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Small-polaron effects on the dc conductivity and thermoelectric power of the one-dimensional Mott semiconductor*

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The effects of intra (molecular) -site vibrations on the dc conductivity, thermoelectric power, and one-electron density of states are calculated and studied. The one-dimensional half-filled-band Hubbard model is coupled locally in space to phonons and the approximation used assumes that the electron bandwidth is small. The one-electron density of states is Gaussian broadened in energy, even for zero bandwidth and zero temperature. Consequently there is a finite density of states at the Fermi energy (in the Mott-Hubbard gap). As temperature increases, the separate peaks in the density of states become less discernible. The dc conductivity exhibits a rounded maximum as a function of temperature and falls off as $T^{-3/2}$ at high temperature. At very low temperatures, below a region of thermally activated behavior, the conductivity begins to rise and diverges as T^{-1}. This behavior is shown to be a consequence of both the electron-phonon coupling and the strong electron-electron interaction. The thermoelectric power is formulated for the strongly interacting model system and it is found that it vanishes—a result that appears to be a consequence of the particle-hole symmetry of the half-filled band.

I. INTRODUCTION

The electrical properties of the high-conductivity tetracyanoquinodimethan (TCNQ) salts[1,2] are not easily understood. There are now at least four salts[3] that display a thermally activated conductivity at low temperatures, followed by a rounded maximum at higher temperature and then a decrease according to some inverse polynomial in temperature. There is no adequate microscopic description of either the low- or high-temperature regimes of these materials. However there are several distinct models that have been applied with limited success.[4]

The roles of electron-electron and electron-lattice interactions have been of particular interest. The electron-electron interaction has been considered mainly in terms of the single-band Hubbard model.[5] In addition to possible structural instabilities in connection with the Peierls instability,[6] the electron-lattice interaction is of interest in connection with intramolecular vibrations[2,7] and small polaron formation.[8]

The theory of a single electron in a narrow band, interacting strongly with intramolecular vibrations, has been investigated intensively by several workers.[9] The role of lattice vibrations in a half-filled band of electrons that are strongly interacting via the short-range Coulomb interaction has been investigated more recently.[7,8,10]

In this paper we consider intramolecular vibrations that are strongly coupled to a very narrow half-filled band of electrons that would otherwise be described as a Mott insulator.[11] (The quarter-filled band which is associated[1] with Ad-TCNQ and Qn-TCNQ is not considered here.) Although this study is motivated by the interesting characteristics of charge-transfer salts based on the acceptor TCNQ, no direct comparison with experiment is given here. In Sec. II the model is defined. The displaced-oscillator canonical transformation is applied to it and the partition function in the atomic limit (zero bandwidth) is obtained. In Sec. III the one-electron spectral weight function is calculated in the atomic limit. The presence of the coupling to the vibrational modes leads to long-range tails in the density of states. In particular, the density of states is finite in the Mott-Hubbard gap. In Sec. IV the electrical conductivity is calculated to second order in the bandwidth. The conductivity displays a rounded maximum as a function of temperature. At high temperatures, the conductivity falls off according to $T^{-3/2}$. At very low temperatures the conductivity diverges as T^{-1}; this result is discussed.

In Sec. V the thermoelectric power is calculated. An expression for the energy current of the model is formulated in site-space. It is found that the thermoelectric power vanishes. This result appears to be a consequence of particle-hole symmetry of the half-filled band. In Sec. VI, the results of Secs. II–V are summarized and discussed.

II. MODEL

The model Hamiltonian for a narrow band of electrons coupled to intramoelcular vibrations is written as follows:

$$H = H_{\mathrm{el}} + H_{\mathrm{ph}} + H' , \tag{2.1}$$

where H_{el} is the single-band Hubbard Hamiltonian[5] given by

$$H_{\mathrm{el}} = -b \sum_{i,\delta,\sigma} C^{\dagger}_{i\sigma} C_{i+\delta\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} . \tag{2.2}$$

Here $C^{\dagger}_{i\sigma}$ ($C_{i\sigma}$) creates (destroys) an electron on the

ith molecular site with spin σ and these operators satisfy the usual anticommutation relations; $n_{i\sigma} = C^\dagger_{i\sigma} C_{i\sigma}$; U is the bare intramolecular Coulomb repulsion; b is the one-electron intermolecular hopping energy. The hopping range is assumed to extend to nearest neighbors only and the δ sum is over the nearest neighbors of the ith spatial site (the summation on i is over the entire lattice). Although the one-dimensional case is of particular interest with regard to the TCNQ salts, the results we obtain are straightforwardly extended to higher dimensions.

The phonon Hamiltonian H_{ph} is taken to be an array of dispersionless Einstein oscillators and is written

$$H_{\text{ph}} = \frac{1}{2}\,\Omega \sum_i (P_i^2 + Q_i^2)\,. \tag{2.3}$$

In Eq. (2.3), Ω is the frequency of the Einstein oscillators and P_i and Q_i are the usual (dimensionless) momentum and displacement coordinates, respectively, and describe the vibrational motion of the ith molecule. The usual commutation relations

$$[Q_i, P_j] = i\delta_{ij}\,, \quad [Q_i, Q_j] = 0\,, \quad [P_i, P_j] = 0\,,$$

are obeyed.

The interaction between the intramolecular vibrations and the electrons is contained in H'. This is given simply as

$$H' = V \sum_i Q_i (n_{i\uparrow} + n_{i\downarrow})\,, \tag{2.4}$$

where V is an appropriately defined coupling constant with dimension of energy. The interaction couples the electronic density on the ith site linearly to the displacement coordinate on that molecular site. The on-site interaction plays an important role in small polaron theories[9] and is an essential piece of the electron-phonon interaction in a narrow-band system.

We assume that the Peierls instability is quenched by the strong intrasite Coulomb repulsion. While it is true that an infinitesimal electron-phonon coupling will lead to a Peierls instability for a noninteracting half-filled band of electrons,[6] this is no longer the case when the electron-electron interaction is taken into account—even in one dimension.[10] Physically, the concomitant electronic charge density wave associated with the Peierls instability forms at the expense of the short-range Coulomb repulsion. If the latter is sufficiently large, then the former is quenched. This is true even at zero temperature.[10]

We shall consider the regime in which the hopping parameter b is the smallest energy in H. Accordingly, we define a zeroth-order Hamiltonian by

$$H_0 = H + b \sum_{i,\delta,\sigma} C^\dagger_{i\sigma} C_{i+\delta\sigma} = U \sum_i n_{i\uparrow} n_{i\downarrow}$$

$$+ V \sum_i Q_i (n_{i\uparrow} + n_{i\downarrow}) + \frac{1}{2}\,\Omega \sum_i (P_i^2 + Q_i^2)\,. \tag{2.5}$$

H_0 is the sum of single-site Hamiltonians, and furthermore its ground state and thermodynamics are solvable as well. The method of solution is well known from the small-polaron problem[9] and its extension to include the first term has been given before.[10]

We write

$$H_0^i = U n_{i\uparrow} n_{i\downarrow} + V Q_i (n_{i\uparrow} + n_{i\downarrow}) + \tfrac{1}{2}\Omega (P_i^2 + Q_i^2) \tag{2.6}$$

and define

$$h_i = e^{i\delta S} H_0^i e^{-i\delta S}\,, \tag{2.7}$$

where

$$S = \sum_i P_i (n_{i\uparrow} + n_{i\downarrow})\,; \tag{2.8}$$

then for

$$\delta = -V/\Omega \tag{2.9}$$

h_i has the form

$$h_i = (U - \Gamma)\, n_{i\uparrow} n_{i\downarrow} - \tfrac{1}{2}\Gamma (n_{i\uparrow} + n_{i\downarrow}) + \tfrac{1}{2}\Omega (P_i^2 + Q_i^2)\,, \tag{2.10}$$

with

$$\Gamma \equiv V^2/\Omega\,. \tag{2.11}$$

S is just the generator of the displaced oscillator canonical transformation. h_i is the canonically equivalent single-site Hamiltonian written in terms of the original electronic and vibrational coordinates. δ is chosen to eliminate the linear electron-lattice coupling. The vibrational Hamiltonian is unchanged, but in the electronic Hamiltonian U is replaced by $U - \Gamma$ and there is a shift in the one-electron energy levels on the molecules by $-\frac{1}{2}\Gamma$. (The latter represents the small-polaron binding energy.[9])

From Eq. (2.10) the ground-state energy $E(N)$ of H_0 is easily calculated as a function of the number particles. The ground-state energy of the half-filled band is

$$E(N_s) = -\tfrac{1}{2}\Gamma N_s\,. \tag{2.12}$$

Here N_s denotes that the number of electrons is equal to the number of sites. We also obtain $E(N_s + 1) = U - \Gamma - \frac{1}{2}(N_s + 1)\Gamma$ and $E(N_s - 1) = -\frac{1}{2}(N_s - 1)\Gamma$. We follow Leib and Wu[12] and define

$$\mu_> = E(N_s + 1) - E(N_s) = U - \tfrac{3}{2}\Gamma \tag{2.13}$$

and

$$\mu_< = E(N_s) - E(N_s - 1) = -\tfrac{1}{2}\Gamma\,. \tag{2.14}$$

The gap related to the addition and removal of an electron about the half-filled band was then given by $\mu_> - \mu_<$.

In this case, we have

$$\mu_> - \mu_< = U - \Gamma . \tag{2.15}$$

As we expected, this gap is just the effective electron-electron interaction on a site. The nonvanishing of $\mu_> - \mu_<$ in the limit $N_s \to \infty$ has been used[12] as a criterion for insulating behavior in the ground state. We shall return to this point later.

The thermodynamics of H_0 is also straightforward. The ground-state partition function Z is given by

$$Z = \mathrm{Tr}e^{-\beta(H_0 - \mu N_{\mathrm{op}})} = \mathrm{Tr}e^{-\beta(h - \mu N_{\mathrm{op}})} .$$

Here μ is the chemical potential and $N_{\mathrm{op}} = \sum_i (n_{i\uparrow} + n_{i\downarrow})$. The last equality is obtained by using the invariance of the trace and N_{op} with respect to the canonical transformation. Z is then written

$$Z = Z_{\mathrm{ph}} Z_{\mathrm{el}}, \tag{2.16}$$

where

$$Z_{\mathrm{ph}} = \mathrm{Tr}\exp\left[-\beta\left(\frac{\Omega}{2}\sum_i (P_i^2 + Q_i^2)\right)\right] = (2\,\mathrm{csch}\tfrac{1}{2}\beta\Omega)^{N_s} ,$$

and

$$\begin{aligned} Z_{\mathrm{el}} &= \left(\sum_{n\uparrow=0}^{1} \sum_{n\downarrow=0}^{1} \exp[-\beta(U-\Gamma)n_\uparrow n_\downarrow \right. \\ &\qquad \left. + \beta(\mu + \tfrac{1}{2}\Gamma)(n_\uparrow + n_\downarrow)]\right)^{N_s} \\ &= (1 + 2e^{\beta(\mu + \Gamma/2)} + e^{\beta(2\mu + 2\Gamma - U)})^{N_s} . \end{aligned} \tag{2.18}$$

The condition that the number of electrons is equal to the number of sites can be expressed as $\langle N_{\mathrm{op}}\rangle = N_s$, where the brackets denote

$$\langle N_{\mathrm{op}}\rangle = \frac{\mathrm{Tr}e^{-\beta(h - \mu N_{\mathrm{op}})} N_{\mathrm{op}}}{\mathrm{Tr}e^{-\beta(h - \mu N_{\mathrm{op}})}} . \tag{2.19}$$

Z_{ph} factors out of this expression and one obtains

$$\langle N_{\mathrm{op}}\rangle = \frac{\partial}{\partial(\beta\mu)} \ln Z_{\mathrm{el}} . \tag{2.20}$$

One easily sees that the number condition is satisfied by setting

$$\mu = \tfrac{1}{2}(U - 2\Gamma) . \tag{2.21}$$

Z_{el} is then given by

$$Z_{\mathrm{el}} = [2(1 + e^{\beta(U-\Gamma)/2})]^{N_s} . \tag{2.22}$$

It is convenient to define

$$U_1 \equiv U - \Gamma , \tag{2.23}$$

$$U_2 \equiv U - 2\Gamma , \tag{2.24}$$

since these combinations will occur repeatedly in that which follows.

III. SPECTRAL WEIGHT FUNCTION

The one-electron spectral weight function $A_{ij}^{\sigma}(\omega)$ is defined[13] as

$$A_{ij}^{\sigma}(\omega) = \int_{-\infty}^{\infty} d\tau\, e^{i\omega\tau} \langle\{C_{i\sigma}(\tau),\, C_{j\sigma}^{\dagger}\}\rangle . \tag{3.1}$$

The operators evolve in time τ according to $C_{i\sigma}(\tau) = e^{iH\tau} C_{i\sigma} e^{-iH\tau}$ and the brackets $\{,\}$ denote the anticommutator.

For a homogeneous system the electronic density of states at frequency ω is conveniently related to the spectral weight function by

$$\rho^{\sigma}(\omega) = (2\pi)^{-1} A_{ii}^{\sigma}(\omega) . \tag{3.2}$$

In the atomic limit ($b \to 0$), Hubbard[5] showed that for the half-filled band of H_{el} [Eq. (2.2)],

$$\rho^{\sigma}(\omega) = \tfrac{1}{2}\delta(\omega) + \tfrac{1}{2}\delta(\omega - U) ; \tag{3.3}$$

we see that the density of states is given by two δ-function peaks, one at $\omega = 0$ and the other at $\omega = U$. This form of the density of states (i.e., two clearly separated nonzero regions) provides the basis for regarding the Mott insulator as a particular type of split-band (or two-band) model with energy gap[14] U (the so-called Mott-Hubbard gap). Although the analogy may be a useful algorithm offering some insight, one must be cautious of the fact that the gap in the noninteracting two-band model is produced by the electron interaction with the periodic crystal potential and that for H_{el} the Mott-Hubbard gap is due to electronic self-correlation. We also note that the existence of somewhat sharp, well-separated peaks in the density of states with negligible weight between the peaks is usually regarded as the hallmark of the insulating state, and conversely that the overlapping of peaks, or existence of substantial weight between peaks is suggestive of a metallic description.

In this section we calculate and study the modification of the density of states (in the limit $b \to 0$) given by Eq. (3.3) due to the presence of the electron-phonon interaction as described by Eq. (2.1).

We write the thermal average in Eq. (3.1) as (for brevity we write N_{op} as N)

$$\langle[C_{i\sigma}(\tau)C_{j\sigma}^{\dagger} + C_{j\sigma}^{\dagger}C_{i\sigma}(\tau)]\rangle = \frac{\mathrm{Tr}e^{-\beta(H_0 - \mu N)}\{C_{i\sigma}(\tau),\, C_{j\sigma}^{\dagger}\}}{\mathrm{Tr}e^{-\beta(H_0 - \mu N)}} . \tag{3.4}$$

We have

$$C_{i\sigma}(\tau) = e^{iH_0\tau} C_{i\sigma} e^{-iH_0\tau} = C_{i\sigma} e^{-i(Un_{i-\sigma} + VQ_i)\tau} , \tag{3.5}$$

and consequently

$$\{C_{i\sigma}(\tau) ,\, C_{j\sigma}^{\dagger}\} = \delta_{ij} e^{-i(Un_{i-\sigma} + VQ_i)\tau} ; \tag{3.6}$$

in Eq. (3.6), δ_{ij} denotes the Kronecker δ function.

In Eq. (3.5) we have treated the time dependence of Q_i to lowest order. This short-time expansion leads directly to Gaussian behavior in the frequency variation of the spectral weight function and conductivity. Although the exact time dependence in Eq. (3.5) can be easily obtained, the resulting form of the frequency behavior of the spectral weight function of the single Einstein oscillator is somewhat pathological from the point of view of describing the vibration relaxation associated with the modes of a TCNQ molecule. The short-time expansion is then taken to represent the relaxation of the molecule and the energy parameters of the Einstein oscillator should be regarded as characteristically typical energies for the relevant vibrational modes.

The thermal average is again a single-site average and it is also useful to perform the displaced oscillator transformation given by Eq. (2.6)–(2.11). We obtain

$$\frac{\mathrm{Tr}\,e^{-\beta(H_0-\mu N)}\,e^{-i(Un_{i-\sigma}+VQ_i)\tau}}{\mathrm{Tr}\,e^{-\beta(H_0-\mu N)}}$$

$$=\frac{\mathrm{Tr}\,e^{-\beta[h-\mu(n_\uparrow+n_\downarrow)]}\,e^{-i\{Un_{-\sigma}+V[Q-(V/\Omega)(n_\sigma+n_{-\sigma})]\}\tau}}{\mathrm{Tr}\,e^{-\beta[h-\mu(n_\uparrow+n_\downarrow)]}}\;; \qquad (3.7)$$

here the spatial-site indices are omitted since the average refers to a single site. The right-hand side of Eq. (3.7) is factored according to

$$\langle e^{-iVQ\tau}\rangle_{\mathrm{ph}}\langle e^{-i(U_1n_{-\sigma}-\Gamma n_\sigma)\tau}\rangle_{\mathrm{el}}\;; \qquad (3.8)$$

here we have used Eqs. (2.11) and (2.23) and defined the averages with respect to the separate vibrational and electronic coordinates by

$$\langle e^{-iVQ\tau}\rangle_{\mathrm{ph}}\equiv Z_{\mathrm{ph}}^{-1}\,\mathrm{Tr}(e^{-\beta[(\Omega/2)(P^2+Q^2)]}e^{-iVQ\tau}) \qquad (3.9)$$

and

$$\langle e^{-i(U_1n_{-\sigma}-\Gamma n_\sigma)\tau}\rangle_{\mathrm{el}}\equiv Z_{\mathrm{el}}^{-1}\,\mathrm{Tr}\,e^{-\beta[U_1n_\uparrow n_\downarrow-(1/2)U_1(n_\uparrow+n_\downarrow)]}$$

$$\times e^{-i(U_1n_{-\sigma}-\Gamma n_\sigma)\tau}\,. \qquad (3.10)$$

Equation (3.9) can be straightforwardly evaluated[15] and gives

$$\langle e^{-iVQ\tau}\rangle_{\mathrm{ph}}=e^{-S\tau^2/2}, \qquad (3.11)$$

where

$$S\equiv\tfrac{1}{2}V^2\coth(\beta\Omega/2)\,. \qquad (3.12)$$

Equation (3.10) is also easily evaluated and gives

$$\langle e^{-i(U_1n_{-\sigma}-\Gamma n_\sigma)\tau}\rangle_{\mathrm{el}}=[2(1+e^{\beta U_1/2})]^{-1}$$

$$\times(1+e^{\beta U_1/2-iU_1\tau}+e^{\beta U_1/2+i\Gamma\tau}+e^{-iU_2\tau})\,. \qquad (3.13)$$

We now combine Eqs. (3.1), (3.4) and (3.6), (3.11) and obtain

$$A_{ij}^\sigma(\omega)=\frac{\delta_{ij}}{2(1+e^{\beta U_1/2})}\int_{-\infty}^{\infty}d\tau\,e^{i\omega\tau-(S/2)x^2}$$

$$\times(1+e^{\beta U_1/2-iU_1\tau}+e^{\beta U_1/2+i\Gamma\tau}+e^{-iU_2\tau})$$

$$=\frac{\delta_{ij}}{(1+e^{\beta U_1/2})}\left(\frac{\pi}{2S}\right)^{1/2}(e^{-\omega^2/2S}+e^{\beta U_1/2}$$

$$\times e^{-(\omega-U_1)^2/2S}+e^{\beta U_1/2}e^{-(\omega+\Gamma)^2/2S}+e^{-(\omega-U_2)^2/2S}). \qquad (3.14)$$

We see that the spectral weight function is temperature dependent and is comprised of four Gaussian-broadened peaks centered at $\omega=0$, U_1, $-\Gamma$, and U_2.

Let us look at the spectral weight function in some interesting limits.

A. $V\to 0$

In the limit $V\to 0$, we use the identity

$$\lim_{a\to 0}(\pi/a)^{1/2}e^{-x^2/a}=\pi\delta(x) \qquad (3.15)$$

and recover

$$A_{ij}^\sigma(\omega)=2\pi\delta_{ij}[\tfrac{1}{2}\delta(\omega)+\tfrac{1}{2}\delta(\omega-U)], \qquad (3.16)$$

the result obtained by Hubbard [5] [Eqs. (3.2) and (3.3)].

B. $T\to 0$

For the limit $T\to 0$ we see from Eq. (3.12) that

$$\lim_{T\to 0}S=\tfrac{1}{2}V^2\,. \qquad (3.17)$$

Equation (3.14) becomes

$$A_{ij}^\sigma(\omega)=\delta_{ij}(\pi/V)^{1/2}(e^{-(\omega-U_1)^2/V^2}+e^{-(\omega+\Gamma)^2/V^2})\,. \qquad (3.18)$$

We see that the electron-phonon coupling leads to a broadening of the δ-function peaks even at zero temperature. One also notes that the peaks that correspond to $\omega=0$ and $\omega=U$ in the absence of V are shifted by $-\Gamma$. Equation (3.18) evolves with increasing V from two well-separated Gaussian peaks centered at $\omega\simeq-\Gamma$ and $\omega\simeq U_1$ for $V\ll U$ to one broad peak centered at $\omega\simeq-\Gamma$ for $V\gg U$. In both of these cases the widths of the peaks [full width at half-maximum (FWHM)] are proportional to $S^{1/2}$. In the further limit $\beta\Omega\ll 1$ the widths are proportional to $(kT)^{1/2}$.

C. $S\to\infty$

As $S\to\infty$ either through $V\to\infty$ or $T\to\infty$, the spectral weight function loses all distinctive features and is comprised of a rather uniform background on any frequency scale that is small compared to $S^{1/2}$.

In addition to the two peaks centered at $\omega\simeq-\Gamma$ and $\omega\simeq U_1$ in Eq. (3.14), two additional satellite peaks centered at $\omega\simeq 0$ and $\omega\simeq U_2$ become appreciable for $\tfrac{1}{2}\beta U_1\sim 1$. The appearance of these peaks can be understood simply as follows. The spectral weight function measures the probability amplitude of adding or removing an electron at a resultant energy change of ω to the system in thermal equilibrium. In terms of the single-site processes relevant to the problem at hand, there are four possibilities: (i) addition of an electron to a site already occupied by an opposite-spin electron; (ii) removal of an electron from a singly-occupied site; (iii) addition of an electron to an empty site; and (iv) removal of an electron from a doubly-occupied site. Processes (iii) and (iv) will be unimportant for $kT\ll U_1$, since doubly-occupied and empty sites will be negligibly populated in the half-filled band. On the other hand, processes (i) and (ii) will be relatively important at all temperatures. The energies associated with those processes can be identified with the peak energies in Eq. (3.14) on sim-

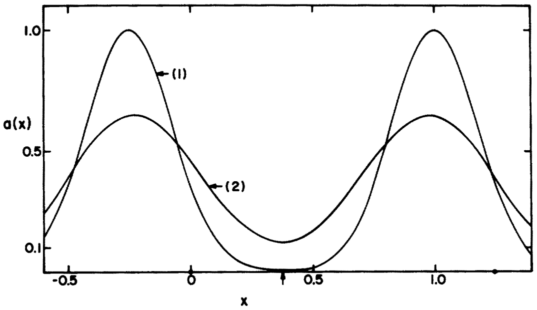

FIG. 1. Spectral weight function is plotted against frequency, both in dimensionless units and for the choice of parameters discussed in the text. Curve (1) gives the spectral weight at zero temperature and curve (2) is for the case $kT=\Omega$. On the x axis, the arrow indicates the position of the chemical potential and the heavy dots (at $x=0$ and $x=1.25$) indicate the positions of the δ functions, Eq. (3.16), in the absence of the electron-phonon coupling.

ple physical grounds. In order to obtain these response energies we need to know the interaction between the added (or removed) electron and the polarons of the interacting system. Equation (2.10) provides us with the polaron-polaron interaction and also the small polaron binding energy. The latter gives the amount energy ($-\frac{1}{2}\Gamma$ per electron) associated with the dressing of the bare electron by the vibrational field. This fact provides us with a method of calculating the energy change in adding or removing an electron from the polaron system. Namely, we add or remove a *polaron*, calculate the energy change from Eq. (2.10), and then, remembering that we are adding a *bare electron*, subtract or put back one electron's worth of small polaron binding energy. Hence process (i) gives a small polaron change of $U_1-\frac{1}{2}\Gamma$; however, since we are adding an electron and not a polaron, we must subtract the small polaron binding energy $[-(-\frac{1}{2}\Gamma)]$ and obtain the energy change of just U_1. In a similar fashion, we find that processes (ii), (iii), and (iv) correspond to energies $-\Gamma$, 0, and U_2, respectively. This argument makes clear on physical grounds the origins of the various terms in Eq. (3.14) and will provide a helpful type of reasoning for the analysis in the later sections.

In Fig. 1, $A^{\sigma}_{ii}(\omega)$ against ω is plotted for $kT=0$ and $kT=\Omega$. The energy parameters are chosen such that $\Gamma=\Omega=\frac{1}{4}U_1$. These values give the behavior of $A^{\sigma}_{ii}(\omega)$ in an interesting case and may not be an unrealistic value for some TCNQ salts. We see that since $U_1=U-\Gamma$ [Eq. (2.23)], we also have in this case $U=5\Omega$. Thus for $\Omega\sim 0.1$ eV,[8] U has a not untypical value that is associated with TCNQ salts provided that it already includes a renormalization from the electronically polarizable donor molecules[16] (in particular for the highly conducting TCNQ salts). The choice $\Gamma=\Omega$ is rather arbitrary but is representative of the interesting intermediate-to-strong coupling regime of the small polaron model.

The spectral weight function and frequency variable are plotted in dimensionless units according to

$$a(x)=[U_1/4(\pi)^{1/2}]A^{\sigma}_{ii}(\omega)$$

and $x=\omega/U_1$. At $kT=0$ (curve 1), the spectral weight function is comprised of two peaks as given by Eq. (3.18). We see that the value of $a(x)$ midway between the two peaks (at $x=\frac{3}{8}$) is approximately 0.004 times the values at the maximum peak heights. We note that $x=\frac{3}{8}$ corresponds to $\omega=\mu$. The FWHM for each peak corresponds to an energy width $\simeq 0.42U_1$. We can define an energy gap G(FWHM) as the energy difference between the lower edge of the upper peak and the upper edge of the lower peak, both at the half-maximum value of the spectral weight function. At $kT=0$, $G(\text{FWHM})\simeq 0.84U_1$.

On the other hand, for $kT=\Omega$, the spectral weight function (curve 2) shows the effects of appreciable thermal broadening. The spectral weight between the two peaks is now much greater; $a(\frac{3}{8})/a(1)\simeq 0.191$. Also the FWHM is about $0.64U_1$ and $G(\text{FWHM})\simeq 0.55U_1$.

The main results of this section are that there is finite spectral weight at the Fermi energy even at $T=0\,^{\circ}\text{K}$, and that the peaks in the spectral weight function broaden with temperature. This latter feature allows us to define (but by no means uniquely) an effective gap G(FWHM) in the density of states. This gap has the property that it decreases with temperature and vanishes at a certain temperature. We discuss the significance of this behavior of the spectral weight function in Sec. VI.

IV. ELECTRICAL CONDUCTIVITY

The electrical conductivity is calculated from

$$\sigma(\omega)=\frac{\tanh(\frac{1}{2}\beta\omega)}{2L\omega}\int_{-\infty}^{\infty}d\tau\, e^{i\omega\tau}\langle[JJ(\tau)+J(\tau)J]\rangle, \tag{4.1}$$

which is an expression for the real part of the electrical conductivity written in symmetric form.[17] L is the crystal volume,

$$\langle JJ(\tau)\rangle=\frac{\mathrm{Tr}(e^{-\beta(H-\mu N)}Je^{iH\tau}Je^{-iH\tau})}{\mathrm{Tr}e^{-\beta(H-\mu N)}}, \tag{4.2}$$

and $\langle J(\tau)J\rangle=\langle JJ(-\tau)\rangle$. J is the current operator, given by

$$J=ieb\sum_{i,\delta,\sigma}(R_i-R_{i+\delta})C^{\dagger}_{i\sigma}C_{i+\delta\sigma}, \tag{4.3}$$

where R_i, $R_{i+\delta}$ are components of the lattice-site position vectors parallel to the external electric field.

If Eq. (4.3) is substituted into Eq. (4.2), $\langle JJ(\tau)\rangle$ becomes

$$\langle JJ(\tau)\rangle = -e^2b^2 \sum_{\substack{i,l\\ \delta,\gamma\\ \sigma,\sigma'}} (R_i - R_{i+\delta}) \frac{(R_l - R_{l+\gamma})\,\mathrm{Tr}(e^{-\beta(H-\mu N)}C^\dagger_{i\sigma}C_{i+\delta\sigma}e^{iH\tau}C^\dagger_{l\sigma'}C_{l+\gamma\sigma'}e^{-iH\tau})}{\mathrm{Tr}\,e^{-\beta(H-\mu N)}} . \tag{4.4}$$

Of course, the difficulty in evaluating the traces comes from H in the exponential. However, as we have seen, in the absence of the electron-hopping term, $H = H_0$ is a simply solvable problem and the traces can be straightforwardly evaluated. The hopping term is treated approximately and this is in the correct spirit of the problem, i.e., the transport properties of the narrow-band Mott semiconductor. The hopping parameter b appears explicitly to second order, since each current operator in the Kubo formula is proportional to the hopping parameter.

With H set equal to H_0 in Eq. (4.4), the techniques used in calculating the spectral weight function in Sec. III can be used to evaluate the conductivity. In particular, with the help of Eq. (3.5) $\langle JJ(\tau)\rangle$ becomes

$$\langle JJ(\tau)\rangle = e^2b^2 \sum_{\substack{i,l\\ \delta,\gamma\\ \sigma,\sigma'}} (R_i - R_{i+\delta})(R_l - R_{l+\gamma})F(\tau), \tag{4.5}$$

where

$$F(\tau) = Z^{-1}\,\mathrm{Tr}\,e^{-\beta(H_0-\mu N)}C^\dagger_{i\sigma}C_{i+\delta\sigma}e^{i(Un_{l-\sigma'}+VQ_l)\tau} \times C^\dagger_{l\sigma'}e^{-i(Un_{l+\gamma-\sigma'}+VQ_{l+\gamma})}C_{l+\gamma\sigma'}, \tag{4.6}$$

and Z is given by Eq. (2.16).

Since H_0 is the sum of single-site Hamiltonians, $F(\tau)$ is equal to zero unless $i+\delta = l$, $i = l+\gamma$, and $\sigma=\sigma'$; that is,

$$\begin{aligned} F(\tau) &= Z^{-1}\delta_{i+\delta,l}\delta_{i,l+\gamma}\delta_{\sigma\sigma'}\,\mathrm{Tr}(e^{-\beta(H_0-\mu N)}n_{i\sigma}(1-n_{l\sigma}) \times e^{i(Un_{l-\sigma}+VQ_l)\tau}e^{-i(Un_{i-\sigma}+VQ_i)\tau}), && (4.7)\\ &= \delta_{i+\delta,l}\delta_{i,l+\gamma}\delta_{\sigma\sigma'}\langle(1-n_{l\sigma})e^{i(Un_{l-\sigma}+VQ_l)\tau}\rangle \times \langle n_{i\sigma}e^{-i(Un_{i-\sigma}+VQ_i)\tau}\rangle . && (4.8)\end{aligned}$$

Here again, the angle brackets denote the thermal average. In particular, the first term of Eq. (4.8) becomes

$$\begin{aligned}\langle(1-n_{l\sigma})e^{i(Un_{l-\sigma}+VQ_l)\tau}\rangle &= \frac{\mathrm{Tr}(e^{-\beta(H^l_0-\mu(n_\uparrow+n_\downarrow))}(1-n_\sigma)e^{i(Un_{-\sigma}+VQ)\tau})}{\mathrm{Tr}\,e^{-\beta(H^l_0-\mu(n_\uparrow+n_\downarrow))}}\\ &= \frac{\mathrm{Tr}\,e^{-\beta(h-\mu(n_\uparrow+n_\downarrow))}(1-n_\sigma)e^{i(Un_{-\sigma}+V(Q-(V/\Omega)(n_\uparrow+n_\downarrow)\tau)}}{\mathrm{Tr}\,e^{-\beta(h-\mu(n_\uparrow+n_\downarrow))}}\\ &= \langle e^{iVQ\tau}\rangle_{\mathrm{ph}}\langle(1-n_\sigma)e^{i(U_1n_{-\sigma}-\Gamma n_\sigma)\tau}\rangle_{\mathrm{el}} . \end{aligned} \tag{4.9}$$

The thermal average of the electron term is evaluated to be

$$\langle(1-n_\sigma)e^{i(U_1n_{-\sigma}-\Gamma n_\sigma)\tau}\rangle_{\mathrm{el}} = (1+e^{iU_1\tau}e^{\beta U_1/2})/2(1+e^{\beta U_1/2}) . \tag{4.10}$$

The electronic contribution to the second term of Eq. (4.8) works out to be

$$\langle n_\sigma e^{-i(U_1n_{-\sigma}-\Gamma n_\sigma)\tau}\rangle_{\mathrm{el}} = e^{i\Gamma\tau}(e^{-iU_1\tau}+e^{\beta U_1/2})/2(1+e^{\beta U_1/2}) . \tag{4.11}$$

We combine Eqs. (4.10) and (4.11) with Eqs. (4.5)–(4.8) and use Eq. (3.11) and then obtain, after a straightforward integration in Eq. (4.1),

$$\sigma(\omega) = \frac{\eta e^2a^2b^2}{(1+e^{\beta U_1/2})^2}\left(\frac{\pi}{4S}\right)^{1/2}\frac{\tanh(\frac{1}{2}\beta\omega)}{\omega} \times(2e^{\beta U_1/2}e^{-(\omega+\Gamma)^2/4S} + e^{-(\omega-U_2)^2/4S} + e^{\beta U_1}e^{-(\omega+U)^2/4S} + \text{terms with } \omega\to-\omega). \tag{4.12}$$

In Eq. (4.12), a is the lattice spacing and $\eta = N_S/L$. For a *single* linear chain $L = N_sa$; for a three-dimensional crystal which can be regarded as being composed of many parallel chains (e.g., TCNQ salts) of length N_sa, $L = N_sa\Sigma$, where Σ is the cross-sectional area of the solid perpendicular to the chain axis.

In the limit $V\to 0$, Eqs. (4.12) and (3.15) imply that

$$\lim_{V\to 0}\sigma(\omega) = \frac{\eta a^2e^2b^2}{(1+e^{\beta U/2})^2} \times\left(2\beta e^{\beta U/2}\delta(\omega) + \frac{e^{\beta U}-1}{U} \times[\delta(\omega+U)+\delta(\omega-U)]\right). \tag{4.13}$$

This is the result obtained by Bari and Kaplan[18] for the Hubbard model in the absence of the electron-lattice coupling. Upon comparison of Eq. (4.13) with Eq. (4.12), one sees that the δ-function peaks of the former become Gaussian peaks in the latter.

The dc conductivity is given by

$$\sigma = \lim_{\omega\to 0}\sigma(\omega) = \frac{\beta\eta a^2e^2b^2}{(1+e^{\beta U_1/2})^2}\left(\frac{\pi}{4S}\right)^{1/2}(2e^{\beta U_1/2}e^{-\Gamma^2/4S} + e^{-U_2^2/4S} + e^{\beta U_1}e^{-U^2/4S}) . \tag{4.14}$$

The leading terms at high temperature behave as

$$\sigma\to C_1\beta^{3/2} - C_2\beta^{5/2}, \tag{4.15}$$

where

$$C_2/C_1 = \tfrac{1}{4}[\Gamma + (U_1^2/\Gamma)]$$

This is to be compared with the case $V = 0$ (Ref. 18), for which the leading term is proportional to β.

The limit $T\to 0$ is at first somewhat surprising; namely, $\sigma\to\infty$. However, as we shall discuss below, this behavior is understood quite readily in terms of the very nature of the Mott semiconductor.

In Fig. 2, the dc conductivity is plotted against temperature for the same values of parameters chosen in Sec. III ($\Gamma = \Omega = \frac{1}{4}U_1$). The following dimensionless variables are introduced:

$$\upsilon = \tfrac{1}{2}\beta\Omega$$

and

$$\sigma_0 = \frac{\Omega U_1}{8\pi^{1/2}\eta e^2 a^2 b^2}\,\sigma \tag{4.16}$$

$$= \frac{\upsilon(\frac{1}{2}\tanh\upsilon)^{1/2}}{(1+e^{4\upsilon})^2}\,(2e^{4\upsilon-\tanh\upsilon/2} + e^{-9\tanh\upsilon/2} + e^{8\upsilon-25\tanh\upsilon/2})\,. \tag{4.17}$$

Except for very low temperatures, the conductivity versus temperature exhibits the same gross features already seen in Ref. 18; i.e., σ is exponentially small at low T, has a rounded maximum, and falls off according to an inverse power-law at high T. For the given choice of parameters the maximum in σ occurs for $kT \simeq 0.3U_1$, slightly less (apart from the renormalization $U \to U_1$) than the value obtained in Ref. 18.

The very low-temperature divergence of σ is seen [from Eq. (4.14), (4.16), or (4.17)] to come from the last term in brackets. From Eq. (4.12), we see that this term can be associated with optical peaks (Gaussian broadened) at $\omega = \pm U$. In the limit $V \to 0$, we see from Eq. (4.13) that these peaks become δ functions and do not contribute to the dc conductivity in that case. However, for $V \neq 0$ the long-ranged Gaussian tails extend down to $\omega = 0$ and give a contribution to σ that is proportional to $e^{-U^2/4S}$. The interesting point is that the contribution from this term in Eq. (4.13) does not vanish as $T \to 0$, unlike the contributions from the first two terms.

This behavior can be understood as follows. In an ordinary noninteracting two-band model of a semiconductor, dc current is carried by thermally activated electrons in the upper band and thermally activated holes in the lower band. Optical properties ($\omega \neq 0$) arise from the mixing of the wave functions of the lower band with those of the upper band by the external electric field. These facts are of course well known. With this perspective let us now turn to the Mott semiconductor. The analogy between the noninteracting two-band system with crystal structure gap between the full and empty band and the single half-filled band with a correlation (Mott-Hubbard) gap that splits off half the states to higher energies is well known. The current operator for the Hubbard model can be written in a certain type of two-band notation.[19] We are referring to the decomposition of the creation and destruction operators according to the projection operators $n_{i-\sigma}$ and $1 - n_{i-\sigma}$. We write

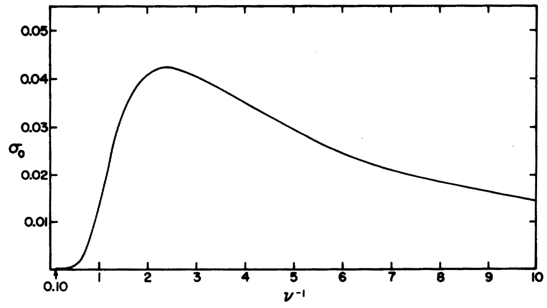

FIG. 2. dc conductivity in dimensionless units [Eq. (4.16)] is plotted against $\nu^{-1} = 2kT/\Omega$ for $\nu^{-1} > 0.10$. As $\nu^{-1} \to 0$, $\sigma_0 \propto \nu$. There is a broad minimum in the range $0.10 < \nu^{-1} < 0.35$ with $\sigma \sim 10^{-5}$.

$$C_{i\sigma} = C_{i\sigma l} + C_{i\sigma u}, \tag{4.18}$$

where

$$C_{i\sigma l} = (1 - n_{i-\sigma})C_{i\sigma}$$

and

$$C_{i\sigma u} = n_{i-\sigma}C_{i\sigma}\,. \tag{4.19}$$

$C_{i\sigma l}$ ($C_{i\sigma u}$) has the interpretation that it destroys an electron on a site that does not (that does) contain an opposite-spin electron. In the limit $b = 0$ for the Hubbard model, these operators have the further interpretation that they destroy electrons in either of the "bands" (lower and upper, respectively) associated with the two δ-function peaks in the spectral weight function.[20] The interpretation is no longer precisely correct when $b \neq 0$ (see Ref. 19 for details) but has had great intuitive appeal for very narrow bands. In terms of the operators we can reexpress the single-band current operator Eq. (4.3) as

$$J = ieb \sum_{i\delta\sigma} (R_i - R_{i+\delta})(C^\dagger_{i\sigma u}C_{i+\delta\,\sigma u} + C^\dagger_{i\sigma l}C_{i+\delta\,\sigma l} + C^\dagger_{i\sigma u}C_{i+\delta\,\sigma l} + C^\dagger_{i\sigma l}C_{i+\delta\,\sigma u})\,. \tag{4.20}$$

The projection-operator decomposition leads to interband hopping terms in Eq. (4.20), in analogy to the interband hopping terms due to interband dipole-moment matrix elements in the noninteracting case. The four terms in Eq. (4.20) relate to conductivity due to thermally excited electrons (first term) in the upper band, conductivity due to thermally excited holes (second term) in the lower band, transitions of electrons from lower band to upper band, and vice versa (third and fourth terms). Of these four terms, only the third gives a contribution to the conductivity at $T = 0\,°\mathrm{K}$. In the absence of the electron-phonon interaction this process requires an energy U, but due to the overlap of the long-range tails of the upper and lower bands (Fig. 1) in the presence of V, the dc conductivity does not vanish as $T \to 0\,°\mathrm{K}$. We note that if the limit $T \to 0\,°\mathrm{K}$ is taken first in Eq. (4.12), the low-frequency conductivity goes as ω^{-1} rather than $\delta(\omega)$, the latter being characteristic of free acceleration behavior.

We now briefly study the dc conductivity in the case of an attractive on-site interaction: $U_1 < 0$. In this case the electronic ground state is not the Mott insulator but consists of doubly occupied and empty sites. An interband transition in this case involves the creation of two singly occupied sites.

In the limit $kT \ll |U_1|$ in Eq. (4.14)

$$\sigma \simeq \beta\eta a^2 e^2 b^2 (\pi/4S)^{1/2} e^{-U_2^2/4S}, \tag{4.21}$$

which diverges at $T = 0\,^\circ\mathrm{K}$. This contribution to σ is related to the fourth term in Eq. (4.20) and the conductivity mechanism is analogous to that related to the third term of Eq. (4.20) for the case $U_1 > 0$. Note that the concepts of upper and lower in Eqs. (4.19) should be reversed for $U_1 < 0$. We point out that this mechanism for the conductivity at low T is not a superconductivity mechanism. On the contrary, from the fourth term in Eq. (4.20) we see that it is pair breaking in the sense that the term "pair" refers to the bound spin-paired electrons on a given site. In the absence of the electron-lattice interaction, the pair-breaking term does not contribute to the conductivity at $\omega = 0$ and explicit pair-hopping[21] gives the lowest order (in the bandwidth) contribution to the dc conductivity.

The case $U_1 = 0$ is also worth noting. In this case Eq. (4.14) becomes

$$\sigma = \beta\eta a^2 e^2 b^2 (\pi/4S)^{1/2} e^{-\Gamma^2/4S}. \tag{4.22}$$

For $kT \gg \Omega$, the exponent becomes $\Gamma^2/4S \to \beta\Gamma/4$ and the conductivity is thermally activated (with activation energy given by the small polaron binding energy) at these temperatures. For very low temperatures σ again behaves as $1/T$. Also, in the case of $U_1 = 0$, the spectral weight function is given by

$$A_{ij}^{\sigma}(\omega) = \delta_{ij}(\pi/2S)^{1/2}\left(e^{-\omega^2/2S} + e^{-(\omega+\Gamma)^2/2S}\right). \tag{4.23}$$

This also reflects the fact that the energy gap is related to the small-polaron binding energy. The essential content of Eq. (4.22) is familiar from small-polaron theory[22] and can be stated in that terminology as follows. At low T the conductivity is band-like; the exponential factor is the familiar oscillator-overlap band-narrowing factor. At higher T the exponential factor becomes a thermal activation factor and controls the temperature dependence of σ. This is the small-polaron hopping regime.

V. THERMOELECTRIC POWER

The thermoelectric power of a solid is a useful transport property to know, since it governs many thermoelectric phenomena[21] (e.g., Peltier effect, Seebeck effect, Thomson effect). In particular, the Seebeck effect gives a direct measure of the thermoelectric power as the ratio of the electric field in a specimen to the thermal gradient that produces the field.

The standard derivations[23] of thermoelectric transport properties proceed from a Boltzmann-equation approach which describes the behavior of free or Bloch electrons under the influence of electric fields, thermal gradients, and weak scattering. On the other hand, we have been considering electrons that are strongly correlated as a result of the dominant short-range interactions. Consequently, the physics has been more easily described in a site-representation rather than in terms of Bloch waves. The application of the Boltzmann-equation approach is therefore not straightforward and it would seem more advantageous to calculate the thermoelectric transport properties directly in the site representation. The quantum-mechanical transport theory[17] is used and site-space analogs of continuum quantities are formulated. We follow closely the method of Schotte,[24] who calculated the thermoelectric properties of a single small polaron according to Holstein's model.[22]

The thermoelectric power or Seebeck coefficient α is given by the relation

$$\alpha = (1/T)(\mu/e - \Xi/\sigma). \tag{5.1}$$

Here μ is the chemical potential, which, in this case is given by Eq. (2.21). e is the electric charge of the electron and is a negative quantity. σ is the dc conductivity; we shall use Eq. (4.14). Ξ is a transport coefficient related to the electrical response associated with a thermal gradient according to the relation

$$\langle J\rangle = \sigma\left[E - \frac{T}{e}\nabla\left(\frac{\mu}{T}\right)\right] + \Xi\left(-\frac{\nabla T}{T}\right). \tag{5.2}$$

The quantum-mechanical expression for Ξ is

$$\Xi = \frac{\beta}{2L}\int_{-\infty}^{\infty} d\tau \langle J J^q(\tau)\rangle. \tag{5.3}$$

The only new quantity in Eq. (5.3) is the energy-current operator J^q $(J^q(\tau) = e^{iH\tau} J^q e^{-iH\tau})$. We denote J_l^q as the energy current associated with the lth site such that $J^q = \sum_l J_l^q$. Similarly the energy density associated with the lth site is written as H_l such that $H = \sum_l H_l$. From Eq. (2.1), we write

$$H_l = H_l^{\mathrm{el}} + H_l^{\mathrm{ph}} + H_l^{\mathrm{el\text{-}ph}}. \tag{5.4}$$

Here

$$H_l^{\mathrm{el}} = -\frac{b}{2}\sum_{\sigma}\left(C_{l+1\,\sigma}^{\dagger} C_{l\sigma} + C_{l\sigma}^{\dagger} C_{l+1\,\sigma} + C_{l\sigma}^{\dagger} C_{l-1\sigma} + C_{l-1\sigma}^{\dagger} C_{l\sigma}\right) + U n_{l\uparrow} n_{l\downarrow}. \tag{5.5}$$

The summation over l in Eq. (5.5) gives the one-dimensional Hubbard model. The densities associated with the phonon Hamiltonian and electron-phonon interaction are

$$H_l^{\mathrm{ph}} = \tfrac{1}{2}\Omega(P_l^2 + Q_l^2) \tag{5.6}$$

and

$$H_l^{\mathrm{el\text{-}ph}} = V Q_l (n_{l\uparrow} + n_{l\downarrow}), \tag{5.7}$$

respectively.

The relation between the energy density and the energy current density is given by the conservation law

$$\frac{\partial H_l}{\partial t} + \mathrm{div} J_l^q = 0 ; \tag{5.8}$$

here the div operator in site space is given by

$$\mathrm{div} J_l^q \equiv (1/a)(J_l^q - J_{l-1}^q) . \tag{5.9}$$

The time derivative of H_l in Eq. (5.8) is calculated from the equation of motion

$$i \frac{\partial H_l}{\partial t} = [H_l, H] .$$

Then from Eqs. (5.8) and (5.9) the energy current is calculated to be

$$\begin{aligned} J_l^q = {} & ib^2 a \sum_\sigma (C_{l+2\sigma}^\dagger C_{l\sigma} - C_{l\sigma}^\dagger C_{l+2\sigma}) \\ & + \frac{ibUa}{2} \sum_\sigma (C_{l+1\sigma}^\dagger C_{l\sigma} - C_{l\sigma}^\dagger C_{l+1\sigma})(n_{l+1-\sigma} + n_{l-\sigma}) \\ & + \frac{ibVa}{2} \sum_\sigma (C_{l+1\sigma}^\dagger C_{l\sigma} - C_{l\sigma}^\dagger C_{l+1\sigma})(Q_{l+1} + Q_l) . \end{aligned} \tag{5.10}$$

The calculation of Ξ in Eq. (5.3) is now straightforward and similar to the calculation of the conductivity in Sec. IV. Ξ is calculated to second order in b. The first term in Eq. (5.10) leads to a b^3 term in Ξ to lowest order but this term actually vanishes. The details of the calculations are given in the Appendix and the final result is

$$\Xi = (U_2/2e)\sigma , \tag{5.11}$$

where, from Eq. (2.24), $U_2 = U - 2\Gamma$ and σ is given by Eq. (4.14). Since the chemical potential μ is equal to $\frac{1}{2}U_2$, we see from Eq. (5.1) that the thermoelectric power is zero.

This result is in agreement with the thermoelectric power of an ordinary two-band intrinsic semiconductor. It is also in agreement with that of a single half-filled metal[25] given by the first term of Eq. (2.2) alone. The vanishing of the thermoelectric power for a half-filled band thus appears to be a somewhat general property related to the particle-hole symmetry[12] of the half-filled band. If the number of electrons is not equal to the number of sites, the thermoelectric power of the non-half-filled band metal for $kT \ll E_F$ is linear in temperature, as expected,[23] and also proportional to

$$E_F[1 - (E_F/2b)^2]^{-1/2} ,$$

where E_F is the zero-temperature Fermi energy. For the half-filled band, E_F is of course zero. α also changes sign as a function of E_F at $E_F = 0$.

On the other hand the thermoelectric power of the near-half-filled band Mott insulator behaves quite differently. Further details for this case will be presented elsewhere.[26]

VI. DISCUSSION AND SUMMARY

The transport properties of a half-filled band of electrons that are interacting strongly with each other through the short-range Coulomb repulsion and also with intramolecular vibrations has been studied. The electronic bandwidth was taken to be the smallest parameter in the problem and the dc conductivity was obtained to second order in this parameter. The thermoelectric power was also calculated and found to be equal to zero, in agreement with the result for a two-band intrinsic semiconductor and is an apparent consequence of particle-hole symmetry of the half-filled band.

The one-electron spectral weight function was calculated and it was found that the coupling to the phonons led to a finite density of states in the nominal Mott-Hubbard gap. With increasing temperature the band tailing became more appreciable and suggested a possible interpretation in terms of a gradual semiconductor-to-nonsemiconductor transition (to the extent that the microscopic features of the density of states of the semiconductor, namely, two distinctive, appreciably nonzero regions, became nondiscernible). Of our calculations of the transport properties, the dc conductivity is a decreasing function of temperature at high T, in qualitative agreement with the behavior found in typical metals (but it is also consistent with the behavior of a semiconductor with a temperature-independent gap; see Ref. 18). The zero thermoelectric power is in agreement with the result for a half-filled-band metal and an ordinary two-band intrinsic semiconductor. However, as noted[26] the thermoelectric power is not typical of a metal for the near-half-filled band.

The results for $T \to 0$ are also interesting.[27] The spectral weight function was shown to have long-range tails even at $T = 0$. As a consequence of this tailing the dc conductivity behaved as $1/T$ (or $1/\omega$) at low T. On the other hand, an explicit calculation of $\mu_> - \mu_<$ in Sec. II yielded a nonzero result in the thermodynamic limit. $\mu_> - \mu_<$ is given [Eqs. (2.13) and (2.14)] by differences in exact ground-state energies; however an electron injected into a specimen from a battery will not in general be in an eigenstate. In particular, Eq. (3.18) predicts that an electron injected onto a given spatial site can be accomodated over a continuous range of energies. In connection with these results we note the conclusion by Leib and Wu[12] that the one-dimensional Hubbard model is an insulator for $U > 0$. Their conclusion is based on the criterion that $\mu_> - \mu_<$ is nonvanishing in the thermodynamic limit. We raise the questions: is it possible that a finite bandwidth will lead to long-range tails in the density of states of the one-dimensional Hubbard model and if so, will the dc conductivity be nonzero?

The dc conductivity behaves as T^{-1} at very low temperature. This behavior was accounted for in terms of the form of the current operator near the atomic limit and the long-range tails in the spectral weight function and optical conductivity. The T^{-1} behavior was found for attractive on-site interactions as well. In this case the large conductivity was related to a pair-breaking mechanism in connection with bound spin-paired electrons on given sites.

In the case that the polarization associated with the vibrational motion exactly cancels the repulsive on-site interaction, the conductivity is easily related to the concepts of small polaron theory. Band-narrowing and thermally activated hopping processes are easily identified.

In conclusion we have attempted to elucidate some of the properties associated with electrical transport in a strongly correlated half-filled band in the presence of strong coupling to intramolecular vibrations.

APPENDIX

In this Appendix, Ξ is evaluated as described in Sec. V. We start from Eqs. (5.3) and (5.10). We have

$$\Xi=-\left(\frac{\beta}{2L}\right)\frac{ea^2b^2}{2}\sum_{n,l}\sum_{\sigma,\sigma'}\int_{-\infty}^{\infty}dt\langle(C^\dagger_{n+1\,\sigma}C_{n\sigma}-C^\dagger_{n\sigma}C_{n+1\,\sigma})$$
$$\times e^{iH\tau}[(C^\dagger_{l+1\,\sigma'}C_{l\sigma'}-C^\dagger_{l\sigma'}C_{l+1\,\sigma'})$$
$$\times[U(n_{l+1-\sigma'}+n_{l-\sigma'})+V(Q_l+Q_{l+1})]]e^{-iH\tau}\rangle. \qquad \text{(A1)}$$

The operators indexed by n are representative of the electrical current operator. The first term in Eq. (5.10) leads to a b^3 in Ξ, to lowest order. However, since the first term in Eq. (5.10) hops the electrons over a distance of two sites and the electrical current operator hops the electrons over a distance of one site, the diagonal matrix elements of the product of these two operators is zero in the atomic limit states.

In Eq. (A1) it is more convenient to calculate the time evolution of the less-complicated electrical current operator. We use the invariance property of the trace and also take $H=H_0$. We use

$$e^{-iH_0\tau}C_{n\sigma}e^{iH_0\tau}=C_{n\sigma}e^{i(Un_{n-\sigma}+VQ_n)\tau}$$

The thermal average in Eq. (A1) is now written

$$\langle(C^\dagger_{n+1\,\sigma}C_{n\sigma}e^{-i[U(n_{n+1-\sigma}-n_{n-1})+V(Q_{n+1}-Q_n)]\tau}-C^\dagger_{n\sigma}C_{n+1\,\sigma}e^{i[U(n_{n+1-\sigma}-n_{n-\sigma})+V(Q_{n+1}-Q_n)]\tau})$$
$$\times(C^\dagger_{l+1\,\sigma'}C_{l\,\sigma'}-C^\dagger_{l\,\sigma'}C_{l+1\,\sigma'})[U(n_{l+1\,-\sigma'}+n_{l-\sigma'})+V(Q_{l+1}+Q_l)]\rangle=-\delta_{\sigma\sigma'}\delta_{nl}\langle(n_{l+1\,\sigma}(1-n_{l\,\sigma})$$
$$\times e^{-i[U(n_{l+1\,-\sigma}-n_{l\,-\sigma})+V(Q_{l+1}-Q_l)]\tau}+n_{l\,\sigma}(1-n_{l+1\,\sigma})e^{i[U(n_{l+1-\sigma}-n_{l-\sigma})+V(Q_{l+1}-Q_l)]\tau})$$
$$\times[U(n_{l+1\,-\sigma}+n_{l\,-\sigma})+V(Q_{l+1}+Q_l)]\rangle=-2\delta_{\sigma\sigma'}\delta_{nl}\langle n_{l+1\,\sigma}(1-n_{l\,\sigma})$$
$$\times e^{-i[U(n_{l+1\,-\sigma}-n_{l\,-\sigma})+V(Q_{l+1}-Q_l)]\tau}[U(n_{l+1\,-\sigma}+n_{l\,-\sigma})+V(Q_{l+1}+Q_l)]\rangle. \qquad \text{(A2)}$$

In the last form in Eq. (A2), the indicated thermal average can be separated into two terms:

$$T_1=U\langle n_{l+1\,\sigma}(1-n_{l\,\sigma})e^{-i[U(n_{l+1\,-\sigma}-n_{l\,-\sigma})+V(Q_{l+1}-Q_l)]\tau}(n_{l+1\,-\sigma}+n_{l\,-\sigma})\rangle \qquad \text{(A3)}$$

and

$$T_2=V\langle n_{l+1\,\sigma}(1-n_{l\,\sigma})e^{-i[U(n_{l+1\,-\sigma}-n_{l\,-\sigma})+V(Q_{l+1}-Q_l)]}(Q_l+Q_{l+1})\rangle \qquad \text{(A4)}$$

Again, we follow the method of Eqs. (2.6)–(2.11) and write

$$T_1=U\langle n_{l+1\,\sigma}(1-n_{l\,\sigma})(n_{l+1\,-\sigma}+n_{l\,-\sigma})e^{-i\tau(U_1n_{l+1\,-\sigma}-\Gamma n_{l+1\,\sigma}+VQ_{l+1}-U_1n_{l\,-\sigma}+\Gamma n_{l\,\sigma}-VQ_l)}\rangle$$
$$=U\langle n_{l+1\,\sigma}n_{l+1\,-\sigma}e^{-i\tau(U_1n_{l+1\,-\sigma}-\Gamma n_{l+1\,\sigma})}\rangle\langle(1-n_{l\,\sigma})e^{i\tau(U_1n_{l\,-\sigma}-\Gamma n_{l\,\sigma})}\rangle e^{-S\tau^2}$$
$$+U\langle n_{l+1\,\sigma}e^{-i\tau(U_1n_{l+1\,-\delta}-\Gamma n_{l+1\,\sigma})}\rangle\langle(1-n_{l\,\sigma})n_{l\,-\sigma}e^{i\tau(U_1n_{l\,-\sigma}-\Gamma n_{l\,\sigma})}\rangle e^{-S\tau^2}$$
$$=\frac{Ue^{-S\tau^2}}{[2(1+e^{\beta U_1/2})]^2}[e^{i\tau(U_1-\Gamma)}+2e^{\beta U_1/2}e^{i\Gamma\tau}+e^{\beta U_1}e^{i\tau(\Gamma+U_1)}]. \qquad \text{(A5)}$$

In a similar manner, again using Eqs. (2.6)–(2.11) we obtain

$$T_2=V\langle n_{l+1\,\sigma}(1-n_{l\,\sigma})e^{-i\tau(U_1n_{l+1\,-\sigma}-\Gamma n_{l+1\,\sigma}+VQ_{l+1}-U_1n_{l\,-\sigma}+\Gamma n_{l\,\sigma}-VQ_l)}(Q_l+Q_{l+1})\rangle$$
$$-\Gamma\langle n_{l+1\,\sigma}(1-n_{l\,\sigma})e^{-i\tau(U_1n_{l+1\,-\sigma}-\Gamma n_{l+1\,\sigma}+VQ_{l+1}-U_1n_{l\,-\sigma}+\Gamma n_{l\,\sigma}-VQ_l)}(n_{l+1\,\sigma}+n_{l+1\,-\sigma}+n_{l\,\sigma}+n_{l\,-\sigma})\rangle. \qquad \text{(A6)}$$

The first term above is zero. This is seen as follows. The thermal average can be separated as (average on electrons)$\times(\langle Q_le^{i\tau VQ_l}\rangle_{\text{ph}}+\langle Q_{l+1}e^{-i\tau VQ_{l+1}}\rangle_{\text{ph}})$. We differentiate Eq. (3.11) with respect to τ and obtain

$$\frac{d}{d\tau}\langle e^{-iVQ\tau}\rangle_{\text{ph}}=-S\tau e^{-S\tau^2/2}; \qquad \text{(A7)}$$

however, Eq. (A7) is also equal to $-iV\langle Q^{-iVQ\tau}\rangle_{\rm ph}$. This implies that

$$\langle Qe^{i\tau VQ}\rangle_{\rm ph}+\langle Qe^{-i\tau VQ}\rangle_{\rm ph}=\frac{i}{V}\left[-S\tau e^{-S\tau^2/2}+S\tau e^{-S\tau^2/2}\right]=0\,. \tag{A8}$$

Hence only the term proportional to Γ remains in Eq. (A6). The last factor $n_{l+1\,\sigma}+n_{l+1\,-\sigma}+n_{l\,\sigma}+n_{l\,-\sigma}$ in that average can be broken up as follows: (i) the term $n_{l\,\sigma}$ does not contribute, since $(1-n_{l\,\sigma})n_{l\,\sigma}=0$; (ii) the term $n_{l+1\,-\sigma}+n_{l\,-\sigma}$ implies the same thermal average encountered in T_1. Hence we get a contribution to T_2 that is just $-(\Gamma/U)T_1$; (iii) the remaining thermal average comes from the term $n_{l+1\,\sigma}$ and since $(n_{l+1\,\sigma})^2=n_{l+1\,\sigma}$, we need to evaluate

$$\begin{aligned}&\langle n_{l+1\,\sigma}(1-n_{l\,\sigma})e^{-i\tau(U_1n_{l+1\,-\sigma}-\Gamma n_{l+1\,\sigma}+VQ_{l+1}-U_1n_{l\,-\sigma}+\Gamma n_{l\,\sigma}-VQ_l)}\rangle\\&\quad=\frac{e^{-S\tau^2}}{[2(1+e^{\beta U_1/2})]^2}\,e^{i\tau\Gamma}(e^{\beta U_1/2}+e^{-i\tau U_1})\,(1+e^{\beta U_1/2}e^{i\tau U_1})\\&\quad=\frac{e^{-S\tau^2}}{[2(1+e^{\beta U_1/2})]^2}\,(e^{i\tau\Gamma(U_1-\Gamma)}+2e^{\beta U_1/2}e^{i\tau\Gamma}+e^{\beta U_1}e^{i\tau(U_1+\Gamma)})\,.\end{aligned} \tag{A9}$$

Again we find that this contribution to T_2 is just $-(\Gamma/U)T_1$. The total contribution to T_2 is $-(2\Gamma/U)T_1$. We use this result and Eqs. (A5) and (A2) to write

$$\Xi=\frac{\beta eb^2\eta a^2}{2(1+e^{\beta U_1/2})^2}\,(U-2\Gamma)\left(\frac{\pi}{4S}\right)^{1/2}(e^{-(U_1-\Gamma)^2/4S}+2e^{\beta U_1/2}e^{-\Gamma^2/4S}+e^{\beta U_1}e^{-U^2/4S})\,.$$

From Eq. (4.14) we see that Ξ is just proportional to the dc conductivity $\Xi=(1/2e)(U-2\Gamma)\sigma$.

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