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Thermoelectric power in half-filled bands*

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We examine the conditions under which a system of interacting electrons exhibits zero thermoelectric power. We show, in particular, that a half-filled-band system described by the one-dimensional Hubbard model has zero thermoelectric power. These results are discussed in relation to the organic charge-transfer salts based on the acceptor molecule TCNQ (tetracyanoquinodimethan).

I. INTRODUCTION

Experimental studies of organic charge-transfer salts have stimulated a substantial theoretical effort to identify the mechanisms primarily responsible for the remarkable properties shown by these materials. In particular, the importance of electron-electron correlations in these systems has been demonstrated experimentally and an attempt has been made to interpret the experimental results for *N*-methylphenazinium-tetracyanoquinodimethan (NMP-TCNQ) on the basis of a one-dimensional Hubbard model.[1] Recent measurements of the thermoelectric power (TEP) of the organic conductor tetrathiofulvalinium-tetracyanoquinodimethan[2] (TTF-TCNQ) have raised new interest in the TEP of many-body systems. The TEP in the fluctuation region above the superconducting transition temperature has been calculated by Maki.[3] Patton and Sham[4] are investigating the TEP near the Peierls transition temperature of a one-dimensional electron-phonon system.

Very recently Bari[5] has considered a one-dimensional system of electrons interacting through a short-range potential and including the coupling of the electrons to a "lattice" described by a set of Einstein oscillators. He calculated the TEP of the system to the lowest order in the electron bandwidth. He found that the TEP vanishes for the case of the half-filled band and speculated that this might be a general property related to the particle-hole symmetry of the half-filled band. We prove below that this is indeed the case.

In Sec. III we show that for a particle-hole symmetric Hamiltonian (the precise meaning of this expression is given in Sec. II) the TEP vanishes identically at all temperatures. This is identical to the behavior of the TEP in an ordinary two-band intrinsic semiconductor. Intuitively this is to be expected, but it is important to establish this result rigorously, since most model Hamiltonians proposed to describe the TCNQ salts are particle-hole symmetric. This is the case, for instance, with the Hubbard Hamiltonian.

As is well known, the Hubbard model has been used to interpret the experimental observations of the charge-transfer salt NMP-TCNQ.[1] The TEP of this salt exhibits a rather interesting temperature dependence.[6] Above 200 K the TEP is small and negative and has a linear temperature dependence with negative slope, suggestive of a metallic system. Below 200 K a change in slope is observed and the electronic contribution appears to decrease sharply. This has been interpreted as due to a transition to a magnetic insulating state. Epstein *et al.*[1] cautioned about this interpretation of the TEP data because of the lack of a detailed transport theory and stressed that related theoretical work would be valuable. This has provided part of the motivation for the present study.

II. PARTICLE-HOLE SYMMETRY

We consider a system of particles described by a Hamiltonian $\mathcal{H}$. In the grand canonical ensemble, appropriate to a system where the average number of particles is given, all thermodynamic averages involve the operator K defined by

$$K = \mathcal{H} - \mu N , \tag{1}$$

where μ is the chemical potential and N is the particle number operator. The thermodynamic average $\langle A \rangle$ of any operator A is given by

$$\langle A \rangle = \mathrm{tr}(\rho A) , \tag{2}$$

where the density operator ρ is defined as

$$\rho = e^{-\beta K} / \mathrm{Tr}\, e^{-\beta K} . \tag{3}$$

If we can find an operator P that commutes with K then it can be shown, using the invariance of the trace under cyclic permutations, that for *any* operator A,

$$\langle A \rangle = \langle PAP^{-1} \rangle . \tag{4}$$

Our method of proof now consists of demonstrating the existence of such an operator P for several model Hamiltonians. Then by use of Eq. (4) we can make definite statements about various thermodynamic averages in systems described by such Hamiltonians.

Without loss of generality, the following discussion is carried out in the site representation. In

this way the application to typical model Hamiltonians describing strongly correlation electrons (e.g., the Hubbard Hamiltonian) will be more transparent. We consider a system of N electrons on a lattice of N_a sites. The electronic Hamiltonian is expressed in terms of operator $C_{i\sigma}^{\dagger}$, $C_{i\sigma}$ which are, respectively, creation and annihilation operators for an electron with spin σ at the ith site. We consider only a single nondegenerate orbital at each site but otherwise the Hamiltonian is left unspecified.

The unitary operator P is defined by its effect on the annihilation operator $C_{j\sigma}$,

$$PC_{j\sigma}P^{-1} = e^{i\phi_j} C_{j\sigma}^{\dagger} , \tag{5}$$

where ϕ_j is a real phase factor which depends on site j. Physically, the operator P interchanges particles and holes. Now if we can choose μ such that P commutes with $K = \mathcal{H} - \mu N$, the symmetry implied by the existence of such an operator P will allow us to make some general statements about the thermodynamic averages and correlation functions in such a system. Assuming we can find such a μ then applying Eq. (4) to the case where A is the number operator $N = \sum_{i,\sigma} n_{i\sigma}$, we find

$$\left\langle \sum_{i,\sigma} n_{i,\sigma} \right\rangle = N_a . \tag{6}$$

Therefore, this choice of μ also ensures that the average number of electrons equals the number of sites in the lattice, i.e., a half-filled band. If we can find such a μ we designate the system as *particle-hole symmetric*.

We can easily show that the half-filled-band nearest-neighbor Hubbard Hamiltonian describes a system which is particle-hole symmetric. The only restriction is to lattices of the alternant type.[7] The Hamiltonian can be written[8]

$$\mathcal{H} = \sum_{\substack{\langle i,j \rangle \\ \sigma}} t_{ij} C_{i\sigma}^{\dagger} C_{j\sigma} + \frac{U}{2} \sum_{i,\sigma} n_{i\sigma} n_{i,-\sigma} , \tag{7}$$

where the sum in the first term is over sites i and j which are nearest-neighbors. From the definition of P it follows that

$$P\left(\sum_{\substack{\langle i,j \rangle \\ \sigma}} t_{ij} C_{i\sigma}^{\dagger} C_{j\sigma} \right) P^{-1} = \sum_{\substack{\langle i,j \rangle \\ \sigma}} t_{ij} C_{i\sigma}^{\dagger} C_{j\sigma} , \tag{8}$$

if we choose the phases such that $\phi_i - \phi_j$ is an odd multiple of π. This condition on the phase differences limits the validity of Eq. (8) to alternant lattices.[9] With this limitation we find

$$P(\mathcal{H} - \mu N)P^{-1} = \mathcal{H} - \mu N , \tag{9a}$$

with

$$\mu = \tfrac{1}{2} U . \tag{9b}$$

Thus for the half-filled-band Hubbard model the chemical potential is $\frac{1}{2} U$ and the system is shown to be particle-hole symmetric.

One can also show (see the Appendix) that for a particle-hole-symmetric system the single-particle density of states is symmetric about the chemical potential.

III. THERMOELECTRIC POWER IN PARTICLE-HOLE SYMMETRIC SYSTEMS

The existence of an operator P which commutes with K implies a relationship between the two-time correlation function of operators A and B. In particular we have

$$\langle A(\tau)B(0) + B(0)A(\tau) \rangle = \langle PA(\tau)B(0)P^{-1} + PB(0)A(\tau)P^{-1} \rangle \tag{10}$$

Using this result we can now proceed to show that the TEP of a particle-hole-symmetric system vanishes. For simplicity we restrict our attention to a linear chain with lattice constant a. The extension to a three-dimensional alternating lattice is straightforward. The thermoelectric power S is written in terms of the Kubo formula for the transport coefficients as[10]

$$S = \frac{-S^{(2)}/S^{(1)} + \mu/e}{T} , \tag{11}$$

where e is the absolute value of the electronic charge and

$$S^{(1)} = \frac{\beta e^2}{2} \int_0^{\infty} \langle VV(\tau) + V(\tau)V \rangle \, d\tau , \tag{12a}$$

$$S^{(2)} = \frac{\beta e}{2} \int_0^{\infty} \langle QV(\tau) + V(\tau)Q \rangle \, d\tau . \tag{12b}$$

Here V and Q are, respectively, the velocity and energy flux operators which can be written in the following manner[11]:

$$\begin{aligned} V &= \lim_{k \to 0} -\frac{1}{\hbar k} \sum_j [n_j, \mathcal{H}] e^{ikaj} , \\ Q &= \lim_{k \to 0} -\frac{1}{\hbar k} \sum_j [h_j, \mathcal{H}] e^{ikaj} , \end{aligned} \tag{13}$$

where h_j is the Hamiltonian density in the site representation and is defined by $\mathcal{H} = \sum_j h_j$. For the Hamiltonian of Eq. (7) we write

$$h_j = \frac{1}{2} \sum_{l,\sigma} t_{jl} (C_{j\sigma}^{\dagger} C_{l\sigma} + C_{l\sigma}^{\dagger} C_{j\sigma}) + U n_{j\uparrow} n_{j\downarrow} .$$

The momentum k is determined by periodic boundary conditions. The time development of the velocity operator is given by

$$V(\tau) = e^{\mathcal{H}\tau} V e^{-\mathcal{H}\tau} = e^{K\tau} V e^{-K\tau} . \tag{14}$$

The second equality follows from the fact that the number operator N commutes with both the velocit operator V and the Hamiltonian $\mathcal{H}$.

From Eqs. (11) and (12) it is clear that the TEP vanishes if

$$\langle QV(\tau)+V(\tau)Q\rangle=\mu\langle VV(\tau)+V(\tau)V\rangle\ . \tag{15}$$

By using the transformation properties of V and Q under the operator P,

$$PVP^{-1}=-V, \tag{16a}$$

$$PQP^{-1}=Q-2\mu V\ , \tag{16b}$$

in combination with Eq. (10), the validity of Eq. (15) can be established and the proof is completed.[12]

IV. DISCUSSION AND CONCLUSION

The study presented in this paper clarifies some aspects of the transport mechanism in high-correlated solids. The established vanishing of the TEP for particle-hole-symmetric systems has implications for understanding the physics of charge-transfer salts. It follows that the behavior of the TEP of salts such as NMP-TCNQ cannot be explained within the context of a half-filled Hubbard model with electron transfer restricted to nearest-neighbor sites.[13] This does not necessarily imply a rejection of the application of the Hubbard model to NMP-TCNQ. On the contrary, our results may indicate how the Hubbard model should be modified in order to account for the experimental behavior of the TEP of NMP-TCNQ. In fact it can be shown[14] that the nearly half-filled narrow-band Hubbard chain exhibits a TEP qualitatively similar to that observed in NMP-TCNQ.

We have investigated the particle-hole symmetry of systems described by a modified Hubbard Hamiltonian. If we augment the Hubbard Hamiltonian to include Coulomb interaction between neighboring sites by means of a term[15]

$$\mathcal{H}'=\frac{1}{2}\sum_{\substack{i,j\\ \sigma,\sigma'}} V_{ij}n_{i,\sigma}n_{j,\sigma'}\ . \tag{17}$$

the particle-hole symmetry is maintained for the half-filled band with the chemical potential given by

$$\mu=\frac{U}{2}+\sum_j V_{ij}\ . \tag{18}$$

Thus the TEP vanishes for this augmented Hubbard model. The TEP also vanishes for the half-filled band if we include a term in the Hamiltonian corresponding to an exchange interaction between electrons on different sites.

The particle-hole symmetry of the half-filled band is not necessarily destroyed by including the coupling of the electrons to the lattice vibrations. Using the results shown above one can prove that the TEP of the system vanishes if this electron-lattice coupling is described by the Hubbard-Holstein Hamiltonian[5,16]

$$\mathcal{H}=\sum_{\substack{\langle i,j\rangle\\ \sigma}} t_{ij}C_{i\sigma}^{\dagger}C_{j\sigma}+\frac{U}{2}\sum_{i,\sigma}n_{i\sigma}n_{i,-\sigma}+\sum_i\left(\frac{p_i^2}{2m}+\frac{m\omega^2}{2}x_i^2\right)-B\sum_{i,\sigma}x_i n_{i\sigma}\ , \tag{19}$$

where x_i and p_i are the coordinates and moments of a set of Einstein oscillators and the last term describes the coupling between the electrons and the oscillators. However, if one allows for "phonon" modulation of the on-site Coulomb interaction by means of a coupling term[17]

$$\mathcal{H}'=-A\sum_{i,\sigma}x_i n_{i\sigma}n_{i,-\sigma}\ , \tag{20}$$

the particle-hole symmetry is destroyed and thus one expects a nonzero TEP. Even in the atomic limit one cannot find an operator P which commutes with $\mathcal{H}-\mu N$ *and* satisfies Eq. (5). This is consistent with the result of Pincus[17] who showed that the electron and hole bands are not symmetric in this case. Finally, we mention that the effect on the TEP due to coupling to the lattice is being studied independently by Bari for a narrow-band Mott semiconductor in the nearly half-filled case. This should add further insight into this fascinating problem.

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APPENDIX

The single-particle spectral weight function $A_{ij}^{\sigma}(\omega)$ is defined[18] as

$$A_{ij}^{\sigma}(\omega)=\int_{-\infty}^{\infty}dt\,e^{i\omega t}\,\langle\{C_{i\sigma}(t),\ C_{j\sigma}(0)\}\rangle\ , \tag{A1}$$

where $C_{i\sigma}(t)=e^{i\mathcal{H}t}\,C_{i\sigma}\,e^{-i\mathcal{H}t}$. If we note that the number operator N commutes with the Hamiltonian we can write

$$C_{i\sigma}(t)=e^{-i\mu t}\,e^{i(\mathcal{H}-\mu N)t}\,C_{i\sigma}\,e^{-i(\mathcal{H}-\mu N)t}\ . \tag{A2}$$

Using this equation and the fact that for particle-hole symmetric systems there exists an operator P [defined in Eq. (5)] which commutes with $\mathcal{H}-\mu N$, we can show that

$$P\,e^{i\mathcal{H}t}\,C_{i\sigma}\,e^{-i\mathcal{H}t}\,C_{i\sigma}^{\dagger}P^{-1}=e^{-2i\mu t}\,e^{i\mathcal{H}t}\,C_{i\sigma}^{\dagger}\,e^{-i\mathcal{H}t}\,C_{i\sigma}\ . \tag{A3}$$

We can then rewrite Eq. (A1), for $i=j$, as

$$A_{ii}^{\sigma}(\omega)=\int_{-\infty}^{\infty}dt\,e^{i(\omega-\mu)t}\,[e^{-i\mu t}\,\langle C_{i\sigma}^{\dagger}(0)\,C_{i\sigma}(-t)\rangle+e^{i\mu t}\langle C_{i\sigma}^{\dagger}(0)\,C_{i\sigma}(t)\rangle]\ . \tag{A4}$$

Note that the term in the brackets is an even function of t. This implies that the single-particle density of state $\rho_\sigma(\omega) = (1/2\pi)A^\sigma_{ii}(\omega)$ is an even function of $(\omega - \mu)$.

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