

## Intersoliton hopping transport of electrons in molecular crystals

I. A. Howard and E. M. Conwell

*Xerox Webster Research Center, 800 Phillips Road, Webster, New York 14580*

(Received 21 December 1983)

Quarter-filled-band quasi-one-dimensional compounds which exhibit large Coulomb repulsion between two electrons on the same site ("large  $U$ ") can support the formation of fractionally charged solitons. Electron hopping between solitons may contribute substantially to transport in these materials. We calculate the intersoliton electron hopping rate for transitions mediated by intramolecular phonons and by acoustic phonons. Acoustic phonons are found to be much less effective and are expected to contribute significantly only when intramolecular phonons are not excited or cannot satisfy conservation of energy. For the case of intramolecular phonons, we consider both hopping of an electron from a soliton pinned by an impurity to a second soliton which then becomes pinned, and hopping between a pair of solitons, one of which remains free to move. [Owing to the large on-chain dielectric constant ( $\sim 100$ – $1000$ ) in these materials, the solitons are probably not bound except at low temperatures.] The transition rates are used to find the hopping mobility for electrons in the soliton levels. Evaluation of the mobility due to the different hopping mechanisms for (N-methylphenazinium)<sub>0.54</sub>(phenazine)<sub>0.46</sub> tetracyanoquinodimethane [(NMP)<sub>0.54</sub>(Phen)<sub>0.46</sub>-(TCNQ)] at a temperature of 100 K suggests that, unlike the polyacetylene case, the predominant process at temperatures  $\geq 100$  K is on-chain hopping, due to the large interchain distances involved. We find a mobility at 100 K of  $0.06$ – $1.03$  cm<sup>2</sup>/V sec due to on-chain hopping, mediated by intramolecular phonons, between pinned and free solitons. This mobility should increase at higher temperatures. The thermoelectric power due to the various electron hopping processes is calculated as well. We find that for hopping processes involving transitions between pinned and free solitons there is a term in the thermopower involving the soliton pinning energy, in addition to the usual term involving electronic energy levels.

## I. INTRODUCTION

There is a large body of evidence that excess charge relative to the commensurate state, up to 6–7%, is accommodated in *trans*-polyacetylene [(CH)<sub>*x*</sub>] by the formation of solitons.<sup>1</sup> Evidence that solitons exist for the same purpose in  $\frac{1}{4}$ -filled-band quasi-one-dimensional crystals with large  $U$  has been given recently, specifically for (N-methylphenazinium)<sub>*x*</sub>(phenazine)<sub>1-*x*</sub> tetracyanoquinodimethane [(NMP)<sub>*x*</sub>(Phen)<sub>1-*x*</sub>-(TCNQ)], with  $0.50 \leq x < 0.55$ .<sup>2</sup> Similar effects might be expected in other crystals of this type, e.g., quinolinium di-tetracyanoquinodimethane [Qn(TCNQ)<sub>2</sub>], acridinium di-tetracyanoquinodimethane [Ad(TCNQ)<sub>2</sub>], etc. Although the Peierls distortion is different in the crystals in that it involves mainly frozen-in internal modes of vibration (site distortion) rather than frozen-in external modes (bond distortion) as in (CH)<sub>*x*</sub>, the soliton wave functions are the same in the two cases, as will be shown in Sec. II.

An important difference, in the context of transport, between the solitons in the crystals and those in polyacetylene is that in the crystals they can only exist charged, specifically with charges  $\pm e/2$ , where  $e$  is the magnitude of the electronic charge.<sup>3</sup> At low concentrations the solitons provide localized electronic levels at midgap,<sup>3,4</sup> as in (CH)<sub>*x*</sub>. At higher concentrations there is a spread of the electronic levels about midgap due to overlap,<sup>5,6</sup> and to the Coulomb field of the randomly distributed charged impurities that give rise to solitons.<sup>6</sup> These effects should

be smaller in the crystals than in polyacetylene, however, for a number of reasons. First, the solitons will overlap less since they are smaller. According to the continuum model,<sup>7</sup> the length of a soliton is  $4ta/\Delta$ , where  $t$  is the transfer integral and  $a$  is the lattice constant. For (NMP)<sub>*x*</sub>(Phen)<sub>1-*x*</sub>-(TCNQ),  $\Delta \approx 900$  K (for  $x = 0.50$  at zero temperature),<sup>2</sup> and  $4t$  has been estimated as 4500 K.<sup>8</sup> Thus  $l \approx 5a$ , considerably less than the length in (CH)<sub>*x*</sub>, which is  $14a$ .<sup>9</sup> The Coulomb field of the impurities will also have a smaller effect due to the very large dielectric constants characteristic of conducting TCNQ salts. In what follows we will generally neglect the level spread.

Solitons are expected to contribute to charge transport due to electron hopping among them. If the solitons are charged and unpinned, then motion in a field could also make a direct contribution to conductivity and other transport properties. We do not expect this contribution to be larger than the hopping contribution, however, for the following reason. Although the materials we deal with have excess electrons, there will, at temperatures above  $T = 0$  K, be some positively charged solitons ( $S^+$ ) on each chain. In an electric field they will block the motion of the negatively charged solitons ( $S^-$ ). Recombination of an adjacent  $S^+S^-$  pair would remove the block only temporarily; we are dealing with a thermal equilibrium situation and another  $S^+S^-$  pair must be generated elsewhere. Electrons hopping in from other chains could unblock the conduction path, but then the rate-limiting step, the step that determines the conductivity

ty, would be the electron hopping.

The hopping conductivity and thermoelectric power were calculated for low soliton concentrations in  $(\text{CH})_x$  by Kivelson.<sup>10-12</sup> In  $(\text{CH})_x$  a charged soliton is pinned by the attraction of the oppositely charged impurity that gave rise to it. An electron can jump with phonon assistance from a localized midgap state on a bound soliton to one on a nearby neutral soliton. As Kivelson points out, since the pinning energy  $E_b$  is large,  $> 0.3$  eV, the jump can only take place when the neutral (mobile) soliton is in the neighborhood of a positively charged impurity. He approximates the electron-phonon coupling by a smooth-peaked function of energy having two parameters. By reasoning that the predominant electron-phonon interaction is with the zone-center optical modes which modulate the dimerization, Kivelson chooses the parameters by matching the peak to the average optical frequency and the peak width to the half-width of the optical-phonon spectrum. The procedure of Miller and Abrahams for calculating the hopping rate between impurities in semiconductors<sup>13</sup> is used to formally calculate the transition rate between an initial soliton with total energy  $E_i$  and a final soliton with total energy  $E_f$ . To find the actual hopping rate it is necessary to average over all possible initial and final energies for the solitons. Since the calculated quantum of vibrational energy is small compared to the binding energy of the solitons, Kivelson takes the distribution of soliton energies, and thus of final energies for the transition, to be continuous.

Intersoliton hopping in the molecular crystals differs in a number of important respects. First, it is quite likely that the solitons are not pinned at room temperature. The Coulomb attraction of a soliton with charge  $\pm e/2$  to a point impurity with charge  $\mp e$  at a distance  $b$  from the chain is given by

$$E_c = \frac{e}{\epsilon_{\perp} \epsilon_{\parallel}^{1/2}} \frac{e}{2} \int_{-\infty}^{\infty} \frac{|\varphi(x)|^2}{(x^2/\epsilon_{\parallel} + b^2/\epsilon_{\perp})^{1/2}} dx, \quad (1.1)$$

where  $\varphi(x)$  is the normalized wave function of the electron on the soliton, and  $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$  are the dielectric constants parallel and perpendicular to the chain, respectively. Since  $\epsilon_{\parallel} \gg \epsilon_{\perp}$  in these molecular crystals,  $E_c$  is well approximated by  $e^2/[2(\epsilon_{\perp} \epsilon_{\parallel})^{1/2} b]$ . For  $(\text{NMP})_x(\text{Phen})_{1-x}$ -TCNQ,  $b$  is of the order of the distance between the NMP and TCNQ chains, equal to 7.7 Å. If we assume  $\epsilon_{\parallel} = 1000$  and  $\epsilon_{\perp} = 3$ , typical values for other compounds in this family,<sup>14</sup> we find  $E_c = 190$  K. Thus the solitons could be bound only at temperatures somewhat less than 190 K. If, as a lower limit,  $\epsilon_{\parallel}$  were 100, the Coulomb energy could be as large as 590 K. If we assume, for definiteness, that the impurities are positively charged, then, of course, even at low temperatures, only negative solitons can be bound and not all of these need be bound since there are more negative solitons than impurities. In what follows we have calculated the hopping rate for three possible low-temperature cases: (1) the electron is initially on a bound soliton and jumps to a free soliton which then becomes bound; (2a) the electron is initially on a bound soliton and jumps to a soliton which remains free; (2b) the electron is initially on a free soliton and jumps to a soliton which then becomes bound. Hop-

ping from a free soliton to a free soliton is also possible and will be taken up in a later paper.

Another difference between our calculation and that of Kivelson is that we have taken the phonon assistance to be by internal or by acoustic modes. In both cases we have the advantage that the frequencies and coupling constants for these modes are known for the TCNQ compounds. The internal modes are expected to have essentially no dispersion. In the impurity problem this would cause the hopping rate to be vanishingly small. Here, however, the motion of the solitons provides a continuum of final states, resulting in a finite hopping rate.

In Sec. II we set up the continuum model Hamiltonian and wave function of an electron bound to an isolated soliton for the case of the Peierls distortion stabilized by internal modes. These are used in Sec. III to establish the appropriate Hamiltonian for a two-soliton system with not much overlap in the presence of impurity potentials. We then find the correct soliton wave functions for this Hamiltonian by the method of Miller and Abrahams. From these and the perturbing potentials due to the acoustic and the internal modes, we obtain the matrix elements for hopping. In Sec. IV the total hopping rate is calculated for the cases of bound and free solitons previously discussed. Once the transition rate is known, the conductivity and thermopower due to intersoliton hopping can be calculated. This is done in Secs. IV and V. In Sec. VI we summarize the conclusions. In the Appendix we discuss the soliton mass for this case and the quantum of vibrational energy of a soliton pinned to an impurity. Experimental comparison will be carried out in a subsequent paper because dc transport, above 80 K at least, involves band electrons and holes as well as hopping in the soliton levels.

## II. HAMILTONIAN AND WAVE FUNCTION FOR ELECTRONS IN SOLITON STATES

To take into account the gap contribution of the internal modes we add to the Hamiltonian of Su, Schrieffer, and Heeger<sup>9</sup> the term for the energy of an electron on the  $n$ th lattice site. To terms linear in the (dimensionless) normal coordinate  $Q_{l,n}$  for the  $l$ th internal vibration on the  $n$ th site, we may write<sup>15</sup> this addition to the Hamiltonian as

$$\sum_{n,s} \epsilon_{ns} = \sum_{n,s} \left[ \epsilon_{0s} + \sum_{l=1}^G \beta_l Q_{l,n} \right] c_{ns}^{\dagger} c_{ns}, \quad (2.1)$$

where  $\epsilon_{0s}$  is the site energy in the absence of excited vibrations,  $\beta_l = (\partial \epsilon_{ns} / \partial Q_{l,n})_0$ , and the summation is over the modes,  $G$  in number, linearly coupled to the electrons.<sup>16</sup> For the half-filled-band case (or  $\frac{1}{4}$ -filled band with large  $U$ ), we take into account the spatial variation of  $Q_{l,n}$  by introducing a staggered order parameter  $\tilde{Q}_{l,n} = (-1)^n Q_{l,n}$ . To derive the continuum  $H$  for this case, it is convenient to introduce the superposition of right- and left-going waves shifted in phase by  $3\pi/4$  from the usual,<sup>7</sup> i.e.,

$$c_{ns} = u_{ns} e^{i3\pi/4} \exp(ik_F n a) - i v_{ns} e^{-i3\pi/4} \exp(-ik_F n a). \quad (2.2)$$

Using the same procedure as Ref. 7 to derive the continuum  $H$  with the added term Eq. (1), and  $c_{ns}$  given by (2.2), we obtain, for the electronic terms,

$$H_{el} = \int dx \psi^\dagger(x) \left[ -2iat\sigma_3 \frac{\partial}{\partial x} - \Delta_{ext}\sigma_2 + \Delta_{int}\sigma_1 \right] \psi(x), \quad (2.3)$$

where  $\Delta_{ext} = 4\alpha\tilde{y}(x)$ ,  $\alpha$  being the derivative of  $t$  with respect to displacement of a lattice point and  $\tilde{y}(x)$  being the staggered displacement parameter,

$$\Delta_{int} = \sum_{l=1}^G \beta_l \tilde{Q}_l = \sum_l \Delta_l(x) \quad (2.4)$$

and

$$\psi(x) = \begin{bmatrix} u(x) \\ v(x) \end{bmatrix}.$$

From Eq. (2.3) we obtain the equations of motion:

$$Eu = -2iat \frac{\partial u}{\partial x} + (\Delta_{int} + i\Delta_{ext})v, \quad (2.5a)$$

$$Ev = 2iat \frac{\partial v}{\partial x} + (\Delta_{int} - i\Delta_{ext})u. \quad (2.5b)$$

In an earlier derivation of the Hamiltonian in the momentum representation,  $\Delta$  was obtained as  $\Delta_{ext} + i\Delta_{int}$ ,<sup>17</sup> the difference here is due to the phase shifted  $u_{ns}$  and  $v_{ns}$  of Eq. (2.2).

For the materials of interest here, as noted earlier, the gap is stabilized mainly by the internal modes, so we drop the term  $\Delta_{ext}$  in Eqs. (2.5a) and (2.5b). Combining them we obtain

$$Ef_- = -2iat \frac{\partial f_+}{\partial x} - i\Delta_{int}(x)f_+, \quad (2.6)$$

where  $f_\pm = u \pm iv$ . For the electronic state on the soliton at midgap we may take  $E=0$ . The resulting equation,

$$\left[ -2at \frac{\partial}{\partial x} - \Delta_{int}(x) \right] f_+ = 0 f_+, \quad (2.7)$$

may be considered the eigenvalue equation for the electron on the soliton; the quantity in large parentheses is the Hamiltonian. Since it is precisely the same equation as would have been obtained if there were only external-mode distortion (and  $u_{ns}$  and  $v_{ns}$  were not phase shifted by  $3\pi/4$ ), it is clear that the electron wave function is the same whether there is internal- or external-mode distortion. To obtain that wave function<sup>7</sup> we choose

$$\Delta(x) = \Delta_0 \tanh(x/\xi_{||}), \quad (2.8)$$

and find the solution

$$f_+ = C \operatorname{sech}(x/\xi_{||}), \quad (2.9)$$

provided

$$\xi_{||} = 2ta/\Delta_0, \quad (2.10)$$

where  $\Delta_0$  is one-half the Peierls gap. We will use  $f_+$  of (2.9) as the wave function for an electron on an isolated soliton. It can be shown that, for the case of the gap sta-

bilized by internal modes, there is no oscillating modulating factor  $\cos(x\pi/2a)$  [ $\sin(\pi x/2a)$  for the antisoliton] in the wave function for the soliton as there is when the gap is stabilized by external modes, as in polyacetylene. Thus the wave function for either soliton or antisoliton has amplitude on both even- and odd-numbered sites, and is given by (2.9).

### III. MATRIX ELEMENTS FOR HOPPING

To calculate the matrix elements we consider the case of one soliton centered at  $x_i=0$ ,  $y_i=0$ , and  $z_i=0$ , a second centered at  $x_j, y_j, z_j$ , sufficiently far away so that the overlap is small, and one charged donor or acceptor nearby. As do Miller and Abrahams,<sup>13</sup> we assume that the Coulomb fields of all the other charged donors or acceptors cancel, on the average. With  $V_a$  the potential energy due to the donor or acceptor charge, we have, using the results of Sec. II,

$$H = -2ta \frac{\partial}{\partial x} - \Delta(x)\delta(y')\delta(z') - \Delta(x-x_j)\delta(y'-y'_j)\delta(z'-z'_j) + V_a, \quad (3.1)$$

where  $x$  is the chain direction,  $y'=y/\xi_1$ ,  $z'=z/\xi_1$  ( $\xi_1$  being the average transverse decay length of the electron wave function), and the Dirac  $\delta$  functions reflect the fact that the soliton lattice distortion has no off-chain (transverse) component. Here, the first term of  $H$  is a kinetic energy term, and  $\Delta(x)$ , the soliton lattice distortion, is taken to have the same form as in the single-soliton Hamiltonian, Eq. (2.8), since soliton overlap is small.

The eigenfunctions of this ground-state two-soliton Hamiltonian in the absence of phonons may be approximated by superpositions of solutions for single-soliton systems. Therefore, we can write solutions as

$$\psi_i = b_1\varphi_i + b_2\varphi_j, \quad b_1 \gg b_2 \quad (3.2a)$$

$$\psi_j = b'_1\varphi_i + b'_2\varphi_j, \quad b'_2 \gg b'_1 \quad (3.2b)$$

where  $\varphi_i$  and  $\varphi_j$  are the wave functions for isolated solitons at  $(x_i, y_i, z_i)$  and  $(x_j, y_j, z_j)$ , respectively. A variational calculation yields

$$b_1/b_2 \simeq (\Delta E_c + J_1 - J_2)/W, \quad (3.3)$$

where

$$J_1 = \langle \varphi_i | -\Delta(x-x_j)\delta(y'-y'_j)\delta(z'-z'_j) | \varphi_i \rangle, \quad (3.4)$$

$$J_2 = \langle \varphi_j | -\Delta(x)\delta(y')\delta(z') | \varphi_j \rangle, \quad (3.5)$$

$$\Delta E_c = | \langle \varphi_i | V_a | \varphi_i \rangle - \langle \varphi_j | V_a | \varphi_j \rangle |, \quad (3.6)$$

and

$$2W = L' + L'' - 2\mathcal{S}J_1 + 2\langle \psi_i | V_a | \psi_j \rangle - 2\mathcal{S}\langle \psi_i | V_a | \psi_i \rangle, \quad (3.7)$$

with

$$L' = \langle \varphi_i | -\Delta(x)\delta(y')\delta(z') | \varphi_j \rangle, \quad (3.8)$$

$$L'' = \langle \varphi_j | -\Delta(x-x_j)\delta(y'-y'_j)\delta(z'-z'_j) | \varphi_i \rangle, \quad (3.9)$$

and

$$\mathcal{S} = \langle \varphi_i | \varphi_j \rangle = \langle \varphi_j | \varphi_i \rangle, \quad (3.10)$$

the overlap integral. The last two terms of (3.7) cancel if  $\epsilon_{||} \gg \epsilon_{\perp}$ , and are subsequently dropped. To evaluate these integrals we need the isolated-soliton wave functions  $\varphi_i$  and  $\varphi_j$ . The on-chain soliton wave function is given in Sec. II. Since the lattice disturbance  $\Delta(x)$  associated with a soliton is strictly one dimensional, we expect the electronic wave function to decay off chain with a decay length  $\xi_{\perp}$  essentially that of the  $p$  orbitals from which the state on the soliton is formed, i.e.,  $\sim 3 \text{ \AA}$ .<sup>18</sup> We can approximate this transverse wave function as an exponential, so that for a soliton centered at  $x_i, y_i, z_i$ ,

$$\begin{aligned} \varphi_i(x_i, y_i, z_i) = & C_{||} \operatorname{sech}[(x - x_i)/\xi_{||}] \\ & \times C_{\perp} \exp\{-[(y - y_i)^2 + (z - z_i)^2]^{1/2}/\xi_{\perp}\}, \end{aligned} \quad (3.11)$$

where  $C_{||} = (2\xi_{||})^{-1/2}$  and  $C_{\perp} = (2/\xi_{\perp})(2\pi)^{-1/2}$  are the on-chain and transverse normalization constants, respectively.

Upon evaluating the integrals for  $J_1, J_2, L', L''$ , and  $\mathcal{S}$ , we find that

$$J_1 = -J_2 \simeq (\Delta_0/2\pi) \tanh(R_{||}/\xi_{||}) \exp(-2R_{\perp}/\xi_{\perp}) \quad (R_{||} \gg \xi_{||}), \quad (3.12)$$

and  $L' = -L''$ , or  $L' + L'' = 0$ . The overlap integral  $\mathcal{S}$  is

$$\begin{aligned} \mathcal{S} = \mathcal{S}_{||} \mathcal{S}_{\perp} = & \exp(-R_{||}/\xi_{||}) (1 + R_{||}/\xi_{||}) \\ & \times (R_{\perp}/\xi_{\perp})^2 \frac{1}{2} K_2(R_{\perp}/\xi_{\perp}) \quad (R_{||} \gg \xi_{||}), \end{aligned} \quad (3.13)$$

where  $K_2$  is the second-order modified Bessel function,  $R_{||}$  is the on-chain component of the distance between soliton centers, and  $R_{\perp}$  is the transverse component of the distance between soliton centers. For  $R_{\perp} \gg \xi_{\perp}$ ,  $K_2$  varies as  $\exp(-R_{\perp}/\xi_{\perp})$ , so the overlap integral decays exponentially, as expected. Since  $W \propto \mathcal{S}$ , we expect that  $W \ll (\Delta E_c + 2J_1)$  and we may write

$$\psi_i \simeq \varphi_i + (b_2/b_1) \varphi_j \simeq \varphi_i - [\mathcal{S} J_1 / (\Delta E_c + 2J_1)] \varphi_j \quad (3.14a)$$

and

$$\psi_j \simeq \varphi_j - (b_2/b_1) \varphi_i \simeq \varphi_j + [\mathcal{S} J_1 / (\Delta E_c + 2J_1)] \varphi_i. \quad (3.14b)$$

The procedure we have followed here, and the results obtained, are closely analogous to those of Miller and Abrahams<sup>13</sup> for the wave functions of an electron on two donor sites in a doped semiconductor in the presence of an ionized acceptor. Once the wave functions  $\psi_i$  and  $\psi_j$  are known, the intersoliton transition rate follows from the matrix elements of the Hamiltonian mixing  $\psi_i$  and  $\psi_j$ . In the remainder of this section we will develop these matrix elements. In Sec. IIIA we deal with transitions assisted by intramolecular-mode phonons. In Sec. IIIB transitions mediated by acoustic phonons are discussed.

### A. Transitions by intramolecular-mode phonons

The total (electronic and vibrational) Hamiltonian for the system consisting of solitons, impurity or dopant molecule, and intramolecular-mode phonons can be written as

$$H = H_e + V_a + H_{\text{int}}, \quad (3.15)$$

where  $H_e$  is the electronic Hamiltonian of the "pure" system (with no impurities or phonons),  $V_a$  is the potential of the impurity or dopant molecule, and  $H_{\text{int}}$  is the intramolecular-mode phonon Hamiltonian.  $H_{\text{int}}$  is the sum of kinetic- and potential-energy terms:

$$H_{\text{int}} = \frac{1}{2} \sum_{n,l} (\hbar/\omega_l) \dot{Q}_{l,n}^2 + \frac{1}{2} \sum_{n,l} \hbar\omega_l Q_{l,n}^2. \quad (3.16)$$

As before,  $n$  is the site index,  $l$  is the mode index,  $\omega_l$  is the mode frequency, and  $Q_{l,n}$  is the dimensionless normal-mode coordinate. We assume that the total wave function can be written as the product of an electronic part  $\psi$ , which is the eigenfunction of  $H_e + V_a$ , and a lattice oscillator wave function  $\Phi$ . Recalling that  $Q_{l,n}$  varies with time as  $\exp(i\omega_l t)$  and that its spatial variation may be written

$$Q_{l,n} = N^{-1/2} \sum_{q} \exp(i\vec{q} \cdot \vec{R}_n) \{2^{-1/2} [b_l(q) + b_l^\dagger(-q)]\}, \quad (3.17)$$

where  $N$  is the number of lattice sites on the chain,  $q$  is the wave vector of the phonon,  $R_n$  is a lattice coordinate, and  $b_l(q)$  and  $b_l^\dagger(-q)$  are the annihilation and creation operators, we find upon taking the matrix elements of (3.16) that, in the continuum limit,

$$\begin{aligned} \langle H_q \rangle & \equiv \langle \Phi_j \psi_j | H_{\text{int}} | \psi_i \Phi_i \rangle \\ & = \sum_l (2\hbar\omega_l / N^{1/2}) \\ & \quad \times \left\{ \frac{n_q^{1/2}}{(n_q + 1)^{1/2}} \right\} \times \langle \psi_j | \exp(2i\vec{q} \cdot \vec{r}) | \psi_i \rangle. \end{aligned} \quad (3.18)$$

Here  $n_q$  is the number of phonons of energy  $\hbar\omega_q$ . The factor  $n_q$  in large curly brackets corresponds to phonon absorption, the factor  $n_q + 1$  to emission.

We evaluate the integral in (3.18) using  $\psi_i$  and  $\psi_j$  derived earlier in this section. Since in practice only the lowest-energy optical mode will be important, we drop the summation over  $l$ . The phonon energy for that mode will be taken as  $\hbar\omega_0$ , independent of  $q$  since, as noted earlier, dispersion is small. The result is

$$\begin{aligned} |\langle H_q \rangle|^2 = & (8/N) [(\hbar\omega_0) \pi q_{||} \xi_{||} (b_2/b_1) \operatorname{csch}(\pi q_{||} \xi_{||})]^2 \\ & \times (1 + q_{\perp}^2 \xi_{\perp}^2)^{-3} \times \left\{ \frac{n_0}{1 + n_0} \right\}, \end{aligned} \quad (3.19)$$

where  $q_{||}, q_{\perp}$  are the components of  $\vec{q}$  parallel and perpendicular to the chain, respectively. To arrive at this, we

have dropped the off-diagonal terms in the matrix element; these give contributions to the transition rate smaller by at least an order of magnitude than the contributions from the diagonal terms. Oscillatory terms varying as  $\sin(q_{\parallel}R_{\parallel})$  or  $\cos(q_{\parallel}R_{\parallel})$  have also been dropped; their contribution to the total conductivity will be small when summed over all  $R_{\parallel}$ . The transition rate  $\nu_{ij}$  between soliton  $i$  and soliton  $j$  is given according to Fermi's golden rule by

$$\nu_{ij} = (2\pi/\hbar) \sum_q |\langle H_q \rangle|^2 \delta(E_j - E_i \pm \hbar\omega_q), \quad (3.20)$$

where  $E_j$  and  $E_i$  are, respectively, the total energies of soliton  $j$  and soliton  $i$ . The plus sign in (3.20) refers to phonon emission, the minus sign to phonon absorption. Changing the summation over  $q$  to an integration over the Brillouin zone, and inserting (3.19) into (3.20), we have for hopping in three dimensions

$$\nu_{ij}^{3D}(E_j, E_i) = \frac{3.3\Omega(\hbar\omega_0)^2}{(\hbar\pi^2\xi_{\parallel}\xi_{\perp}^2)} (b_2/b_1)_{3D}^2 \delta(E_j - E_i \pm \hbar\omega_0) \times \left\{ \begin{matrix} n_0 \\ 1+n_0 \end{matrix} \right\}, \quad (3.21)$$

where  $\Omega$  is the volume of a unit cell. To obtain Eq. (3.21) the integral over  $q_{\parallel}$  was evaluated approximately in regions of small ( $q_{\parallel}\xi_{\parallel}$ ) and large ( $q_{\parallel}\xi_{\parallel}$ ) by using the polynomial and the exponential expansions of  $\text{csch}(\pi q_{\parallel}\xi_{\parallel})$ , respectively. In addition, the factor  $1 - (1 + \xi_{\perp}^2 \pi^2 / b^2)^{-2}$  has been approximated by unity, which is reasonable for the cases we consider. For later use we also write the transition rate for the case of on-chain hopping and  $q = q_{\parallel}$ :

$$\nu_{ij}^{1D}(E_j, E_i) = [26.4a(\hbar\omega_0)^2 / (\hbar\pi\xi_{\parallel})] (b_2/b_1)_{1D}^2 \times \delta(E_j - E_i \pm \hbar\omega_0) \times \left\{ \begin{matrix} n_0 \\ 1+n_0 \end{matrix} \right\}, \quad (3.22)$$

where  $(b_2/b_1)_{1D}$  is evaluated by setting  $R_{\perp} = 0$  in (3.12)–(3.14).

To find the total transition rate  $\bar{\nu}$  for intersoliton hopping due to intramolecular phonons, one must sum  $\nu_{ij}$  over all  $E_j$  and  $E_i$ . This summation will be carried out in Sec. IV, where the total rate  $\bar{\nu}$  will then be used to find the mobility of electrons in the soliton levels.

### B. Transitions by acoustic-mode phonons

Intersoliton hopping can also be mediated by acoustic-mode phonons. In analogy to (3.15) we may write the Hamiltonian for that case as<sup>12</sup>

$$H = H_e + V_a + U(R) + \sum_n P_n^2 / (2M), \quad (3.23)$$

where  $U(R)$  is the potential energy of the molecules along the chain,  $M$  is the mass of a molecule, and  $\vec{P}_n = i\hbar\vec{\nabla}_n$ , the momentum operator. The development of the matrix element  $\langle H_q \rangle$  proceeds along the lines of Kivelson's matrix element for external modes.<sup>12</sup> For the case of on-chain hopping due to longitudinal modes with  $\vec{q}$  parallel

to the chain direction or transverse modes with  $\vec{q}$  perpendicular to the chain direction

$$\begin{aligned} \langle H_q \rangle &= \sum_n (\psi_j^* \vec{P}_n \psi_i) \cdot \int \Phi_j(\vec{P}_n/M) \Phi_i d\tau \\ &= (\hbar\omega_q/2MN)^{1/2} \times \left\{ \begin{matrix} n_q^{1/2} \\ (1+n_q)^{1/2} \end{matrix} \right\} \\ &\quad \times \hbar \int_{-\infty}^{\infty} dx e^{\pm iqx} (\psi_j^* \nabla_x \psi_i). \end{aligned} \quad (3.24)$$

Here the factor  $e^{+iqx}$  corresponds to absorption of a phonon, while  $e^{-iqx}$  corresponds to phonon emission. When the spatial integral in (3.24) is evaluated with the use of the electronic wave functions (3.14a) and (3.14b), the result is

$$\begin{aligned} |\langle H_q \rangle|^2 &= [\hbar\omega_q/(MN)] [(\hbar\pi/4\xi_{\parallel})(q\xi_{\parallel})^2 \\ &\quad \times (b_2/b_1)_{1D} \text{csch}(\pi\xi_{\parallel}q/2)]^2 \times \left\{ \begin{matrix} n_q \\ 1+n_q \end{matrix} \right\}. \end{aligned} \quad (3.25)$$

Here, as in the intramolecular-mode case, off-diagonal terms and terms oscillatory in  $R_{\parallel}$  have been dropped, since their contributions to the conductivity will be very small compared to the remaining terms. To find  $\nu_{ij}$ , we insert Eq. (3.25) into Eq. (3.20), setting  $\hbar\omega_q = \hbar c_0 q$ , where  $c_0$  is the velocity of longitudinal or transverse waves. Integrating over  $q$ , we find

$$\begin{aligned} \nu_{ij}^{1D} &= (\pi^2 a \Delta E / M c_0 \xi_{\parallel}^2) (\xi_{\parallel} \Delta E / 2\hbar c_0)^4 (b_2/b_1)_{1D}^2 \\ &\quad \times \text{csch}^2(\pi\xi_{\parallel}\Delta E/2\hbar c_0) \times \left\{ \begin{matrix} n(\Delta E) \\ 1+n(\Delta E) \end{matrix} \right\}, \end{aligned} \quad (3.26)$$

where  $\Delta E = |E_j - E_i|$ .

Having derived the rates  $\nu_{ij}$  for the cases of intramolecular- and acoustic-phonon-assisted hopping, we proceed in Sec. IV to average over the possible soliton energies  $E_i$  and  $E_j$  to find the total transition rates  $\nu_{ij}$ , and subsequently the intersoliton electron mobilities for the two cases.

## IV. TOTAL TRANSITION RATES AND MOBILITIES

The hopping rate  $\nu_{ij}(E_j, E_i)$  established in the preceding section is the probability per unit time of a transition from soliton  $i$  to an empty soliton  $j$ , when the initial state energy is  $E_i$  and the final-state energy is  $E_j$ . The actual hopping rate from  $i$  to  $j$  is the sum of  $\nu_{ij}(E_j, E_i)$  over all initial states  $E_i$ , weighted by the probability of their occurrence  $p_i(E_i)$ , and all final states  $E_j$  weighted by their probability  $\bar{p}_j(E_j)$ . The total hopping rate  $\bar{\nu}_{ij}$  between all pairs of states,  $(E_j, E_i)$  is then

$$\bar{\nu}_{ij} = \int \int \nu_{ij}(E_j, E_i) p_i(E_i) \bar{p}_j(E_j) dE_i dE_j. \quad (4.1)$$

Given the hopping rate  $\bar{\nu}_{ij}$ , one can approximate the hop-

ping mobility  $\mu$  for electrons in the soliton levels by

$$\mu \simeq |e| \bar{v}_{ij} R^2 / (kT) \quad (4.2)$$

from the Einstein relation. Here  $R$  is the average hopping distance.

#### A. Intramolecular modes

First we will consider transitions from an initially bound soliton to a soliton which is near a positive impurity or dopant and thus becomes bound in the final state, after receiving the electron. If the Coulomb attraction  $E_c$  [see Eq. (1.1)] of the soliton to the dopant is large, and the quantum of vibrational energy  $\hbar\omega_v$  is small, it is appropriate to speak of a continuum of soliton energy levels in the Coulomb potential well of the donor or impurity, as Kivelson does.<sup>10-12</sup> In that case  $p_i(E_i)$  is given by<sup>12</sup>

$$p_i(E_i) = \rho_i(E_i) \exp(-E_i/kT) / Z_i(T), \quad (4.3)$$

where  $\rho_i(E_i)$  is the density of states of the negatively charged soliton in the potential well of the dopant and  $Z_i(T)$  is the corresponding partition function. Likewise, for  $\bar{p}_j(E_j)$  we have<sup>12</sup>

$$\bar{p}_j(E_j) = \rho_j(E_j) / Z_j, \quad (4.4)$$

where  $\rho_j(E_j)$  is the density of states of the final-state soliton, and  $Z_j$  is the partition function for the free soliton  $j$  that exists before the electron's hop from soliton  $i$ . Since we consider the bound soliton to have a continuous distribution of energy levels between  $-E_b = -E_c + \hbar\omega_v/2$  and the top of the well, which we take to have zero energy, we have

$$\rho_i(E_i) = \frac{\Theta(-E_i)\Theta(E_i + E_b)}{(\hbar\omega_v)}. \quad (4.5)$$

Here  $\Theta$  is the unit step function. The partition function  $Z_i(T)$ , which follows from (4.5), is now

$$Z_i(T) \simeq (kT/\hbar\omega_v) \exp(E_b/kT) \quad (4.6)$$

for  $E_b \gg kT$ .

As shown in the Appendix, we expect a free soliton to have essentially zero kinetic energy compared to  $kT$  at 100 K and above. We may then take the partition function  $Z_j$  as the total number of free-soliton states. With  $N$  the number of sites on a chain, and  $n_s$  the number of solitons on a chain, we can approximate the number of states as the average number of sites available to each soliton, so that

$$Z_j \simeq N/n_s. \quad (4.7)$$

Using (3.22), (4.1), and (4.3)–(4.7), we can then evaluate  $\bar{v}$  for  $E_j = E_i - \hbar\omega_0$  (that is, for phonon emission) to obtain (case 1a)

$$\bar{v}_{\text{em}}^{3D} = (3.3\Omega\omega_0^2 n_s / \pi^2 \xi_{\parallel}^2 \omega_v N) (b_2/b_1)_{3D}^2 \times \exp(-E_b/kT) \{ \exp[(E_b - \hbar\omega_0)/kT] - 1 \} (1 + n_0), \quad (4.8)$$

and likewise, for  $E_j = E_i + \hbar\omega_0$  (phonon absorption) we

obtain (case 1b)

$$\bar{v}_{\text{abs}}^{3D} = [3.3\Omega\omega_0^2 n_s / (\pi^2 \xi_{\parallel}^2 \omega_v N)] (b_2/b_1)_{3D}^2 \times \{ 1 - \exp[(\hbar\omega_0 - E_b)/kT] \} n_0. \quad (4.9)$$

In (4.8) and (4.9),  $(b_2/b_1)_{3D}$  is evaluated for  $\Delta E_c = \hbar\omega_0$ . The sum of (4.8) and (4.9) gives the total transition rate for intersoliton hopping assisted by internal modes between solitons bound in deep wells with many levels, case 1. To obtain the corresponding 1D quantities we use the relationship

$$\bar{v}^{1D} = \bar{v}^{3D} (8\pi \xi_{\perp}^2 a / \Omega) (b_2/b_1)_{1D}^2 / (b_2/b_1)_{3D}^2.$$

To have an idea of the magnitude of  $v_{ij}$  we apply these results to the case of (NMP)<sub>x</sub>(Phen)<sub>1-x</sub>-TCNQ. We first find that, in contrast to polyacetylene, off-chain or 3D hopping is negligible compared to 1D hopping. Using Eqs. (3.3), (3.12), and (3.13), with  $\Delta E_c = \hbar\omega_0$ , we find

$$\frac{(b_2/b_1)_{3D}}{(b_2/b_1)_{1D}} \simeq \frac{1}{2} (R_{\perp} / \xi_{\perp})^2 K_2(R_{\perp} / \xi_{\perp}) \exp(-2R_{\perp} / \xi_{\perp}). \quad (4.10)$$

The interchain distances are 7.6 and 16.3 Å. The latter distance is so large that we can clearly neglect hopping in that direction. Taking into account the finite extent of the molecule, and the fact that the electron wave function is spread throughout, we may take  $R_{\perp}$  as small as 6 Å in the former direction, giving  $R_{\perp} / \xi_{\perp} = 2$ . Evaluating (4.10) and inserting the result in the above expression for  $\bar{v}^{1D}$ , we find  $\bar{v}^{3D} \sim 10^{-4} \bar{v}^{1D}$  for even the closest chain. Thus the relatively large interchain distance results in such poor overlap that on-chain jumping is greatly favored.

As explained in the Appendix, for (NMP)<sub>x</sub>(Phen)<sub>1-x</sub>-TCNQ it is likely that there are  $\sim 10$  vibrational levels in the potential well of a soliton bound to an impurity; this would justify use of a continuum model for states in the well. For (NMP)<sub>0.54</sub>(Phen)<sub>0.46</sub>-TCNQ at 100 K, we have calculated from (4.8) and (4.9) the total transition rates  $\bar{v}_{\text{abs}}^{1D}$  and  $\bar{v}_{\text{em}}^{1D}$ , at this temperature  $\Delta/k \simeq 690$  K (Ref. 8) for  $(n_s/N) = 0.08$ ,<sup>3</sup> and with a bandwidth  $4t/k = 4500$  K,<sup>8</sup>  $\xi_{\parallel} = 3.26a = 12.6$  Å. We may take  $R_{\parallel}$  as the average distance between two solitons,  $12.5a = 48.3$  Å, so that  $(R_{\parallel} / \xi_{\parallel}) = 3.83$ . Then, with  $E_b$  of 250 K and  $(\hbar\omega_0/k) = 210$  K, the lowest-energy intramolecular mode for TCNQ,<sup>16</sup> we find  $(b_2/b_1)_{1D} = 0.0267$ . This results in rates of  $\bar{v}_{\text{abs}}^{1D} = 2.17 \times 10^9 \text{ sec}^{-1}$  and  $\bar{v}_{\text{em}}^{1D} = 2.17 \times 10^9 \text{ sec}^{-1}$ , which give a total mobility of  $\mu \simeq 5.6 \times 10^{-2} \text{ cm}^2/\text{V sec}$  for this process.

If  $E_c$  is not much larger than  $\hbar\omega_v$ , then there may be only one soliton level in the potential well. We cannot consider hopping transitions from a bound soliton to a final-state bound soliton in this case, since the system lacks the necessary continuum of final states for a hopping transition. Hopping could occur for this case, however, if electrons make transitions from the single bound-state energy level to an (initially unoccupied) free soliton, which has a continuum of kinetic energy levels, or vice versa.

We thus take up the case of hopping from a bound soliton to a free soliton and its reverse, hopping from a free

soliton to a soliton that becomes bound in the final state near an impurity, assuming there is only one level in the potential well of the bound soliton. This level is taken to be at energy  $-E_b$ , where, as before, the zero of energy is at the top of the well. For the density of states in (4.3) we then have simply

$$\rho_i(E_i) = \delta(E_i + E_b), \quad (4.11)$$

and for the corresponding partition function,

$$Z_i(T) = \exp(E_b/kT). \quad (4.12)$$

The free soliton which is the final state of the electron is assumed to be sufficiently far away that the net Coulomb repulsion due to the charged ion and the other soliton may be neglected. It then has a continuum of levels between zero energy and  $E_k$ , a maximum kinetic energy (see the Appendix). For the density of states in (4.4) we then have

$$\rho_j(E_j) = [N/(n_s E_k)] \Theta(E_j) \Theta(-E_j + E_k). \quad (4.13)$$

The partition function for the free solitons is given by (4.7) as before. The hop from the bound soliton to the free soliton involves phonon absorption, i.e.,  $E_j = E_i + \hbar\omega_0$ . Thus, using (3.22) and (4.1), we have for the bound-soliton-free-soliton transition via phonon absorption for 1D hopping and  $q = q_{||}$  (case 2a)

$$\bar{\nu}_{\text{abs}}^{\text{1D}} = [26.4a / (\pi \xi_{||} \hbar E_k)] (\hbar\omega_0)^2 (b_2/b_1)_{\text{1D}}^2 n_0. \quad (4.14)$$

For the transition from a free soliton to a free soliton which becomes bound to an impurity in the final state, phonon emission is required, and  $E_j = E_i - \hbar\omega_0$ . Use of (3.22) and (4.1) leads to (case 2b)

$$\bar{\nu}_{\text{em}}^{\text{1D}} = [26.4a n_s / (\pi \xi_{||} \hbar E_k N)] (\hbar\omega_0)^2 (b_2/b_1)_{\text{1D}}^2 (1 + n_0). \quad (4.15)$$

The above expressions are valid for  $0 \leq \hbar\omega_0 - E_b \leq E_k$ ; that is, the difference in the phonon energy and the bound-soliton energy level in the well must be no larger than the maximum allowed kinetic energy of the free soliton. Since, as explained in the Appendix, we can expect  $E_k$  to be small [ $\sim 30$  K for  $(\text{NMP})_x(\text{Phen})_{1-x}$ -(TCNQ)], this would mean that for intersoliton hopping to take place via intramolecular phonons, the intramolecular phonon energy and the soliton binding energy must be rather closely matched. This restriction is due to some of the idealizations made in the calculation, notably neglecting the Coulomb potential energy of the free soliton and allowing for the presence of only one impurity. In a real material, one would expect an inhomogeneous distribution of impurities. Particularly when the concentration is not very low, this will result in a range of binding energies for the bound soliton and of potential energies for the free soliton. In addition, if there are intermolecular modes close in energy to  $\hbar\omega_0$ , more than one mode may participate in the intersoliton transitions.

We now evaluate the on-chain hopping rate for the case  $x = 0.54$  at  $T = 100$  K. We have previously found that  $(b_2/b_1)_{\text{1D}} = 0.0267$  for this case. With  $E_k = 30$  K, these values inserted in Eqs. (4.14) and (4.15) lead to  $\bar{\nu}_{\text{abs}}^{\text{1D}} = 4.9 \times 10^{10} \text{ sec}^{-1}$  and  $\bar{\nu}_{\text{em}}^{\text{1D}} = 3.2 \times 10^{10} \text{ sec}^{-1}$ . Since

the electron can go from the bound to the free soliton only by absorption, and from free to bound only by emission, to obtain  $\mu$  from Eq. (4.2) we insert for  $\bar{\nu}_{ij}$  the average of  $\bar{\nu}_{\text{em}}$  and  $\bar{\nu}_{\text{abs}}$ . The result is  $\mu = 1.03 \text{ cm}^2/\text{V sec}$  at 100 K.

Finally, we consider hopping between bound and free solitons when  $E_c$  is large compared to  $\hbar\omega_0$ , i.e., when there is an effective continuum of levels in the well. We then use the density of states and partition function given by Eqs. (4.5) and (4.6) for the bound soliton, in place of Eqs. (4.11) and (4.12). The rest of the derivation is identical to that of the previous case. Taking  $\hbar\omega_0 < E_b$ , we have

$$\begin{aligned} \bar{\nu}_{\text{abs}}^{\text{1D}} &= [26.4a / (\pi \xi_{||} \hbar E_k)] (\hbar\omega_0)^2 (b_2/b_2)_{\text{1D}}^2 \\ &\times \exp[(\hbar\omega_0 - E_b)/kT] [1 - \exp(-E_k/kT)] n_0 \end{aligned} \quad (4.16)$$

and

$$\begin{aligned} \bar{\nu}_{\text{em}}^{\text{1D}} &= [26.4a \omega_0^2 k T n_s / (\pi \xi_{||} E_k \omega_0 N)] (b_2/b_1)_{\text{1D}}^2 \\ &\times [1 - \exp(-E_k/kT)] (1 + n_0). \end{aligned} \quad (4.17)$$

If we evaluate this case for the  $(\text{NMP})_{0.54}(\text{Phen})_{0.46}$ -(TCNQ) parameters used previously, (4.16) gives  $\bar{\nu}_{\text{abs}}^{\text{1D}} = 8.59 \times 10^9 \text{ sec}^{-1}$  and (4.17) gives  $\bar{\nu}_{\text{em}}^{\text{1D}} = 4.6 \times 10^{10} \text{ sec}^{-1}$ , so that  $\mu \approx 0.70 \text{ cm}^2/\text{V sec}$  at 100 K.

Although the mobilities for all the hopping processes considered are likely to be smaller than that of the conduction-band electrons, intersoliton hopping may nonetheless make an important contribution to transport since there are few electrons in the conduction band at the temperatures we have considered.

We consider now the acoustic-mode case. From (3.26) we see that  $\nu_{ij}(E_j, E_i)$  has a complicated dependence on  $E_i$  and  $E_j$ ; we can use (3.26), however, to obtain an estimate of  $\mu$  for  $(\text{NMP})_x(\text{Phen})_{1-x}$ -(TCNQ). The relation  $\hbar\omega_q = \hbar c_0 q$  is applicable only below  $(\hbar\omega_q/k) \approx 80$  K for TCNQ-based compounds of this type. We can evaluate (3.26) for a phonon of  $\hbar\omega_q/k = 50$  K, at a temperature of  $T = 50$  K, to have an idea of the magnitude of  $\nu_{ij}(E_j, E_i)$ . We will apply the calculation to the case  $x = 0.54$ . Previous calculations<sup>8</sup> have predicted a Peierls half-gap  $\Delta/k \approx 710$  K and a soliton half-length  $\xi_{||} = 12 \text{ \AA}$  for  $(\text{NMP})_{0.54}(\text{Phen})_{0.46}$ -(TCNQ) at this temperature. If the speed of sound is  $3 \times 10^5 \text{ cm/sec}$ , and the mass  $M$  of the TCNQ molecule  $\sim 3.41 \times 10^{-22} \text{ g}$ , then for  $R_{||} = 12.5a$  the average distance between two solitons, the calculated hopping rate from Eq. (3.26) is  $\nu_{ij}^{\text{1D}}(50 \text{ K}) = 1.649 \times 10^4 \text{ sec}^{-1}$ , corresponding to  $\mu = 8.25 \times 10^{-7} \text{ cm}^2/\text{V sec}$ . When the contribution of the transverse modes is included, this is multiplied by a factor of 3. If we allow the solitons to approach as closely as possible before hopping,  $\mu$  is multiplied by a factor of 3.4. Thus the mobility is exceedingly small for this process. The reasons for this small value are the large mass of the ions, which makes the vibration amplitude small, and the weak coupling to the acoustic modes.

## V. THERMOELECTRIC POWER

Since Kivelson has derived the thermoelectric power for case 1,<sup>12</sup> we will first address case 2, transitions between

free and bound solitons, the latter having only one bound level in the potential well of the impurity. We will also calculate the thermopower for transitions between free solitons. The method used is that of Emin.<sup>19</sup>

Denoting the hopping rate from site  $i$  to site  $j$  by  $\bar{v}_{ij}$ , as calculated in Sec. IV, and the probability of electron occupation of site  $i$  by  $f_i$ , we can write the net particle (electron) current  $\Gamma_{ij} - \Gamma_{ji}$  from soliton  $i$  to soliton  $j$  as

$$\Gamma_{ij} - \Gamma_{ji} = f_i(1 - f_j)\bar{v}_{ij} - f_j(1 - f_i)\bar{v}_{ji}. \quad (5.1)$$

The distribution functions  $f_i, f_j$  here must reflect the fact that each soliton site may have a multiplicity of states; these states differ in nature according to whether the soliton is positively charged and free, or negatively charged (occupied), in which case, according to the situation considered, it may be either pinned or free. Allowing  $Z_0$  to denote the partition function of the empty (positive) soliton, and  $Z_i$  the partition function of the occupied (negative) soliton, we have<sup>20</sup>

$$f_i = \left\{ 1 + \frac{1}{2} (Z_0/Z_1)_i \exp[(\epsilon_i - \mu)/kT_i] \right\}^{-1}, \quad (5.2)$$

where  $\epsilon_i$  is the electronic energy level on site  $i$ , and  $(Z_0/Z_1)_i$  is the ratio of the partition functions calculated by using the soliton energy levels of site  $i$ . The factor  $\frac{1}{2}$  here reflects the fact that the electronic state, although it has a degeneracy of 2, may be occupied by just one electron due to the very large Coulomb repulsion for a second electron.

In thermal equilibrium (which we denote by a superscript zero)  $\Gamma_{ij}^0 - \Gamma_{ji}^0 = 0$ , leading to

$$\bar{v}_{ij}^0 / \bar{v}_{ji}^0 = f_j^0(1 - f_i^0) / f_i^0(1 - f_j^0). \quad (5.3)$$

Before finding the thermopower we will show that Eq. (5.3) is satisfied with  $f$  given by (5.2). For the case that soliton  $i$  is initially bound, with a single energy level in the potential well at  $E_b$ , by the partition function  $Z_{1i}$  is given by Eq. (4.12). After the transition soliton  $i$  is free and the partition function  $Z_{0i}$  is given by Eq. (4.7). Inserting these in Eq. (5.2), we obtain

$$f_i^0 = \left\{ 1 + \frac{1}{2} (N/n_s) \exp[(-E_b + \epsilon_i - \mu)/kT] \right\}^{-1}. \quad (5.4)$$

Soliton  $j$ , on the other hand, is free before and after the transition, making  $(Z_0/Z_1)_j$  in Eq. (5.2) unity. With these results for  $f_i^0$  and  $f_j^0$  we obtain

$$\bar{v}_{ij}^0 / \bar{v}_{ji}^0 = (N/n_s) \exp[(-E_b + \epsilon_i - \epsilon_j)/kT]. \quad (5.5)$$

The left-hand side of Eq. (5.5) was evaluated in Sec. IV,  $\bar{v}_{ij}^0$  being given by Eq. (4.14) and  $\bar{v}_{ji}^0$  being given by Eq. (4.15). Using these expressions, we obtain

$$\bar{v}_{ij}^0 / \bar{v}_{ji}^0 = (N/n_s) n_0 / (1 + n_0) = (N/n_s) \exp(-\hbar\omega_0/kT). \quad (5.6)$$

Since the kinetic energy of the soliton is small compared to  $E_b$ , and we are taking  $\epsilon_i = \epsilon_j$ , conservation of energy requires that  $E_b \simeq \hbar\omega_0$ , making (5.5) equal to (5.6), as required by detailed balancing.

To find the thermopower we assume that there is a temperature gradient  $\Delta T$ , with site  $i$  at  $T_i$  and site  $j$  at  $T_j$ , such that the average temperature  $T$  is

$$T = (T_i + T_j)/2 = (T + \delta T_i + T + \delta T_j)/2. \quad (5.7)$$

Thus  $\delta T_i = -\delta T_j$  and  $\Delta T = 2\delta T_i$ . The presence of the gradient will shift the hopping rates  $\bar{v}$  and the distribution functions  $f_{i,j}$ , and will give rise to a potential difference between the sites. The "new" particle current can be approximated for small gradients by expansion of  $\bar{v}_{ij}$ ,  $\bar{v}_{ji}$ ,  $f_i$ , and  $f_j$  in Eq. (5.1). To first order in  $\delta T_i$ ,  $\delta T_j$ ,  $\delta\mu_i$ , and  $\delta\mu_j$ , the changes in these quantities are

$$\delta f_i = \left. \frac{\partial f_i}{\partial T_i} \right|_{T_i=T} \delta T_i + \left. \frac{\partial f_i}{\partial \mu_i} \right|_{\mu_i=\mu_0} \delta \mu_i, \quad (5.8)$$

where  $\mu_0$  is the thermal equilibrium value and

$$\begin{aligned} \delta \bar{v}_{ij} = & \left. \frac{\partial \bar{v}_{ij}}{\partial T_i} \right|_{T_i=T} \delta T_i + \left. \frac{\partial \bar{v}_{ij}}{\partial T_j} \right|_{T_j=T} \delta T_j \\ & + \left. \frac{\partial \bar{v}_{ij}}{\partial (E_{\text{tot}}^i - E_{\text{tot}}^j)} \right|_{E_{\text{tot}}^i - E_{\text{tot}}^j = \hbar\omega_0} eV_{ij}, \end{aligned} \quad (5.9)$$

where  $E_{\text{tot}}$  is a total site energy for  $i$  or  $j$ . The current  $\Gamma_{ij} - \Gamma_{ji}$  in the presence of the thermal gradients is evaluated by using  $f_i$  of (5.2) in (5.8), and  $\bar{v}_{ij}$  and  $\bar{v}_{ji}$  from (4.13) and (4.14) in (5.9), with the condition of detailed balance (5.3) used to eliminate the thermal equilibrium terms. In (5.9) the temperature derivatives of  $\bar{v}_{ij}$  cancel each other since the electron interacts with the same phonon reservoir at  $i$  and  $j$ . The thermopower  $Q_{ij}$  is defined as the ratio of the open-circuit ( $I=0$ ) difference in electrochemical potential between the sites  $i$  and  $j$  to the temperature gradient  $T_j - T_i$ . Setting  $\Gamma_{ij} - \Gamma_{ji}$  equal to zero, we find for this ratio,

$$Q_{ij} = \left[ \frac{eV_{ij} + \delta\mu_i - \delta\mu_j}{e\Delta T} \right]_{I=0} \quad (5.10)$$

$$= \frac{k}{e} \left[ -\frac{E_b}{2kT} + \frac{(\epsilon_i + \epsilon_j)/2 - \mu}{kT} \right] \quad (5.11)$$

for case 2.

We take the electronic levels  $\epsilon_i$  and  $\epsilon_j$  in this and subsequent expressions to be at midgap, i.e., at zero energy. Then, since each pair of solitons has the same spectrum of levels, we may take  $Q_{ij} = Q$ , the thermopower of the sample.<sup>12</sup>

This expression differs from the usual hopping formula for the thermopower<sup>19</sup> by the presence of the term  $-E_b/2kT$ . Basically, the extra term arises from the fact that the statistical weight  $(Z_0/Z_1)_i$  of the level on  $i$  is a function of  $T_i$ ; this reflects the fact that the probability of an electron's being trapped on the site is a function of  $T$ , dependent on the factor  $E_b/kT$ . As  $T$  rises, the effect of this factor [see Eq. (5.4)] is to make  $f_i$  decrease. Since there is less probability of finding an electron on  $i$ , the current  $\Gamma_{ij}$  [the first term of (5.1)] decreases, while  $\Gamma_{ji}$  (second term) increases. This would tend to decrease the voltage developed, for a given  $\Delta T$ , between sites  $i$  and  $j$ , and thus to decrease  $Q$ .

For the case of transitions between free solitons, the thermopower is somewhat simplified by the fact that the empty and filled soliton states have the same statistical distribution of energy levels. Thus  $(Z_0/Z_1)_i = (Z_0/$



$Z_1)_j=1$ , and the distribution function is the usual one for a large- $U$  case. Evaluation of  $Q$  can be carried out by using (5.8)–(5.10) with the result that

$$Q = \frac{k}{e} \left[ \frac{(\epsilon_i + \epsilon_j)/2 - \mu}{kT} \right]. \quad (5.12)$$

This is the usual result for hopping thermopower.<sup>19</sup>

The thermopower for case 1, hopping between bound solitons with a spectrum of energy levels, has been considered by Kivelson for the case of lightly doped polyacetylene. He finds<sup>10,12,21</sup> for the case 1 that

$$Q = \frac{k}{e} \left[ \frac{\bar{\epsilon}}{kT} + \frac{(\epsilon_i + \epsilon_j)/2 - \mu}{kT} \right], \quad (5.13)$$

where

$$\bar{\epsilon} = \bar{v}_{ij}^{-1} \int dE_i dE_j E_i p_i(E_i) \bar{p}_j(E_j) \exp(-E_i/kT) v_{ij}(E_i, E_j) \quad (5.14)$$

is an average, weighted by hopping frequency, of the soliton energy on a given site. This expression is still applicable for the case of soliton hopping in large- $U$  molecular crystals. We note here that Emin and Ngai<sup>22</sup> have criticized Kivelson's result, stating that there will be no term in the thermopower such as the first in (5.13) if sites  $i$  and  $j$  have "equivalent coupling to the atomic vibrations." This statement is true, however, only for a single state on each site; for a multiplicity of states, as in the present case, there will, in general, be a term in  $Q$  besides the one involving the difference between the average electronic energy level and  $\mu$ , as was seen earlier in Eq. (5.11).

## VI. CONCLUSIONS

In view of the large dielectric constants that have been measured in quasi-one-dimensional molecular crystals, it is probable that the solitons are not bound at room temperature and for a considerable range of temperatures below. Nevertheless, we do not expect moving solitons to contribute much to dc conductivity above very low temperatures ( $< 50$  K in samples with low doping), since the small gaps and very long chains [compared to  $(\text{CH})_x$ ] in these crystals mean that there will be some solitons of the opposite sign on the chain to block motion in the electric field. Nor do we see any way of unblocking the motion. Intersoliton hopping of electrons onto another chain, an important process in  $(\text{CH})_x$ , will not be important for these materials due to the small transverse extent of the bound electron wave function compared to the interchain spacing. Recombination of a pair of oppositely charged solitons will result in the thermal generation of another such pair on the chain, since we are dealing with the thermal equilibrium situation. Thus the only contribution we see solitons making to dc conductivity, except for very low temperatures, is due to intersoliton hopping of electrons.

Hopping rates for both internal and external modes were found to depend, as expected, on the square of the overlap integral for the electron wave functions and on phonon abundance. It is the former factor which makes

the interchain hopping so small. In addition, for the acoustic modes the hopping rate depends on  $(q\xi_{||})^4 \exp(-\pi q\xi_{||})$ , so that the coupling to these modes is weak for both small and large  $q$ . Also, the amplitude of motion is small for the acoustic modes due to the inverse dependence on the molecular mass. Thus acoustic-mode-assisted hopping is expected to be quite ineffective. For the internal modes the hopping rate depends on the square of the phonon energy, which is substantial. For  $(\text{NMP})_{0.54}(\text{Phen})_{0.46}(\text{TCNQ})$  at 100 K, for instance, we calculate hopping rates of  $\sim 10^9 - 10^{10} \text{ sec}^{-1}$ , depending on whether the electron hops between pinned solitons or between a pinned and a free soliton, for internal-mode-assisted hopping. This leads to mobilities in the range  $10^{-2}$  to  $1.03 \text{ cm}^2/\text{V sec}$ , as compared to the mobility of  $\sim 10^{-6} \text{ cm}^2/\text{V sec}$  that follows from the transition rate of  $\sim 1.649 \times 10^4 \text{ sec}^{-1}$  calculated for acoustic-phonon-assisted hopping.

We find that the thermoelectric power generated by intersoliton hopping processes contains, in general, a term arising from the soliton energies as well as the usual term involving the difference between electronic energies and the Fermi energy. The additional term arises from the existence of a multiplicity of possible states for a given soliton. In the case of hopping between pinned solitons, this term is Kivelson's<sup>12</sup>  $\bar{\epsilon}/kT$ ; for hopping between pinned solitons of energy  $-E_b$  and free solitons of essentially zero energy, the analogous term is  $E_b/(2kT)$ . In the case of hopping between free solitons there is no extra term. Detailed comparison of these results with experimental conductivity and thermopower data for  $(\text{NMP})_x(\text{Phen})_{1-x}(\text{TCNQ})$  will be carried out in a later publication.

## ACKNOWLEDGMENTS

The authors would like to acknowledge useful and stimulating discussions with A. J. Epstein and S. Kivelson.

## APPENDIX

The mass of a soliton stabilized by external modes was found to be<sup>7,9</sup>

$$M_S^{\text{ext}} = \frac{4}{3} \frac{Mu_0^2}{3a\xi_{||}}, \quad (A1)$$

where  $u_0$  is the dimerization amplitude. We follow a similar procedure to determine the mass of a soliton stabilized by internal modes. The expression in Eq. (3.16) for the kinetic energy may be written in the continuum model, with the use of Eq. (2.4), as

$$T = (\hbar/2) \sum_l (\omega_l \beta_l^2)^{-1} \int (dx/a) \dot{\Delta}_l^2(x). \quad (A2)$$

Assuming that, for each (independent) normal mode,

$$\Delta_l = \Delta_{l0} \tanh[(x - v_s t)/\xi_{||}], \quad (A3)$$

we obtain, from (A1),

$$T = (v_s^2/2)(4\hbar/3a\xi_{||}) \sum_l \Delta_{l0}^2/(\omega_l \beta_l^2). \quad (A4)$$

Thus the mass of the soliton in this case is given by

$$M_S^{\text{int}} = (4\hbar/3a\xi_{\parallel}) \sum_I \Delta_{I0}^2 / (\omega_I \beta_I^2) = \frac{4}{3} \sum_I (Q_I')^2 / (a\xi_{\parallel}). \quad (\text{A5})$$

The expression at the right, similar in form to that for the external mode case, is obtained by introducing normal-mode coordinates,  $Q_I' \equiv (\hbar/\omega_I)^{1/2} Q_I$ , which have dimensions of  $(\text{mass})^{1/2} \times \text{length}$ .

To evaluate (A5) it is convenient to eliminate  $\Delta_{I0}$  by use of the relation<sup>15</sup>

$$\Delta_{I0} = (\beta_I^2 / \omega_I) \Delta_{\text{int}} / \left[ \sum_I (\beta_I^2 / \omega_I) \right]. \quad (\text{A6})$$

With  $\Delta_{\text{int}}$  taken as the observed half-gap, and the values of  $\beta_I$  and  $\omega_I$  tabulated by Etemad<sup>23</sup> for the  $a_g$  internal modes of TCNQ [from tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ)], we can calculate  $M_S^{\text{int}}$  for  $(\text{NMP})_x(\text{Phen})_{1-x}$ -(TCNQ). For an empty soliton in a lightly doped sample, where  $\Delta_{\text{int}} \approx 900$  K, we find from (A5) and (A6)  $M_S^{\text{int}} = 1.57m_e$ , where  $m_e$  is the electron mass. In the case of an occupied soliton we must add  $1m_e$  to  $M_S^{\text{int}}$ . For larger doping and higher temperatures  $M_S^{\text{int}}$  would be less. These are small masses and it is quite possible that there are other contributions of the same order of magnitude from other sources of Peierls distortion—acoustic modes and librions—and from anharmonic effects. A periodic interchain potential that increases the Peierls gap would also add to the soliton mass.

Given the soliton mass, one can calculate the oscillation energy  $\hbar\omega_v$  of a pinned soliton about an impurity. The

oscillation frequency is  $\omega_v = (k_b/M_S)^{1/2}$ , where  $k_b = \partial^2 E_c / \partial x_S^2$  evaluated at  $x_S = 0$  and  $E_c(x_S)$  is the Coulomb energy for a soliton centered not at  $x = 0$  but at  $x = x_S$  at a perpendicular distance  $b$  from the impurity. If we approximate the soliton wave function  $\varphi(x - x_S)$  by a constant from  $x_S - \xi_{\parallel}$  to  $x_S + \xi_{\parallel}$ , we can use Eq. (1.1) to find  $E_c(x_S)$ . We find then, for the force constant,

$$k_b = (e^2 \epsilon_{\perp}^{1/2} / 2\epsilon_{\parallel}^{3/2} b^3) (1 + \xi_{\parallel}^2 \epsilon_{\perp} / b^2 \epsilon_{\parallel})^{-3/2}. \quad (\text{A7})$$

Using the previously derived mass of an occupied soliton in  $(\text{NMP})_x(\text{Phen})_{1-x}$ -(TCNQ) and taking  $\epsilon_{\parallel} = 10^3$ , we obtain  $\hbar\omega_v \approx 18$  K. Since the corresponding depth of the potential well, as calculated in the Introduction, is  $\sim 190$  K, this would indicate  $\sim 10$  vibrational levels in the well. For this case one will be able to reasonably approximate the soliton density of states in the well by a continuum, as Kivelson<sup>12</sup> does for  $(\text{CH})_x$ .

When considering hopping transitions to or from free solitons as in Sec. IV, one must know the width of the kinetic energy distribution for free solitons. We take the maximum kinetic energy to be

$$T_{\text{max}} \approx \frac{1}{2} M_S \pi^2 \xi_{\parallel}^2 \lambda c_0^2 / 2a^2,$$

(Ref. 24), where  $c_0$  is the speed of sound in the crystal. For  $c_0 \approx 3 \times 10^5$  cm/sec we find  $T_{\text{max}}/k \approx 30$  K if  $\lambda = 0.887$ . (This is the value of  $\lambda$  needed to reproduce the experimentally seen gap  $2\Delta_0/k = 1800$  K at  $T = 0$  from the Peierls equation. If we use the value  $\lambda \approx 0.35$  calculated by Etemad<sup>23</sup> for the TCNQ chain, we obtain  $T_{\text{max}}/k \approx 52$  K). This  $T_{\text{max}}$  is smaller than  $kT$  over most of the temperature range of interest in studying hopping.

<sup>1</sup>See, for example, Proceedings of the International Conference on Low-Dimensional Conductors, 1981, Boulder, Colorado [Mol. Cryst. Liq. Cryst. **77**, 1 (1981)].

<sup>2</sup>A. J. Epstein, J. W. Kaufer, H. Rommelmann, I. A. Howard, E. M. Conwell, J. S. Miller, J. P. Pouget, and R. Comes, Phys. Rev. Lett. **49**, 1037 (1982).

<sup>3</sup>M. J. Rice and E. J. Mele, in Proceedings of the International Conference on Low-Dimensional Conductors, August 9–14, 1981, Boulder, Colorado [Mol. Cryst. Liq. Cryst. **77**, 223 (1981)]; E. J. Mele and M. J. Rice, Phys. Rev. B **25**, 1339 (1982).

<sup>4</sup>It has been pointed out by S. Kivelson [Phys. Rev. B **28**, 2653 (1983)] that even in the regime of pure site distortion the solitons do not have charge conjugation symmetry (as they do for pure bond distortion), with the result that a filled soliton level is below midgap while an empty one is above. The reason for this is that a nonvanishing average site distortion, which could be expected to result from placing an electron on a soliton or removing it, contributes to the internal energy of the soliton. An estimate of the size of this effect by Kivelson indicates that it need not be negligible. However, there is experimental evidence for  $(\text{NMP})_x(\text{Phen})_{1-x}$ -(TCNQ) that this level splitting is small. Below the high-temperature intrinsic region where the conductivity  $\sigma \propto \exp(-\Delta/kT)$ ,  $\Delta$  being the half-gap, there is a temperature regime where, within experimental error,  $\sigma \propto \exp(-\Delta/2kT)$ . The lower-temperature slope would

not be one-half of the upper if the soliton levels were significantly split.

<sup>5</sup>W. P. Su, Solid State Commun. **47**, 947 (1983).

<sup>6</sup>E. J. Mele and M. J. Rice, Phys. Rev. B **23**, 5397 (1981).

<sup>7</sup>H. Takayama, Y.-R. Lin-Liu, and K. Maki, Phys. Rev. B **21**, 2388 (1980).

<sup>8</sup>I. A. Howard and E. M. Conwell, Phys. Rev. B **27**, 6205 (1983).

<sup>9</sup>W.-P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. B **22**, 2099 (1980).

<sup>10</sup>S. Kivelson, Phys. Rev. Lett. **46**, 1344 (1981).

<sup>11</sup>S. Kivelson, in Proceedings of the International Conference on Low-Dimensional Conductors, August 9–14, 1981, Boulder, Colorado [Mol. Cryst. Liq. Cryst. **77**, 65 (1981)].

<sup>12</sup>S. Kivelson, Phys. Rev. B **25**, 3798 (1982).

<sup>13</sup>A. Miller and E. Abrahams, Phys. Rev. **120**, 745 (1960).

<sup>14</sup>I. F. Shchegolev, Phys. Status Solidi A **12**, 9 (1972).

<sup>15</sup>M. J. Rice, C. B. Duke, and N. O. Lipari, Solid State Commun. **17**, 1089 (1975).

<sup>16</sup>N. O. Lipari, M. J. Rice, C. B. Duke, R. Bozio, A. Girlando, and C. Pecile, Int. J. Quantum Chem. **11**, 583 (1977).

<sup>17</sup>E. M. Conwell and N. C. Banik, Phys. Rev. B **27**, 7420 (1983).

<sup>18</sup>G. Herzberg, *Electronic Spectra of Polyatomic Molecules* (Van Nostrand, Princeton, 1966), p. 302.

<sup>19</sup>D. Emin, Phys. Rev. Lett. **35**, 882 (1975).

<sup>20</sup>As explained by Landsberg [P. T. Landsberg, in *Handbook on Semiconductors*, edited by W. Paul (North-Holland, Amster-

dam, 1982), Vol. I], the probability of finding a site in state  $r$  ( $r=0$  for an empty site,  $=1$  for an unoccupied site) is

$$P(r) = g_r (e^{\mu/kT})^r Z_r / \left[ \sum_{s=0}^1 (e^{\mu/kT})^s Z_s \right],$$

where  $g_r$  is the degeneracy of charge state  $r$ . For  $r=1$ ,  $P(1)$  is the occupation probability  $f$ . Therefore,

$$f = P(1) = [1 + \frac{1}{2} (Z_0/Z_1) e^{-\mu/kT}]^{-1} \\ = \{1 + \frac{1}{2} (Z_0/Z_1)_i \exp[(\epsilon_i - \mu)/kT]\}^{-1},$$

where

$$Z_1 = \sum_n \exp(-\epsilon_{el}/kT) \exp(-E_{sol}^n/kT) \\ \equiv (Z_1)_i \exp(-\epsilon_{el}/kT),$$

$\epsilon_{el}$  refers to the electronic energy level on the soliton, and  $E_{sol}^n$  is the  $n$ th energy level of the soliton itself. Since electronic energy levels are not occupied for the empty soliton site,  $Z_0 = (Z_0)_i$ .

<sup>21</sup>Note that this result is correct even though Kivelson has used an incorrect distribution function, the equation below (31) in Ref. 12. Also, his Eq. (35) in this reference for the temperature has two typographical errors:  $e/k_B$  should be  $k_B/e$  and the  $+$  sign before  $\ln[n^{(0)}/(1-n^{(0)})]$  should be a  $-$  sign.

<sup>22</sup>D. Emin and K. L. Ngai, in Proceedings of the International Conference on Physics and Chemistry of Conducting Polymers, 1982, Les Arcs, France [J. Phys. (Paris) Colloq. **44**, C3-471 (1983)].

<sup>23</sup>S. Etemad, Phys. Rev. B **24**, 4959 (1981).

<sup>24</sup>A. R. Bishop, D. K. Campbell, P. S. Lomdahl, B. Horowitz, and S. R. Phillpot, Phys. Rev. Lett. **52**, 671 (1984).