,⁸ but may be as large as $E_b \sim 1\text{eV}$. Thus, free soliton conduction is unlikely to be important at room temperature or below. E_b also determines the energy scale of variation of $\rho(E_i, E_f)$. Since only this scale is important, in Ref. 1 it was found adequate to adopt a simple form

$$\rho(E_i, E_f) = \text{const. for } E_b < E_i, E_f < 0$$

subject to the normalization condition

$$\int dE_i dE_f \rho(E_i, E_f) = N^2$$

where N = the a number of carbons per chain.

Next, the nature of the localized electronic state can be calculated. The in-chain wave function decay length, as in SSH, was found to be $\xi_{||} \approx (2t_0/\Delta_0)$ where Δ_0 is the half band gap energy and $2t_0$ is the valence band width. It is also straightforward to show that $\xi_{\perp} = b/\ln(\Delta_0/t_{\perp})$ for a state at mid-gap so long as $\Delta_0 \gg t_{\perp}$ where t_{\perp} is the interchain resonance energy.

Finally, we reiterate a peculiarity of the SSH model, namely that the energy of the mid-gap state is rigorously 0 in the absence of an impurity potential. Thus, although in typical problems in phonon-assisted hopping, the phonons are assumed to modulate the energy of the localized electronic state, no such electron-phonon coupling exists in the pure soliton system. Although the impurity potential breaks the electron-hole symmetry which is responsible for the absence of coupling, the coupling in the presence of an impurity is still expected to be weak. SSH estimate that the binding energy of a charged soliton to an impurity is increased by less than 10% due to the change in the soliton width produced by the interaction with the impurity. This change in energy is the "polaron binding energy" in the conventional sense. Since this energy is small in magnitude compared to the scale of variation of $\rho(E_i, E_f)$ it can be shown that the only effect of multiphonon processes is to smooth out any charge features in $\rho(E_i, E_f)$ and $\tilde{g}(E)$. We are thus left with the problem of calculating the one-phonon transition rate.

(Note as an aside that in systems in which charge conjugation symmetry does not forbid this type of electron-phonon coupling, the situation is very different. Here the soliton changes its shape, and hence its energy, drastically depending on its occupancy. The resulting "polaron binding energy" E_p will show up in the temperature dependence of $\gamma(T)$. At high temperatures, at least we expect $\gamma(T) \sim \gamma_0 \exp[-E_p/2kT]$. We can speculate that the conductivity activation energy observed in TTF - TCNQ just off commensurability $n = 3$ may be due to ISH of this sort.)

At this point the only remaining task is to calculate $g(E)$. To calculate $g(E)$ explicitly we need to know the phonon wave functions in the presence of a soliton. While these can be found numerically in the same way as the

phonon spectrum was computed by Melé and Rice⁷ this is not an easy task. Rather than embark on a lengthy computer calculation, the strategy adopted in Ref. 1 was to find as many constraints on $g(E)$ as could be derived without explicit knowledge of the phonon wave functions, and then to assume a smooth functional form for $g(E)$ which satisfies those constraints and contains one free parameter to be determined from experiment. The justification for this procedure, and in particular for the assumption of smoothness, is that at experimentally relevant temperatures, a substantial range of energies contributes to the integral in Eq. (2). Thus, any fine structure of $g(E)$ will tend to be averaged out. The results of these calculations, then, represent a one free parameter empirical fit to experiment. This fit has been employed successfully by Epstein et al¹⁰ to interpret the AC conductivity and by Moses et al¹¹ to interpret the thermopower and the pressure dependence of the DC conductivity.

In keeping with the phenomenological approach of the present paper, we will not consider the details of this fitting procedure. Rather we shall ask on general grounds what we expect for the temperature dependence of $\gamma(T)$ and $\varepsilon(T)$. First, we note that the electrons are most strongly coupled to the zone center optical phonons of energy $\hbar\omega_0 \approx 0.15\text{eV}$ which modulate the dimerization. Thus, for temperatures small compared to $\hbar\omega_0$, we expect $\gamma(T)$ to be a rapidly falling function of T . In fact, if the phonon band were narrow, as in a molecular crystal, we would expect to find $\gamma(T) \sim \gamma_0 \exp(-\hbar\omega_0/kT)$. Since the phonon band in $(\text{CH})_x$ is moderately wide, and includes an acoustic band which extends to quite high energies ($\sim 0.05\text{eV}$), and since, moreover, there are various factors mentioned previously which tend to smooth out the integral in Eq. (2), we do not expect $\gamma(T)$ to have a well defined activation energy in $(\text{CH})_x$. We rather expect that the characteristic hopping energy is determined by kT , so $\gamma(T) \sim T^x$ and $\varepsilon(T) \sim A kT$. Of course, A and x will at best be constants over limited range of temperatures. Nonetheless, a subactivated conductivity and a weakly temperature dependent thermopower are clearly to be expected.

VI. CONCLUSIONS: ESSENTIAL EXPERIMENTAL SIGNATURES OF ISH

We have now surveyed the phenomenology of ISH. The theory has proven remarkably successful in explaining a large number of transport experiments in $(\text{CH})_x$. In this

final section, we would like to focus on those experimentally accessible qualitative predictions of the theory which are characteristic signatures of ISH and are not terribly sensitive to the complicated, model dependent microscopic calculations required to obtain quantitative predictions.

The first and foremost characteristic of ISH is that it relies on the presence of both charged and neutral solitons in the vicinity of the impurity centers. Thus, on isomerizing from *cis* to *trans* $(CH)_x$, we expect to see qualitative changes in the transport coefficients although the gross electronic structure does not change much. In the following paper, evidence is presented that such a change does indeed occur. More than any other piece of evidence, the strong dependence on isomerization supports the contention that solitons play an important role in the conduction process.

Next, and equally central, we expect to see the characteristics of hopping transport; a strongly frequency and electric field dependent electrical conductivity, dispersive transport, etc. In addition, we expect to see an extremely rapid rise in the conductivity with impurity concentration, since σ depends exponentially on $c_{im}^{-1/3}$. This tells us that the hopping centers are in some way associated with impurity sites. All of these features have been observed in *trans* $(CH)_x$.

Lastly, there are the several predictions that reflect the fact that the activation energy for hopping is predominantly a result of dynamical, as opposed to static, disorder. Among the consequence of this are: the fact that the conductivity in Eq. (7a) factors into a temperature dependent and a concentration (and/or pressure) dependent part, the fact that the same factor, $\Gamma(T)$, determines the temperature dependence of the DC and AC conductivities, the fact that the heat transport, $\bar{\epsilon}/kT$, is independent of impurity concentration, and the fact that the dispersion in the transient photoconductivity is temperature independent. With varying degrees of uncertainty, all of these predictions have been confirmed as well.

We thus conclude that it seems increasingly likely that the dominant conduction process in *trans* $(CH)_x$, at least at dopant concentrations below a few tenths of a percent, is intersoliton hopping. We further suggest that the same conduction process may be expected to be important in other materials which have similar soliton-like charge excitations.

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REFERENCES

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1. S. Kivelson, Phys. Rev. Lett. 46, 1344 (1981). Also Phys. Rev. B (submitted).
2. W.P. Su, J.R. Schrieffer, and A.J. Heeger, Phys. Rev. Lett. 42, 1698, (1979) and Phys. Rev. B22, 20999 (1980).
3. W.P. Su and J.R. Schrieffer, Proc. Natl. Acad. Sci. U.S.A. 77, 5626 (1980). Also D.K. Campbell and A.R. Bishop (preprint).
4. W.P. Su and J.R. Schrieffer, Phys. Rev. Lett. 46, 741 (1981).
5. Here we are considering, for instance, an electron hopping from a polaron with charge $+e$ (hence with one localized electron) to a "dipolaron" with charge $+2e$ (hence with no localized electrons). This process differs from normal polaron hopping in that the lattice distortions have an integrity independent of occupancy. Both polarons exist before and after the electronic transition.
6. Although large polarons can, in principle, hop from one chain to another, the lattice distortion associated with the polaron is large both in magnitude and in spatial extent, so the quantum tunneling probability of the polaron is probably vanishingly small. Phonon assisted hopping of a polaron is, in principle, possible, but at least in $(CH)_x$, the polaron binding energy is several tenths of an eV, so the hopping rate is also very small at room temperature and below. Thus, a large polaron may be expected to be anomalously one dimensional. This observation serves to strengthen the analogy between intersoliton and interpolaron hopping.
7. E.J. Mele and M.J. Rice, Phys. Rev. Lett. 45, 926 (1980).
8. This estimate was made by assuming that the coulomb potential is screened as it would be in a continuous dielectric medium with $\epsilon_{||}=10$ and $\epsilon_{\perp}=1$. See L.D. Landau and E. Lifshitz, Electrodynamics of Continuous Media (Pergamon Press, Oxford, 1960) pg. 61.

9. See for example, P.N. Butcher and K.H. Hauden, *Philos. Mag.* 36, 657 (1977).
10. A.J. Epstein, H. Rommelmann, M. Abkowitz, and H.W. Gibson (following paper).
11. D. Moses, A. Denenstein, A. Pron, A.J. Heeger, and A.G. MacDiarmid (preprint).
12. H. Scher and E. Montroll, *Phys. Rev.* B7, 4491 (1973). Also G. Pfister and H. Scher, *Adv. Phys.* 27, 747 (1978).
13. S. Kivelson, *Phys. Rev.* B21, 5755 (1980).
14. S. Etemad - private communication. Also S. Etemad, L. Lauchlan, T-C. Chung, A.S. Heeger and A.G. MacDiarmid (manuscript).