

Thermopower in the correlated hopping regime

P. M. Chaikin*

Department of Physics, University of California, Los Angeles, California 90024

G. Beni

Bell Laboratories, Murray Hill, New Jersey 07974

(Received 16 June 1975)

The high-temperature limit for the thermopower of a system of interacting localized carriers is governed entirely by the entropy change per added carrier. The calculation of this quantity reduces to a simple combinatorial problem dependent only on the density of carriers and the interactions stronger than the thermal energy. We have thus been able to generalize the Heikes formula to include several cases of interacting Fermi systems with spin.

I. INTRODUCTION

There has been a great deal of recent interest in metallo-organic compounds which have relatively high conductivity and quasi-one-dimensionality.^{1,2} Thermoelectric power is a very useful experiment in studying these substances as it sheds light on both the conduction process and on the thermodynamics.^{3,4} In general, these compounds [as exemplified by the tetracyanoquinodimethan (TCNQ) salts] have narrow bandwidths (transfer integral $t \approx 0.01-0.1$ eV) and sizable on-site Coulomb interactions ($U_0 \approx 0.1-1$ eV). It has therefore appeared reasonable to discuss their properties in terms of the narrow-band Hubbard model, and indeed much work has been done along these lines primarily to explain the conductivity, specific heat, and magnetic properties of these salts.⁵ Actually, the theoretical treatment of the transport phenomena in these systems is still very incomplete since the details of the motion of the charge carriers are not sufficiently well characterized.

The Seebeck coefficient has been calculated in the atomic limit of the Hubbard model⁶ and for infinite U_0 but finite bandwidth.⁷ The purpose of this paper is to add some physical insight into the previous results, and more importantly to extend them to the cases of any number of near-neighbor interactions and for attractive on-site interaction. The unifying feature of the models discussed in the present work is that the charge carriers are treated as localized interacting particles.

The neglect of all the effects connected with the kinetic energy of the carriers results in a constant thermopower at high temperatures. Its sign and magnitude are determined solely by the constraints as to the occupancy of states and the density of electrons in the system. In this limit the calculation is reduced to a combinatorial problem, which is easily solvable.

Using our results and knowing the electron den-

sity, it should now be possible to learn the strengths of the Coulomb interactions at different distances by measuring the thermopower as a function of temperature. Conversely, if the strength of the interactions are known, say, from conductivity and thermodynamic measurements, we should be able to infer the electron density. In the materials in question this is an extremely important and elusive quantity which equals the amount of charge transfer from cation to anion chains. The plan of the paper is as follows. In Sec. II we briefly review the theory of the Seebeck coefficient of narrow-band semiconductors and metals and rederive the Heikes formula using a slightly different approach. In Sec. III we extend the calculations including interactions and in Sec. IV we conclude with a brief discussion.

II. NONINTERACTING SYSTEMS

A. Formalism

While in broad-band systems one usually makes use of the Boltzmann equation to derive the transport properties, in narrow-band materials this treatment may be insufficient. In treating systems with large many-body interactions it is not appropriate to use the one-electron Boltzmann transport theory. We turn instead to the Kubo formalism for the transport coefficients of an interacting system.⁸ The thermoelectric power is given by

$$S = - \frac{S^{(2)}/S^{(1)} + \mu/e}{T}, \quad (1)$$

where e is the absolute value of the electron charge and

$$S^{(2)} = \frac{1}{2} \beta e \int_0^\infty \left\{ \text{Tr} \left[\exp \beta \left(\mu \sum_i n_i - H \right) \right] \times [Qv(\tau) + v(\tau)Q] \right\} d\tau,$$

$$S^{(1)} = \frac{1}{2} \beta e^2 \int_0^\infty \left\{ \text{Tr} \left[\exp \beta \left(\mu \sum_i n_i - H \right) \right] \times [vv(\tau) + v(\tau)v] \right\} d\tau, \quad (2)$$

where β is $1/k_B T$, H is the Hamiltonian, μ is the chemical potential, and v and Q are, respectively, the velocity and energy flux operators. At high temperature βH will be zero for any finite terms in the Hamiltonian. On the other hand, terms in the Hamiltonian which are large (infinite) in comparison to the temperature will not contribute to the trace and therefore will serve only to constrain the possible configurations. The entire temperature dependence of the integrands for $S^{(2)}$ and $S^{(1)}$ is then given by the $\beta\mu$ terms in the exponentials with all state configurations contributing equally. However, from the definition of the chemical potential

$$\frac{\mu}{T} = - \left(\frac{\partial \sigma}{\partial N} \right)_{E,V}, \quad (3)$$

where σ is the entropy of the system, N is the number of particles, and E and V are, respectively, the internal energy and volume.

As β goes to zero we can calculate the entropy of the system in terms of the degeneracy g of the high-temperature state,

$$\sigma = k_B \ln g \quad \text{and} \quad (4)$$

$$\frac{\mu}{T} = - k_B \left(\frac{\partial \ln g}{\partial N} \right)_{E,V}.$$

Thus $\beta\mu$ goes to a temperature-independent value. From Eq. (2) we see that quite generally the ratio of $S^{(2)}/S^{(1)}$ becomes temperature independent as $T \rightarrow \infty$. We then have

$$S(T \rightarrow \infty) \rightarrow - \frac{S^{(2)}/S^{(1)}}{T} + \frac{\mu}{eT} \rightarrow - \frac{\mu}{eT} = - \frac{k_B}{e} \frac{\partial \ln g}{\partial N}. \quad (5)$$

In this limit it is clear why the thermopower is often said to measure the "entropy per carrier."

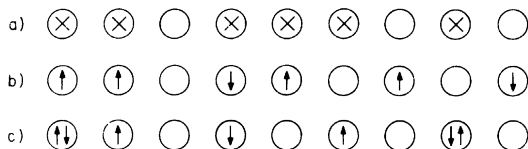


FIG. 1. Possible high-temperature site configuration of (a) spinless fermions; (b) electrons with an infinite on-site repulsion; and (c) electrons with no interactions.

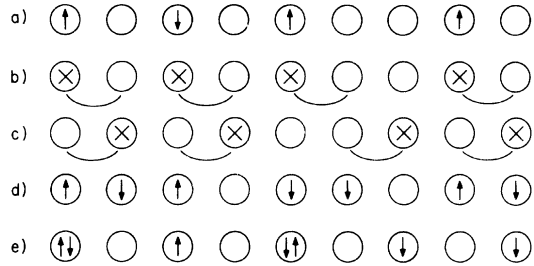


FIG. 2. (a) Possible high-temperature site configuration of electrons with infinite nearest-neighbor repulsion; (b) and (c) pairings used in the combinatorial program for Fig. 2(a) (see text); (d) possible electron configuration for $1 > \rho > 1/2$ and $U_0 - 2U_1 > 0$; and (e) for $1 > \rho > 1/2$, and $U_0 - 2U_1 < 0$.

It is convenient to discuss our results in terms of temperature regions in which the results are applicable as compared to the energy parameters of the extended Hubbard model (see Table I). We write the extended Hubbard Hamiltonian

$$H = -t \sum_{i,\sigma} (C_{i,\sigma}^\dagger C_{i+1,\sigma} + C_{i+1,\sigma}^\dagger C_{i,\sigma}) + U_0 \sum_{i,\sigma} n_{i\sigma} n_{i-\sigma} + \sum_{i,j,\sigma,\sigma'} U_{j\sigma} n_{i\sigma} n_{i+j,\sigma'}, \quad (6)$$

where t is the transfer matrix element, U_0 is the on-site Coulomb interaction, U_j is the Coulomb interaction between electrons on sites j units apart, $C_{i,\sigma}^\dagger$ and $C_{i,\sigma}$ are, respectively, electron site and spin creation and annihilation operators, and $n_{j\sigma}$ is the number operator for spin σ .

The degeneracy is calculated for a system with N_A sites and N electrons distributed randomly but with certain restrictions. In all of the following examples we take the high-temperature limit ($t \ll kT$) and treat only the one-dimensional case. Typical configurations of the high-temperature state are illustrated in Figs. 1–3.

B. Heikes formula

For spinless Fermions no two particles can occupy the same site and the degeneracy is [Fig. 1(a)]

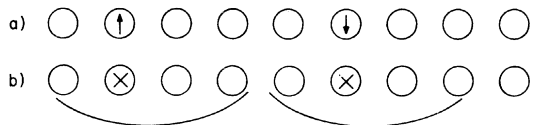


FIG. 3. (a) Possible high-temperature site configuration of electrons with infinite third-nearest-neighbor interactions; (b) grouping used in the combinatorial problem for Fig. 3(a).

$$g = N_A! / N! (N_A - N)! . \quad (7)$$

Using Stirlings approximation, and differentiating with respect to N , we have immediately

$$S(T \rightarrow \infty) \rightarrow - (k_B / e) \ln[(1 - \rho) / \rho] , \quad (8)$$

where ρ is the ratio of particles to sites ($\rho = N / N_A$). Equation (8) represents the well-known Heikes formula.⁹ It is interesting to note that it should only be physically applicable to systems in enormous magnetic fields (systems where temperature is large compared to any energy other than $g\mu_B H$), or to electrons paired with a strong binding energy such that $k_B T \ll E_{\text{binding}}$. (In this case $\rho = 2N / N_A$, see Sec. III E.)

III. INTERACTING SYSTEMS

A. $k_B T \gg U_0$ (fermions with spin)

The simplest generalization of Heikes formula is obtained when we consider a system of fermions with spin at infinite temperature. In this situation the spin-up electrons may be distributed randomly among the N_A sites, and independently so may the spin-down electrons. The number of spin-up electrons may run from 0 to N (the total number of electrons). Here we must sum over the states with different number of up and down electrons [Fig. 1(c)]

$$g = \sum_{N_1=0}^N \left(\frac{N_A!}{N_1! (N_A - N_1)!} \frac{N_A!}{N_1! (N_A - N_1)!} \right) , \quad N_1 + N_2 = N . \quad (9)$$

The thermopower is then

$$S(T \rightarrow \infty) = - (k_B / e) \ln[(2 - \rho) / \rho] . \quad (10)$$

B. $k_B T \ll U_0$ (on-site repulsion)

A similar problem is that of electrons in a system with a large electron-electron repulsion (U_0) so that two electrons with either spins parallel or opposed are forbidden double occupancy of a single site. In this case there are N electrons to put on N_A sites and each electron may have spin up or down [Fig. 1(b)],

$$g = N_A! 2^N / N! (N_A - N)! , \quad (11)$$

which leads to

$$S(T \rightarrow \infty) = - (k_B / e) \ln[2(1 - \rho) / \rho] .$$

C. $kT \ll U_0, U_1$ (nearest-neighbor interactions)

We now include nearest-neighbor repulsion and work this case out in detail. For second and more distant neighbors we will only consider the lowest density cases. From analogy with the treatment for first neighbors it should be clear how to proceed to higher-density cases.

For less than one electron on every other site

($\rho < \frac{1}{2}$) the degenerate states will all involve situations in which no adjacent sites are occupied [Fig. 2(a)]. We can separate the spin degrees of freedom from the spatial configuration remembering to multiply by 2^N later. There are several ways to solve for the configurational degeneracy all involving transformation of the problem (for instance, from a site problem to a bond problem), however, the most illustrative way for our extension to further neighbors is shown in Fig. 2(b). We note that if we take each electron only in a pair with an unoccupied site to its right, there will never be adjacent sites occupied.

Each pair is then a new "particle" (red ball) of which there are N . The remaining unpaired empty sites are black balls and there are $N_A - 2N$ of them. The configurational degeneracy is the number of ways of arranging the different colored balls,

$$"g_c" = (N_A - N)! / N! (N_A - 2N)! . \quad (12)$$

Including the spin degeneracy we have

$$"g" = 2^N (N_A - N)! / N! (N_A - 2N)! , \quad (13)$$

which leads to the following expression for the thermopower:

$$S(T \rightarrow \infty) = - (k/e) \ln[2(1 - 2\rho)^2 / \rho(1 - \rho)] . \quad (14)$$

There is, however, a pathology to the problem. By our way of counting we have excluded any state in which the last space is occupied. To correct for this we move the empty space to the left of the electron and count all states in which the last space has an electron [Fig. 2(c)]. None of these have previously been counted. The additional degeneracy

TABLE I. Thermopower as a function of charge density ρ for different temperature ranges as compared to extended Hubbard-model parameters [see Eq. (6)].

Region of applicability	Thermopower
$kT \gg U_0, U_j, t$	$-\frac{k}{ e } \ln \frac{2-\rho}{\rho}$
$U_0 \gg kT \gg U_j, t$	$-\frac{k}{ e } \ln \frac{2(1-\rho)}{\rho}$
$U_0 > U_1 \gg kT \gg U_{j>1}, t$	$-\frac{k}{ e } \ln \frac{2(1-2\rho)^2}{\rho(1-\rho)}$
$U_0 > U_1 \gg U_2 \gg kT \gg U_{j>2}, t$	$-\frac{k}{ e } \ln \frac{2(1-3\rho)^3}{\rho(1-2\rho)^2}$
$U_0 > U_1 \dots U_b \gg kT \gg U_{j>b}, t$	$-\frac{k}{ e } \ln \frac{2(1-b\rho-\rho)^{b+1}}{\rho(1-b\rho)^b}$
Attractive U_0	
$ U_0 \gg kT \gg U_j, t$	$-\frac{k}{2 e } \ln \frac{2-\rho}{\rho}$

is given by Eq. (12) with $N'_A = N_A - 2$ and $N' = N - 1$,

$$g'_c = (N_A - N - 1)! / (N - 1)! (N_A - 2N)! . \quad (15)$$

Adding this to Eq. (12) we have the full configurational degeneracy

$$g_c = "g_c" + g'_c = N_A (N_A - N - 1)! / N! (N_A - 2N)! . \quad (16)$$

This leads to Eq. (14) for the thermopower if we neglect terms of the order $1/N$. Similar results will hold for the nearest-neighbor calculations which follow. We will therefore neglect the end-point effects in the rest of the calculations presented here.

For an electron density between one per site and one-per-two sites ($1 > \rho > \frac{1}{2}$) there are two cases of interest. If the on-site Coulomb repulsion is greater than twice the nearest-neighbor interaction ($U_0 - 2U_1 > 0$), the configurations will be as shown in Fig. 2(d) with no two empty sites (holes) as nearest neighbors.¹⁰ The configurational degeneracy is then the same as in Eq. (16) with the substitution of holes for electrons: $N_h = N_A - N$,

$$g_c = \frac{N_A (N_A - N_h - 1)!}{(N_h)! (N_A - 2N_h)!} = \frac{N_A (N - 1)!}{(N_A - N)! (2N - N_A)!} . \quad (17)$$

The spin degeneracy is, however, still the degeneracy of the electrons so that

$$g = N_A (N - 1)! 2^N / (N_A - N)! (2N - N_A)! , \quad (18)$$

and the resulting thermopower is (for $U_0 - 2U_1 \gg kT$, $1 > \rho > \frac{1}{2}$)

$$S(T \rightarrow \infty) \rightarrow - (k/e) \ln[2\rho(1 - \rho)/(2\rho - 1)^2] . \quad (19)$$

If the near-neighbor interaction is strong ($U_0 - 2U_1 < 0$) the resulting state will involve a charge-density wave as illustrated in Fig. 2(e). The empty sites may either be odd or even numbered (shifted uniformly by one site), which introduces a factor of two in g . There are $\frac{1}{2}N_A$ occupied sites of which $N - \frac{1}{2}N_A$ are doubly occupied (with no spin degeneracy) and $N_A - N$ are singly occupied (spin degeneracy 2). We arrange the $N_A - N$ singles on the $\frac{1}{2}N_A$ sites and obtain

$$g = 2(\frac{1}{2}N_A)! 2^{N_A - N} / (N_A - N)! (N - \frac{1}{2}N_A)! , \quad (20)$$

which leads to a thermopower ($KT \ll 2U_1 - U_0$, $1 > \rho > \frac{1}{2}$)

$$S(T \rightarrow \infty) \rightarrow - (k/e) \ln[(1 - \rho)/(2\rho - 1)] . \quad (21)$$

If we assume that the interactions are electron-hole symmetric, we find the thermopower for any $\rho > 1$ by inverting Eqs. (11), (14), (19), or (21).¹¹

D. $kT \ll U_0, U_b$ (further-neighbor interaction)

If near-neighbor interactions are repulsive to a certain distance (and negligible thereafter), we

calculate the Seebeck coefficient as follows. Suppose the repulsion cuts off at b sites so there must be b empty sites between two occupied ones. Figure 3(a) illustrates the case of $b = 3$. We transform the problem to "red balls" containing $b + 1$ sites [as in Fig. 3(b)] and empty sites "black balls." The combinatorial problem then gives

$$g = (N_A - bN)! 2^N / (N)! (N_A - (b + 1)N)! , \quad (22)$$

where we have included the spin degeneracy. For densities of $\rho < 1/(b + 1)$ the thermopower is then

$$S(T \rightarrow \infty) \rightarrow - \frac{k}{e} \ln \frac{2[1 - (b + 1)\rho]^{b+1}}{\rho(1 - b\rho)^b} . \quad (23)$$

E. Attractive on-site interaction

An additional simple case to calculate is that for an attractive static electron-electron interaction.¹² The attraction leads directly to pair formation and the problem is reduced to placing $\frac{1}{2}N$ pairs on N_A sites with no spin degeneracy. We directly have

$$g = N_A! / (\frac{1}{2}N)! (N_A - \frac{1}{2})! \quad (24)$$

and

$$S(T \rightarrow \infty) \rightarrow - \frac{1}{2}(k/e) \ln[(2 - \rho)/\rho] . \quad (25)$$

Note that this is just what we would get from Heikes formula [Eq. (8)] if we take $\rho' = \frac{1}{2}\rho$ and remember that each electron is one-half the equivalent Heikes particle so the entropy per carrier is one-half.

We have assumed throughout that the transfer matrix element was negligible compared to the temperature. If we neglect the interaction terms, we find that for $t \gg K_B T$ we have only one configuration, the degenerate electron gas, and the resulting thermopower is zero (e.g., for a metal as $T \rightarrow 0$). For $t \ll kT$ we regain the previous calculations.

IV. CONCLUSION

We have calculated the thermoelectric power in the high-temperature saturation limit for a number of different electron-electron interactions, and hence have arrived at a generalization of the Heikes equation. We believe that there has been a great deal of misuse of the Heikes formula [Eq. (8)] both in dealing with doped semiconductors and with narrow-band systems. Although the spin degeneracy of the localized electrons has been pointed out previously in the literature,¹³ many recent papers have continued to neglect this contribution to the thermoelectric power. The true range of direct validity for Eq. (8) is only for electrons in extremely high magnetic fields. We therefore expect that the most useful of the equations we have developed will be those for Fermions with spin [Eq. (10)] and including strong on-site repulsion [Eq. (11)]. These describe the more usual conditions for localized electrons. If we now try to compare some of these

concepts to experimental results, we must look for systems with fairly narrow bandwidths whose thermoelectric power saturates to a constant value as temperature is raised. Of the tetracyanoquinodimethan (TCNQ) compounds it is found that all of the 2:1 complex salts on which there is good data have a thermopower which reaches a constant value of about $-60 \mu\text{V}/\text{K}$. Assuming a charge transfer commensurate with the stoichiometry we have an electron density of $\rho = \frac{1}{2}$ on the TCNQ chains (the cation chains contain only closed-shell electron configurations). Equation (10) for uncorrelated electrons then gives $-(k/e) \ln 3$ or $-90 \mu\text{V}/\text{K}$, whereas Eq. (11) for correlated electrons gives $-60 \mu\text{V}/\text{K}$. We believe this is extremely strong evidence for a sizeable on-site Coulomb interaction in these salts.

In addition, the slight deviations from $-60 \mu\text{V}/\text{K}$ observed in quinolinium-(TCNQ)₂, and several other salts^{1,4} may be analyzed in terms of Eq. (11) to determine the amount of charge transfer and how this differs from the stoichiometry. In the case of Q-(TCNQ)₂ the fit of the high-temperature thermopower implies that $\rho = 0.475$ or 5% of untransferred charge remaining on the quinolinium chains. This is in agreement with the low-temperature "Curie tail" which is seen in susceptibility and appears to be an intrinsic property of the crystal rather than an impurity effect.

In the calculation of the thermoelectric power for the simple Hubbard model in the atomic limit it has previously been noted that for a one-half-filled band ($\rho = 1$) the correct value at all temperatures is zero.⁶ The result of the combinatorial problem de-

rived in the present paper has a divergent thermopower for infinite on-site interaction with $\rho = 1$. The discrepancy comes about in the present case from the complete exclusion of the upper Hubbard band. As ρ approaches unity, the states of energy $U (= \infty)$ have increasing importance. A comment is, therefore, in order as to the range of validity of Eq. (11) as $\rho \rightarrow 1$.

We have assumed throughout this work that the energy-transport term in Eq. (1) [$S^{(2)}/TS^{(1)}$] is small compared to the entropy term (μ/eT). An examination of these two terms in the finite temperature calculation of Ref. 6 shows that the entropy term dominates as $U/T \rightarrow \infty$ as long as $1 - \rho \gg e^{-bU/2}$. When further-neighbor interactions (U_b) are included as in Eq. (23) we find divergencies when $\rho = 1/(b+1)$. Although the thermopower has not been calculated as a function of temperature in these cases we would guess our result to be valid in the limit $[1 - (b+1)\rho] \gg e^{-bU_b/2}$.

The calculations we have done are for a particular Hamiltonian and for one-dimensional electronic systems. However, the general method described in Eqs. (1)-(5) should be appropriate for any system in which the Hamiltonian can be separated into terms much higher or lower than the temperature. The dimensionality restrictions in our calculations appear in the configurations allowed in the computation of the degeneracy. In fact, Eqs. (10), (11), and (25), which only involve on-site interactions, are valid for any number of dimensions. Near-neighbor interactions will not be the same in higher dimensions.

*Research supported by the National Science Foundation through Grant No. GH37250.

¹I. F. Schegolev, Phys. Status Solidi **12**, 9 (1972).

²H. R. Zeller, in *Advances in Solid State Physics*, edited by H. J. Queisser (Pergamon, New York, 1973), Vol. XIII.

³P. M. Chaikin, J. F. Kwak, T. E. Jones, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. **31**, 601 (1973).

⁴J. F. Kwak, G. Beni, and P. M. Chaikin, preceding paper, B **13**, 641 (1975).

⁵A. J. Epstein, S. Etemad, A. F. Garito, and A. J. Heeger, Phys. Rev. B **5**, 952 (1972).

⁶G. Beni, Phys. Rev. B **10**, 2186 (1974).

⁷J. F. Kwak and G. Beni, following paper, B **13**, 652 (1975).

⁸R. Kubo, J. Phys. Soc. Jpn. **12**, 1203 (1957).

⁹I. G. Austin and N. F. Mott, Adv. Phys. **18**, 41 (1969).

¹⁰G. Beni and P. Pincus, Phys. Rev. B **9**, 2963 (1974).

¹¹G. Beni and C. Coll (unpublished).

¹²C. Coll, P. M. Chaikin, and P. Pincus, Solid State Commun. **12**, 1265 (1973).

¹³R. Heikes, *Buhl International Conference on Materials*, edited by E. R. Shatz (Gordon and Breach, New York, 1974).