PHYSICAL REVIEW B VOLUME 21, NUMBER 10 15 MAY 1980

Mott's formula for the thermopower and the Wiedemann-Franz law

M. Jonson* and G. D. Mahan
Physics Department, Indiana University, Bloomington, Indiana 47405

(Received 13 June 1979)

The Mott formula for the thermopower, $S=(\pi^2/3)(k_B^2T/e)\sigma'/\sigma$, and the Wiedemann-Franz law, $K/\sigma T=(k_B/e)^2(\pi^2/3)$, are shown to be exact for independent electrons interacting with static impurities and phonons treated in the adiabatic approximation. This is true irrespective of the interaction strength. These results are derived using a Green's-function technique that emphasizes the importance of corrections to the free-electron heat current operator. These corrections have frequently been neglected in the past. The Green's-function technique is well suited for going beyond the adiabatic phonon approximation, and the implications of doing so are briefly discussed.

I. INTRODUCTION

It has been known for some time that for a system of independent electrons interacting with static scatterers, the Mott formula[1] for the thermoelectric power S,

$$S=\frac{\pi^2}{3}\left(\frac{k_B^2T}{e}\right)\left(\frac{d\ln\sigma(\epsilon)}{d\epsilon}\right)_{\epsilon=0} \tag{1}$$

and

$$\sigma=\int_{-\infty}^{\infty}d\epsilon\left(-\frac{\partial n_F}{\partial\epsilon}\right)\sigma(\epsilon)\,, \tag{2}$$

is exact for arbitrary values of the interaction strength. It is also known that the Wiedemann-Franz law,[2] which relates the electrical conductivity σ to the (electronic part of the) thermal conductivity K by the relation

$$K/\sigma T=(k_B/e)^2(\pi^2/3)\,, \tag{3}$$

is exact for the same system.

These exact results were first derived by Chester and Thellung[3] using a wave-function formulation of quantum mechanics. The purpose of this note is to rederive Eqs. (1) and (3) using a Green's-function technique. The motivation for this is mainly pedagogical. However, the present derivation also serves to emphasize the importance of letting the various interactions modify the free-electron form of the heat current operator. This point has frequently been overlooked in the past. A further merit of the Green's-function technique is that it provides a basis for treating electrons interacting with time dependent objects such as phonons. In this case Eqs. (1) and (3) are not exact; no similar exact results have been found, but based on the results of the present approach certain general conclusions can be drawn.

II. dc TRANSPORT COEFFICIENTS

Transport coefficients like the electrical conductivity σ, the thermoelectric power S, and the thermal conductivity K are related to response functions $L_{\alpha\beta}^{ij}$, where[4]

$$\vec{j}_\alpha=L_{\alpha\beta}^{11}[-(1/T)\nabla_\beta(\mu+eV)]+L_{\alpha\beta}^{12}\nabla_\beta(1/T)\,, \tag{4}$$

$$\vec{j}_{Q,\alpha}=L_{\alpha\beta}^{21}[-(1/T)\nabla_\beta(\mu+eV)]+L_{\alpha\beta}^{22}\nabla_\beta(1/T)\,. \tag{5}$$

There $\vec{j}_\alpha(\vec{j}_{Q,\alpha})$ is the α component of the electrical (thermal) current, μ is the chemical potential, and V is an electrostatic potential. The response functions $L_{\alpha\beta}^{ij}$ (which are diagonal in $\alpha\beta$ for isotropic systems) are given by Kubo formulas, which in the Matsubara notation take the form[4]

$$L^{ij}(i\omega)=-\frac{iT}{(i\omega)d\Omega}\int_0^\beta d\tau\, e^{i\omega\tau}\langle T_\tau\vec{j}_i(\tau)\cdot\vec{j}_j(0)\rangle\,, \tag{6}$$

where d is the dimensionality and Ω is the volume of the system, $\beta=1/k_BT$, and T_τ indicates an ordering of the current operators with respect to the complex "time" τ. The retarded response functions that determine the transport coefficients are obtained from $L^{ij}(i\omega)$ by the analytical continuation $i\omega\to\omega+i\delta$.

From Eqs. (4) and (5) one finds that if the chemical potential is constant,

$$\sigma=e^2L^{11}/T\,, \tag{7}$$

$$S\equiv-\frac{\Delta V}{\Delta T}=\frac{1}{eT}\frac{L^{12}}{L^{11}}\,, \tag{8}$$

and

$$K=\frac{1}{T^2}\left(L^{22}-\frac{L^{12}L^{21}}{L^{11}}\right). \tag{9}$$

Using Eqs. (7) and (9) we can furthermore define L, the Lorenz number, as

$$L=\frac{K}{\sigma T}=\frac{1}{e^2T^2}\frac{(L^{11}L^{22}-L^{12}L^{21})}{(L^{11})^2}\,. \tag{10}$$

[In Eqs. (7)–(10), $L^{ij} \equiv \lim_{\omega\to 0} \mathrm{Re} L^{ij}(\omega + i\delta)$.] For many metals L is approximately a constant, and we shall now proceed to show that in fact $L = \frac{1}{3}\pi^2 \times (k_B/e)^2$ for a model system of independent electrons interacting with static impurities and phonons treated in the adiabatic (static) approximation. We shall also show that the Mott formula [Eq. (1)] holds for the same model system. The first step will be to derive the current operators that appear in Eq. (6). This will be done in the next section.

III. THE ENERGY CURRENT AND THE ADIABATIC PHONON APPROXIMATION

In order to calculate the response functions L^{ij} of Eq. (6) we have to find the proper expressions for the particle current $\vec{j}$ and the energy current $\vec{j}_E$, the latter being related to the heat current $\vec{j}_Q$ by the simple formula

$$\vec{j}_q = \vec{j}_E - \mu \vec{j}\,, \tag{11}$$

where μ is the chemical potential.

We shall consider a many-body system of independent electrons interacting with static impurities and phonons as described by the Hamiltonian

$$H = \sum_k \epsilon_k c_k^\dagger c_k + \frac{1}{\Omega} \sum_q V^{\mathrm{imp}}(q) \rho^{\mathrm{imp}}(q) + \sum_{q\lambda} W_\lambda(q) Q_\lambda(q) \rho(q)\,, \tag{12}$$

where $\rho(q)$ is the electron density operator, $W_\lambda(q)$ is the electron-phonon interaction, and $Q_\lambda(q)$ is the phonon displacement operator

$$Q_\lambda(q) = (2M\omega_{\lambda_q})^{-1/2} (a_{\lambda_q} + a^\dagger_{\lambda,-q})\,. \tag{13}$$

The particle current operator corresponding to Eq. (12) is just

$$\vec{j} = \sum_k \vec{v}_k c_k^\dagger c_k\,, \tag{14}$$

where $\vec{v}_k \equiv \vec{k}/m$ is the velocity. The energy current operator is nontrivial but is readily derived for instance by choosing a real-space representation for the Hamiltonian of Eq. (12)

$$H = \sum_{i\delta} t_\delta c^\dagger_{i+\delta} c_i + \sum_{ij} V^{\mathrm{imp}}_{ij} n^{\mathrm{imp}}_j n_i + \sum_{ij\lambda} W^\lambda_{ij} Q^\lambda_j n_i\,, \tag{15}$$

where

$$c_i^\dagger = \frac{1}{\sqrt{N}} \sum_k e^{i\vec{k}\cdot\vec{R}_i} c_k^\dagger\,,$$

$$t_\delta = \sum_k \epsilon_k e^{-i\vec{k}\cdot\vec{\delta}}\,,$$

and V^{imp}_{ij}, n^{imp}_j, W^λ_{ij}, and Q^λ_j are related to the respective Fourier components in Eq. (12) in the usual way.

The energy current is now found as the time derivative of an energy position operator $\vec{R}$ (Ref. 5):

$$\vec{R} = \sum_i \vec{R}_i h_i\,, \quad H = \sum_i h_i\,, \tag{16}$$

$$\vec{j}_E = \dot{\vec{R}} = -i[\vec{R}, H] = -i \sum_{ij} \vec{R}_i [h_i, h_j]\,, \tag{17}$$

with an obvious definition of h_i. On performing the commutation operations implied by Eq. (17) and transforming back to the Fourier-space representation one finds that[6] (noting that $\vec{v}_k = \nabla_k \epsilon_k = i\sum_\delta \vec{\delta} t_\delta e^{i\vec{k}\cdot\vec{\delta}}$)

$$\vec{j}_E = \sum_k \epsilon_k \vec{v}_k c_k^\dagger c_k + \frac{1}{\Omega} \sum_q V^{\mathrm{imp}}(q) \rho^{\mathrm{imp}}(q) \vec{j}(q) + \sum_{q\lambda} W_\lambda(q) Q_\lambda(q) \vec{j}(q) - \frac{i}{M} \sum_{q\lambda} [\nabla_q W_\lambda(q)] P_\lambda(q) \rho(q)\,, \tag{18}$$

where

$$\vec{j}(q) = \sum_k (\vec{v}_k + \vec{v}_q/2) c^\dagger_{k+q} c_k \tag{19}$$

and

$$P_\lambda(q) = M\dot{Q}_\lambda(q) = -i(M\omega_{\lambda_q}/2)^{1/2} (a_{\lambda,-q} - a^\dagger_{\lambda_q}) \tag{20}$$

is the phonon momentum operator.

We note that the first term of Eq. (18) is the energy current of free electrons while the last three terms represent corrections due to the interactions between the electrons and static impurities and phonons, respectively. As we shall see, these correction terms are important and in particular retaining them (in a form consistent with the adiabatic phonon approximation) is essential to proving the Mott formula and the Wiedemann-Franz law.

The electron-phonon interaction makes the evaluation of the response functions $L^{ij}(i\omega)$ difficult. This is because of the dynamics, i.e., the time dependence of the phonons. However, in the so-called adiabatic phonon approximation we can find formally exact results for $L^{ij}(i\omega)$. Consider systems of high conductivity, like most metals. In such a system an electron quickly travels past any particular ion; i.e., the time spent in the vicinity of any ion is small compared to a typical period of ion (phonon) vibration, so that the electron sees essentially static, displaced ions. It is then tempting to neglect the time dependence of the phonons altogether. This is known as the adiabatic or static phonon approximation and it makes the phonon momentum operator $P_\lambda(q)$ in Eq. (18) zero while $W_\lambda(q)Q_\lambda(q)$ of Eqs. (12) and (18) acts like a random static potential that adds to the impurity potential. The electrons see a total static potential $U(q)$, where

$$U(q)=\frac{1}{\Omega}V^{\text{imp}}(q)\rho^{\text{imp}}(q)+\sum_\lambda W_\lambda(q)Q_\lambda^{\text{ad}}(q)\,. \tag{21}$$

We shall proceed in the next section to calculate the response functions L^{ij} in this approximation and postpone a discussion of its validity to Sec. V.

IV. EVALUATION OF THE RESPONSE FUNCTIONS L^{ij}

We start by considering the response function L^{11} which is related to the conductivity by Eq. (7). On combining Eqs. (6) and (14) one finds that

$$L^{11}(i\omega)=-\frac{iT}{(i\omega)d\Omega}\int_0^\beta d\tau\, e^{i\omega\tau}\times\sum_{kk'}\vec{v}_k\cdot\vec{v}_{k'}\times\langle T_\tau c_k^\dagger(\tau)c_k(\tau)c_{k'}^\dagger(0)c_{k'}(0)\rangle\,. \tag{22}$$

In the adiabatic phonon approximation the Hamiltonian [Eq. (12)] is quadratic in the electron operators while the phonon operators can be treated as c numbers. This means that the Hamiltonian can in principle be diagonalized and Wick's theorem can be applied to Eq. (22) (Ref. 7) where the statistical average $\langle c_k^\dagger(\tau)c_k(\tau)c_{k'}^\dagger(0)c_{k'}(0)\rangle$ then can be expressed as a sum of contractions so that

$$L^{11}(i\omega)=-\frac{iT}{(i\omega)d\Omega}\sum_{kk'}\vec{v}_k\cdot\vec{v}_{k'}\left(\langle n_k\rangle\langle n_{k'}\rangle\,\delta(i\omega)-\frac{1}{\beta}\sum_{ip}\mathcal{G}_{kk'}(ip+iw)\mathcal{G}_{k'k}(ip)\right), \tag{23}$$

where the off-diagonal temperature Green's function $\mathcal{G}_{kk'}(ip)$ are defined as

$$\mathcal{G}_{kk'}(ip)=\int_0^\beta d\tau\, e^{ip\tau}\mathcal{G}_{kk'}(\tau)\quad \mathcal{G}_{kk'}(\tau)=-\langle T_\tau c_k(\tau)c_{k'}(0)\rangle\,.$$

The first term of Eq. (23) does not contribute to $L^{11}\equiv\operatorname{Re}L^{11}(\omega+i\delta)$ and will therefore be omitted. In the second term we have used off-diagonal Green's functions. We may instead introduce a vertex function Λ_k, where

$$\sum_{k'}\vec{v}_{k'}\mathcal{G}_{kk'}(ip+i\omega)\mathcal{G}_{k'k}(ip)=\mathcal{G}_k(ip+i\omega)\mathcal{G}_k(ip)\vec{\Lambda}_k(ip+i\omega,ip)\,. \tag{24}$$

The vertex function will obey an integral equation

$$\vec{\Lambda}_k(ip,ip+i\omega)=\vec{v}_k+\frac{1}{\Omega}\sum_{k'}W_{kk'}(ip,ip+i\omega)\mathcal{G}_{k'}(ip)\mathcal{G}_{k'}(ip+i\omega)\vec{\Lambda}_{k'}(ip,ip+i\omega)\,, \tag{25}$$

where $W_{kk'}$ is a generalized scattering function. The Matsubara sum over ip in Eq. (24) can now be performed to give the following result (see Appendix):

$$\sigma=\frac{e^2}{T}L^{11}\equiv\int_{-\infty}^{\infty}d\epsilon\left(-\frac{\partial n_F}{\partial\epsilon}\right)\sigma(\epsilon)\,, \tag{26}$$

$$\sigma(\epsilon)=\frac{e^2}{2\pi}\sum_k\vec{v}_k\left\{\frac{A_k(\epsilon)}{2\Gamma_k(\epsilon)}\vec{\Lambda}_k(\epsilon-i\delta,\epsilon+i\delta)-\operatorname{Re}\left[\mathcal{G}_k(\epsilon-i\delta)^2\left(\vec{v}_k+\frac{1}{m}\nabla_k\Sigma_k(\epsilon-i\delta)\right)\right]\right\}, \tag{27}$$

where A_k is the electron spectral function, Σ_k is the electron self-energy, and $-\Gamma_k$ is its imaginary part.

Equation (27) together with Eq. (25) constitute a formally exact result and was first obtained by Langer.[8] An actual calculation without retreating to some approximation scheme or other would be a formidable but at least, in principle, a doable task.

In order to calculate the next response function L^{12}, we need the heat current. This can be written as

$$\vec{j}_Q=\sum_k\vec{v}_k\xi_k c_k^\dagger c_k+\sum_q U(q)\vec{j}(q)\,, \tag{28}$$

with $\xi_k=\epsilon_k-\mu$ and $U(q)$ given by Eq. (21). One finds then that

$$L^{12}(i\omega)=\frac{iT}{(i\omega)\Omega d}\frac{1}{\beta}\sum_{ip}\sum_{kk'}\left(\vec{v}_k\xi_k\vec{v}_{k'}\mathcal{G}_{kk'}(ip+i\omega)\mathcal{G}_{kk'}(ip)+\sum_q U(q)(\vec{v}_k+\vec{v}_q/2)\cdot\vec{v}_{k'}\mathcal{G}_{kk'}(ip+i\omega)\mathcal{G}_{k',k+q}(ip)\right), \tag{29}$$

where we have followed the same steps that lead to Eq. (23) for $L^{11}(i\omega)$. We want to turn Eq. (29) around so that it contains a factor like ip, the energy variable, rather than ξ_k, the free-electron energy of a state of momentum $\vec{k}$. To achieve this we shall use the Dyson equation for the off-diagonal Green's function $\mathcal{G}_{kk'}$. The Dyson equation can be stated in two different but equivalent forms,

$$\mathcal{G}_{kk'}(ip) = \mathcal{G}_k^0(ip)\delta_{k,k'} + \mathcal{G}_k^0(ip)\sum_q U(q)\mathcal{G}_{k-q,k'}(ip) \tag{30}$$

and

$$\mathcal{G}_{k'k}(ip) = \mathcal{G}_k^0(ip)\delta_{k,k'} + \mathcal{G}_k^0(ip)\sum_q U(q)\mathcal{G}_{k',k+q}(ip)\,, \tag{31}$$

where

$$\mathcal{G}_k^0(ip) = 1/(ip - \xi_k) \qquad\qquad (32$$

is the free-electron Green's function. If we write the factor $\vec{v}_k + \vec{v}_q/2$ that appears in the second term of Eq. (29) as $\frac{1}{2}\vec{v}_k + \frac{1}{2}(\vec{v}_k + \vec{v}_q)$ and make the variable substitution $\vec{k} \to \vec{k} - \vec{q}$ in the part that will now be multiplied by $\frac{1}{2}(\vec{v}_k + \vec{v}_q)$ we find that the last term of Eq. (29) can be written as

$$\tfrac{1}{2}\vec{v}_k \cdot \vec{v}_{k'} \sum_q U(q)[\mathcal{G}_{k,k'}(ip + i\omega)\mathcal{G}_{k',k+q}(ip) + \mathcal{G}_{k-q,k'}(ip + i\omega)\mathcal{G}_{k',k}(ip)]\,. \tag{33}$$

After this rearrangement we can use the Dyson equations (30) and (31) to solve for $\Sigma_q U(q)\mathcal{G}_{k',k+q}$ and $\Sigma_q U(q)\mathcal{G}_{k-q,k'}$ so that

$$L^{12}(i\omega) = \frac{iT}{(i\omega)\Omega d}\,\frac{1}{\beta}\sum_{ip}\left(\sum_{kk'}\,[\tfrac{1}{2}(ip) + \tfrac{1}{2}(ip + i\omega)]\vec{v}_k \cdot \vec{v}_{k'}\mathcal{G}_{kk'}(ip + i)\mathcal{G}_{k'k}(ip) - \tfrac{1}{2}\sum_k v_k^2\,[\mathcal{G}_k(ip + i\omega) + \mathcal{G}_k(ip)]\right)\,, \tag{34}$$

where we have used Eq. (32). Performing the Matsubara sum over frequency in the last term of Eq. (34) gives

$$\frac{iT}{(i\omega)\Omega d}\sum_k v_k^2 \int_{-\infty}^{\infty}\frac{d\epsilon}{2\pi}\,n_F(\epsilon)A_k(\epsilon)\,,$$

which does not contribute to $\mathrm{Re}L^{12}(\omega + i\delta)$. We are left with a final result for $L^{12}(i\omega)$ that looks very much like Eq. (23) for L^{11} except for the energy factor $\frac{1}{2}ip + \frac{1}{2}(ip + i\omega)$! Indeed, performing the Matsubara sum allows us to state the following result:

$$\frac{e^2}{T}L^{12} = \int_{-\infty}^{\infty} d\epsilon\left(-\frac{\partial n_F}{\partial \epsilon}\right)\epsilon\sigma(\epsilon)\,, \tag{35}$$

where $\sigma(\epsilon)$ is given by Eq. (27) and an extra factor of ϵ appears relative to Eq. (26) for L^{11}.

Finally we need to calculate $L^{22}(i\omega)$. We can draw on our previous results by decomposing the heat current into a kinetic energy part $j_{Q,\mathrm{KE}}$ and a potential energy part $j_{Q,\mathrm{PE}}$ corresponding to the two terms of Eq. (28). This decomposition allows us to write

$$\begin{aligned}L^{22}(i\omega) = -\frac{iT}{(i\omega)\Omega d}\int_0^\beta d\tau\, e^{i\omega\tau}[\langle T_\tau\vec{j}_{Q,\mathrm{KE}}(\tau)\cdot\vec{j}_{Q,\mathrm{KE}}(0)\rangle + \langle T_\tau\vec{j}_{Q,\mathrm{KE}}(\tau)\cdot\vec{j}_{E,\mathrm{PE}}(0)\rangle \\ + \langle T_\tau\vec{j}_{Q,\mathrm{PE}}(\tau)\cdot\vec{j}_{Q,\mathrm{KE}}(0)\rangle + \langle T_\tau\vec{j}_{Q,\mathrm{PE}}(\tau)\cdot\vec{j}_{Q,\mathrm{PE}}(0)\rangle]\,.\end{aligned} \tag{36}$$

On inspection we realize that the first term of Eq. (36) will be given by Eq. (23) for $L^{11}(i\omega)$ except for an additional factor of $\xi_k\xi_{k'}$ coming from the difference in $\vec{j}_{Q,\mathrm{KE}}$ and $\vec{j}$. Furthermore the second and third terms will by given by Eq. (34) for $L^{12}(i\omega)$ except for an additional factor of $\xi_{k'}$. We are then left with the last term of Eq. (36) which we denote by $L_4^{22}(i\omega)$, where

$$L_4^{22}(i\omega) = \frac{iT}{(i\omega)\Omega d}\sum_{kk'}\sum_{qq'} U(q)U(q')[\tfrac{1}{2}\vec{v}_k + \tfrac{1}{2}(\vec{v}_k + \vec{v}_q)]\cdot[\tfrac{1}{2}\vec{v}_{k'} + \tfrac{1}{2}(\vec{v}_{k'} + \vec{v}_{q'})]\,\frac{1}{\beta}\sum_{ip}\mathcal{G}_{k,k'+q'}(ip + i\omega)\mathcal{G}_{k',k+q}(ip)\,. \tag{37}$$

If we expand the square brackets

$$[\tfrac{1}{2}\vec{v}_k+\tfrac{1}{2}(\vec{v}_k+\vec{v}_q)]\cdot[\vec{v}_{k'}+\tfrac{1}{2}(\vec{v}_{k'}+\vec{v}_{q'})]=\tfrac{1}{4}\vec{v}_k\cdot\vec{v}_{k'}+\tfrac{1}{4}\vec{v}_k\cdot(\vec{v}_{k'}+\vec{v}_{q'})+\tfrac{1}{4}(\vec{v}_k+\vec{v}_q)\cdot\vec{v}_{k'}+\tfrac{1}{4}(\vec{v}_k+\vec{v}_q)\cdot(\vec{v}_{k'}+\vec{v}_{q'})$$

and make variable transformations so that all four terms that arise contain the factor $\frac{1}{4}\vec{v}_k\cdot\vec{v}_{k'}$, Eq. (37) takes the form

$$\begin{aligned}L_4^{22}(i\omega)=\frac{iT}{(i\omega)\Omega d}\sum_{kk'}\sum_{qq'}U(q)U(q')\tfrac{1}{4}\vec{v}_{k'}\cdot\vec{v}_{k'}\\ \times\frac{1}{\beta}\sum_{ip}[\mathcal{G}_{k,k'+q'}(ip+i\omega)\mathcal{G}_{k',k+q}(ip)+\mathcal{G}_{k-q,k'+q'}(ip+i\omega)\mathcal{G}_{k',k}(ip)\\ +\mathcal{G}_{k,k'}(ip+i\omega)\mathcal{G}_{k'-q',k+q}(ip)+\mathcal{G}_{k-q,k'}(ip+i\omega)\mathcal{G}_{k'-q',k}(ip)].\end{aligned}\tag{38}$$

Repeated use of the Dysons equations [Eqs. (30) and (31)], Eq. (32), and relabeling of dummy indices enables us to rewrite this as

$$\begin{aligned}L_4^{22}(i\omega)=\frac{iT}{(i\omega)\Omega d}\sum_{kk'}\vec{v}_k\cdot\vec{v}_{k'}\,\frac{1}{\beta}\sum_{ip}\{[\tfrac{1}{2}(ip-\xi_k)+\tfrac{1}{2}(ip+i\omega-\xi_k)][\tfrac{1}{2}(ip-\xi_{k'})+\tfrac{1}{2}(ip+i\omega-\xi_{k'})]\\ \times\mathcal{G}_{kk'}(ip+i\omega)\mathcal{G}_{k'k}(ip)+2(ip-\xi_k)\mathcal{G}_k(ip)\delta_{k,k'}+\cdots\},\end{aligned}\tag{39}$$

where the ellipsis represents purely real constants.

On performing the Matsubara sums, the second term of Eq. (39) gives a contribution

$$\frac{iT}{(i\omega)\Omega d}\sum_k v_k^2\int_{-\infty}^{\infty}\frac{d\epsilon}{2\pi}n_F(\epsilon)(\epsilon-\xi_k)A_k(\epsilon)$$

which does not contribute to $\mathrm{Re}L^{22}(\omega+i\delta)$. We can now combine all four contributions of Eq. (36) to $L^{22}(i\omega)$ to get

$$L^{22}(i\omega)=\frac{iT}{(i\omega)\Omega d}\sum_{kk'}\vec{v}_k\cdot\vec{v}_{k'}\,\frac{1}{\beta}\sum_{ip}[\tfrac{1}{2}ip+\tfrac{1}{2}(ip+i\omega)]^2\mathcal{G}_{kk'}(ip+i\omega)\mathcal{G}_{k'k}(ip).\tag{40}$$

This, again, looks much like Eq. (23) for L^{11} except for the factor $[\frac{1}{2}ip+\frac{1}{2}(ip+i\omega)]^2$. After performing the Matsubara sum we obtain

$$\frac{e^2}{T}L^{22}=\int_{-\infty}^{\infty}d\epsilon\left(-\frac{\partial n_F}{\partial\epsilon}\right)\epsilon^2\sigma(\epsilon),\tag{41}$$

with $\sigma(\epsilon)$ given by Eq. (27) and two factors of the energy variable appearing.

To derive the Mott formula [Eq. (1)] and the Wiedemann-Franz law [Eq. (3)] from the above results for $L^{11}, L^{12}, L^{21}=L^{12}$, and L^{22} we use the Sommerfeld expansion[9]

$$\int_{-\infty}^{\infty}d\epsilon\left(-\frac{\partial n_F}{\partial\epsilon}\right)\epsilon^n\sigma(\epsilon)\cong\sigma(0)\delta_{n,0}+\frac{\pi^2}{6}(k_BT)^2[n(n-1)\epsilon^{n-2}\sigma(\epsilon)+2n\epsilon^{n-1}\sigma'(\epsilon)+\epsilon^n\sigma''(\epsilon)]_{\epsilon=0}.\tag{42}$$

Using Eq. (42) in conjunction with Eqs. (35) and (41), we find that

$$L^{12}=\frac{T}{e^2}\frac{\pi^2}{3}(k_BT)^2\sigma'(0)$$

and

$$L^{22}=\frac{T}{e^2}\frac{\pi^2}{3}(k_BT)^2\sigma(0).$$

Finally the Mott formula [Eq. (1)] follows from Eq. (8) and the Wiedemann Franz law from Eq. (10) with $L=(\pi^2/3)(k_B/e)^2$.

The exact evaluation of the correlation functions L^{11}, L^{12}, and L^{22} shows that they differ only by the additional factors of ϵ and ϵ^2 in the integral over $d\epsilon$. In Green's-function language, the particle is assigned a wave vector $\vec{k}$ and an energy ϵ, and the Green's functions $\mathcal{G}(k,\epsilon)$ provides the relationship between them. Thus we associate ϵ as the energy variable of the thermal currents. The correlation function L^{12} has one factor of the heat current, and has one power of ϵ; L^{22} has two factors of the energy current, and has two powers of ϵ. This is an intuitively reasonable result, that each factor of the energy current merely adds another power of the energy variable to the integrand. This exact result can only be found by including all of the terms in the energy current when it is expressed in wave-vector notation as in (18).

V. CONCLUSIONS

We have shown that the Mott formula for the thermopower and Wiedemann-Franz law are exact for a system of independent electrons interacting with static impurities and adiabatic (static) phonons. Those exact results were derived using a Green's-function technique, and we emphasize again that it is important to use a heat current operator that is consistent with the Hamiltonian that describes the system. Any interaction term in the Hamiltonian will be reflected in the heat current operator.

The adiabatic phonon approximation is adequate in some situations but dubious in others. This can be illustrated from the form of the electron-phonon self-energy.

$$\Sigma_k^{\text{el-ph}}(\epsilon)=\int\frac{d^3q}{(2\pi)^3}\sum_\lambda|M_\lambda(q)|^2\left(\frac{1-n_F(\xi_{k+q})+n_B(\omega_{\lambda q})}{\epsilon-\xi_{k+q}-\omega_{\lambda q}+i\delta}+\frac{n_F(\xi_{k+q})+n_B(\omega_{\lambda q})}{\epsilon-\xi_{k+q}+\omega_{\lambda q}+i\delta}\right). \tag{43}$$

Neglecting the time dependence of the phonons, i.e., making the adiabatic phonon approximation, amounts to dropping the phonon frequencies $\omega_{\lambda q}$ from the denominators of Eq. (43) in which case

$$\Sigma_k^{\text{el-ph}}(\epsilon)\to\int\frac{d^3q}{(2\pi)^3}\sum_\lambda|M_\lambda(q)|^2\frac{2n_B(\omega_{\lambda q})+1}{\epsilon-\xi_{k+q}+i\delta}, \tag{44}$$

i.e., the Fermi factors n_F cancel. As the phonon frequencies are small this is a reasonable approximation for the electron-phonon energy itself. However, it makes an important difference in the energy derivative as the Fermi factors make

$$\frac{d}{d\epsilon}\Sigma_k^{\text{el-ph}}\sim\Sigma^{\text{el-ph}}/\omega_D, \tag{45}$$

whereas in the adiabatic approximation

$$\frac{d}{d\epsilon}\Sigma_k^{\text{el-ph}}\sim\Sigma^{\text{el-ph}}/E_F, \tag{46}$$

where ω_D and E_F are the Debye and Fermi energies, respectively.

The result of Eq. (45) is of order 1 and leads to the large electron-phonon mass enhancement. Noting that the Mott formula contains an energy derivative, it is reasonable to assume that the adiabatic approximation is poor for the thermopower and that this transport coefficient is affected by the electron-phonon mass enhancement. This question has been a subject of recent controversy.[10]

Jonson and Girvin[11] have found that the electrical conductivity of a model tight-binding system was adequately given by the adiabatic approximation provided the conductivity was well above the limit where Anderson localization occurs. The same should be true for the thermal conductivity as neither K nor σ, in contrast to the thermopower, depend on variation of electron properties around the Fermi level. The Wiedemann-Franz law might therefore hold to a good approximation even when the dynamics of the phonons is retained. This is indeed true for many metals at and above room temperature[12] where the energy change in inelastic electron-phonon collisions is small compared to k_BT.[13] For lower temperatures the Lorenz number becomes temperature dependent and the adiabatic approximation breaks down.

Finally we would like to add a comment on the numerical importance of retaining the correct energy current operator. Clearly, for good metals, where the static impurity potential can be treated as a small perturbation, the Boltzmann equation is valid and the correction to the energy current operator has only subsidiary numerical importance (being of order Γ/E_F).[10] Recently, however, there has been a considerable interest in poorly conducting metals. This is partly due to their interesting transport properties, such as the anomalous thermoelectric power of some metallic glasses reported by Nagel.[14] For these strongly disordered metals (their residual resistivity may be as high as 200 μohm cm) it appears to be essential to go beyond perturbation theory in treating the static impurity scattering.[11] In fact, in order to explain the negative temperature coefficient of resistivity observed in many of these metals it seems necessary to go beyond the Boltzmann equation formalism.[15] In this context we believe the present results, which have been proved valid for arbitrary interaction strength, to be useful. In particular, the static impurity correction to the energy current operator should be numerically significant.

ACKNOWLEDGMENTS

It is a pleasure to thank S. M. Girvin for many useful discussions. This research was supported by the NSF through Grant No. DMR 77-11305.

APPENDIX

The Matsubara sums that have to be evaluated in Eqs. (23), (34), and (40) can all be written in the form

$$S(i\omega)=\frac{i}{(i\omega)}\frac{1}{\beta}\sum_{ip}P_k(ip,ip+i\omega), \tag{A1}$$

where

$$P_k(ip, ip+i\omega)=[\tfrac{1}{2}(ip)+\tfrac{1}{2}(ip+i\omega)]^n\mathcal{G}_k(ip)$$
$$\times\,\mathcal{G}_k(ip+i\omega)\Lambda_k(ip, ip+i\omega)\,. \qquad \text{(A2)}$$

The sum over fermion frequencies (ip) in (A1) can be converted to an integral

$$S(i\omega)=-\frac{1}{(i\omega)}\int_\Gamma \frac{dz}{2\pi}\, n_F(z)P_k(z, z+i\omega)\,, \qquad \text{(A3)}$$

where Γ is a path from $(\delta-i\infty)$ to $(\delta+i\infty)$ and from $(-\delta+i\infty)$ to $(-\delta-i\infty)$ in the complex z plane. $P_k(z, z+i\omega)$ has branch cuts along $z=\epsilon$ and $\epsilon-i\omega$; i.e., deforming the contour of integration gives

$$S(\omega+i\delta)=-\frac{1}{\omega}\int_{-\infty}^{\infty}\frac{d\epsilon}{2\pi}n_F(\epsilon)[P(\epsilon+i\delta, \epsilon+\omega+i\delta)-P(\epsilon-i\delta, \epsilon+\omega+i\delta)$$
$$+P(\epsilon-\omega-i\delta, \epsilon+i\delta)-P(\epsilon-\omega-i\delta, \epsilon-i\delta)]\,. \qquad \text{(A4)}$$

Making the variable transformation $\epsilon\rightarrow\epsilon+\omega$ in the last two terms we find in the $\omega\rightarrow 0$ limit for the real part of $S(\omega+i\delta)$

$$\text{Re}S=\int_{-\infty}^{\infty}d\epsilon\;-\frac{\partial n_F}{\partial\epsilon}\,\epsilon^n f(\epsilon)\,, \qquad \text{(A5)}$$

where

$$f(\epsilon)=\text{Re}\,[\mathcal{G}_k(\epsilon-i\delta)\mathcal{G}_k(\epsilon+i\delta)\Lambda_k(\epsilon-i\delta, \epsilon+i\sigma)$$
$$-\mathcal{G}_k(\epsilon-i\delta)\mathcal{G}_k(\epsilon-i\delta)\Lambda_k(\epsilon-i\delta, \epsilon-i\delta)]\,. \qquad \text{(A6)}$$

Using the relations

$$\mathcal{G}_k(\epsilon\pm i\delta)=1/[\epsilon\pm i\delta-\xi_k-\Sigma_k(\epsilon\pm i\delta)]\,,$$
$$\Gamma_k(\epsilon)=-\text{Im}\Sigma_k(\epsilon-i\delta)\,,$$
$$A_k(\epsilon)=-2\,\text{Im}\mathcal{G}_k(\epsilon-i\delta)\,,$$

and the Ward identity

$$\vec{\Lambda}_k(\epsilon-i\delta, \epsilon-i\delta)=\vec{v}_k+(1/m)\nabla_k\Sigma_k(\epsilon-i\delta)\,,$$

leads to the expression [Eq. (27)] for $\sigma(\epsilon)$.

---

*On leave from the Institute of Theoretical Physics, CTH, Fack, S-41296 Göteborg, Sweden.

[1] N. F. Mott and E. A. Davis, *Electronic Processes in Non-crystalline Materials* (Clarendon, Oxford, 1971), p. 47.

[2] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart and Winston, New York, 1976).

[3] G. V. Chester and A. Thellung, Proc. R. Soc. London 77, 1005 (1961).

[4] R. D. Barnard, *Thermoelectricity in Metals and Alloys* (Taylor and Francis, London, 1972).

[5] In the definition Eq. (16) of the energy position operator $\vec{R}$, the electron-phonon bond was assumed to be at the electron site $\vec{R}_i$. This is ambiguous. If the bond instead is placed at $\vec{R}_i+\eta(\vec{R}_j-\vec{R}_i)$, $0\leq\eta\leq 1$, where $\vec{R}_j$ is the location of the phonon displacement, an extra term proportional to η appears in the energy current. However, it turns out that this term can be written as a perfect time derivative. After a partial time integration in Eq. (6) we observe that such a term vanishes in the static limit.

[6] This correct expression for the energy current was first derived (although in a different manner) by A. Vilenkin and P. L. Taylor, Phys. Rev. B 18, 5260 (1978).

[7] S. Doniach and E. H. Sondheimer, *Green's Functions for Solid State Physicists* (Benjamin, London, 1974), Chap. 5.6.

[8] J. S. Langer, Phys. Rev. 120, 714 (1960).

[9] See Appendix C of Ref. 2.

[10] A. Wilenkin and P. L. Taylor, Phys. Rev. Lett. 42, 597 (1979); S. K. Lyo, Phys. Rev. B 17, 2545 (1978); J. L. Opsal, B. J. Thaler, and J. Bass, Phys. Rev. Lett. 36, 1211 (1976); R. E. Prange and L. P. Kadanoff, Phys. Rev. 134, A566 (1964).

[11] M. Jonson and S. M. Girvin, Phys. Rev. Lett. 43, 1447 (1979).

[12] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1966), p. 222.

[13] See Ref. 2, p. 323.

[14] S. R. Nagel, Phys. Rev. Lett. 41, 990 (1978).

[15] S. M. Girvin and M. Jonson, unpublished.