RAPID COMMUNICATIONS

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Optimal thermoelectric figure of merit of a molecular junction

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We show that a molecular junction can give large values of the thermoelectric figure of merit ZT, and so it could be used as a solid-state energy-conversion device that operates close to the Carnot efficiency. The mechanism is similar to the Mahan-Sofo model for bulk thermoelectrics—the Lorenz number goes to zero violating the Wiedemann-Franz law while the thermopower remains nonzero. The molecular state through which charge is transported must be weakly coupled to the leads, and the energy level of the state must be of order k_BT away from the Fermi energy of the leads. In practice, the figure of merit is limited by the phonon thermal conductance; we show that the largest possible $ZT \sim (\tilde{G}_{\text{th}}^{\text{ph}})^{-1/2}$, where $\tilde{G}_{\text{th}}^{\text{ph}}$ is the phonon thermal conductance divided by the thermal conductance quantum.

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Electrical transport in mesoscopic and nanoscale systems has been a major focus of recent work in physics, chemistry, and materials science.[1] In contrast, thermal transport has been much less intensively studied despite a number of fascinating results including the observation in 2000 of the quantum of thermal conductance.[2,3] Thermal and thermoelectric transport are also relevant to technological questions of great importance, such as the construction of solid-state energy-conversion devices.

The efficiency of such devices is determined by the thermoelectric figure of merit[4] ZT, which is defined as

$$ZT = \frac{GS^2}{G_{\text{th}}^{\text{el}}/T + G_{\text{th}}^{\text{ph}}/T}. \tag{1}$$

Here G is the charge conductance, S is the thermopower, $G_{\text{th}}^{\text{el}}$ is the electron thermal conductance, and $G_{\text{th}}^{\text{ph}}$ is the phonon thermal conductance. As $ZT \to \infty$, the device attains the Carnot efficiency. The figure of merit of the semiconductors typically used for thermoelectric applications is approximately 1; ZT values of 2 or 3 would lead to a considerable increase in commercial utility and are being sought in several types of materials.

Theoretical[5,6] and experimental[7] studies of semiconductor nanowires have shown that phonon confinement can lead to a lower phonon thermal conductance and so to a higher ZT. Nanostructured materials, such as quantum dot superlattices,[8] can also have strong scattering of phonons. Certain strongly correlated oxides, such as sodium cobaltate,[9–11] are promising candidate materials by virtue of their metal-like electrical conductivity combined with high thermopower at room temperature or below. Another set of candidates, molecular junctions,[12,13] are promising as both phonon and electron properties may contribute to increasing ZT. The order of magnitude of the maximum phonon thermal conductance through a junction should be set by the thermal conductance quantum. However, due to a density-of-states mismatch between the phonons in the leads and the phonon modes of the molecule, the true phonon thermal conductance might be much smaller. The electronic properties of such junctions are the subject of this Rapid Communication.

Improvements of standard density-functional methods are needed to give unambiguous predictions for the transport properties of molecular systems,[14,15] especially when correlations between electrons are significant. It is therefore valuable to understand transport in simplified models incorporating intramolecular correlations, such as the Anderson model reviewed below, both as a check on the accuracy of new *ab initio* methods and to guide both experiment and numerics to where high ZT may occur.

Here we find the figure of merit of a molecular junction starting from the Anderson model for the molecule and leads, which is valid under the assumption that a single molecular level dominates transport. If the lifetime τ of an electron in the molecular state satisfies $\tau \ll \hbar/(k_BT)$, it is generally true[16,17] that $ZT \ll 1$. We concentrate therefore on the regime $\tau \gg \hbar/(k_BT)$. Physically, this corresponds to a wave function for the level that is strongly localized on the molecule so that the state is weakly coupled to the leads. In Ref. 18 it was shown that for the Anderson model in this limit of weak coupling to the leads, with strong interactions, and by ignoring the phonon contribution to the thermal conductance, the figure of merit becomes infinite. Here we find that the phenomenon is surprisingly general—it is also true in the limit of weak interactions. We clarify the mechanism in both cases by comparison to the work of Mahan and Sofo[19] on bulk thermoelectrics. (The mechanism, a violation of the Wiedemann-Franz law, has previously been studied in quantum dots in different parameter regimes in Refs. 20–22.) Also, by carrying the calculation for the electron-only ZT to higher order in the coupling to the leads, we find the optimal value of ZT once the phonon contribution is included. Finally, we suggest a candidate molecule in which high ZT might be observed.

The Anderson model is defined by the Hamiltonian

$$H = -t \sum_{j>0, j<-1, \sigma} (c_{j+1,\sigma}^{\dagger} c_{j,\sigma} + \text{H.c.}) - \sum_{\sigma} [t_R'(c_{1,\sigma}^{\dagger} c_{0,\sigma} + \text{H.c.}) + t_L'(c_{0,\sigma}^{\dagger} c_{-1,\sigma} + \text{H.c.})] + \varepsilon_d (n_{0\uparrow} + n_{0\downarrow}) + U n_{0\uparrow} n_{0\downarrow}. \tag{2}$$

The label σ represents the spin of the electrons; j is the site index, with the molecule represented by the site at $j=0$. The amplitude to hop from the molecule to the right (left) lead is given by $t'_{R(L)}$, and the leads are represented by the sites at $j>0$ and $j<0$. The energy needed to place a single electron on the molecule is ε_d, which can be tuned by gate voltage. The electron-electron repulsion within the molecule results in an additional energy cost of U to add two electrons to the molecular site. The hopping within the leads is t, which gives a band structure $E(k)=-2t\cos ka$, where a is the lattice spacing.

As a first step, we find the transport properties with no electronic repulsion ($U=0$) when the transmission function of the impurity can be found by solving the single-particle Schrödinger equation. The result is

$$\mathcal{T}_\sigma(E)=\frac{\Gamma_L\Gamma_R(1-E^2/4t^2)}{\bar{\Gamma}^2(1-E^2/4t^2)+[E(1-\bar{\Gamma}/2t)-\varepsilon_d]^2}, \tag{3}$$

where E is the incident energy, $\Gamma_{L(R)}=2t'^2_{L(R)}/t$, and $\bar{\Gamma}=(\Gamma_L+\Gamma_R)/2$. Close to the band center, and with $\Gamma_{L,R}\ll t$, the familiar Lorentzian transmission results,

$$\mathcal{T}_\sigma(E)=\frac{\Gamma_L\Gamma_R}{\bar{\Gamma}}\frac{\bar{\Gamma}}{\bar{\Gamma}^2+(E-\varepsilon_d)^2}. \tag{4}$$

The hybridization energy, $\bar{\Gamma}$, sets the lifetime, τ, of an electron on the molecule through $\tau=\hbar/\bar{\Gamma}$. We first use this form of $\mathcal{T}_\sigma(E)$ to treat the noninteracting case.

Within the Landauer formalism the transmission function determines the charge current I and the heat current due to the electrons I_Q^{el} through the relations

$$I=-\frac{e}{h}\int_{-2t}^{2t}dE[\mathcal{T}_\uparrow(E)+\mathcal{T}_\downarrow(E)][f_L^0(E)-f_R^0(E)], \tag{5}$$

$$I_Q^{\mathrm{el}}=\frac{1}{h}\int_{-2t}^{2t}dE(E-\mu)[\mathcal{T}_\uparrow(E)+\mathcal{T}_\downarrow(E)][f_L^0(E)-f_R^0(E)]. \tag{6}$$

Here $-e$ is the electron charge, and the function f_L^0 is defined by $f_L^0(E)=(e^{(E-\mu_L)/(k_BT_L)}+1)^{-1}$, where μ_L and T_L are the chemical potential and temperature in the left lead (and similarly for f_R^0). At linear response, and for chemical potential away from the band edges,

$$I=-\frac{2e}{h}\frac{\gamma_L\gamma_R}{\bar{\gamma}}[\mathcal{F}_0(\bar{\gamma},\delta)eV+\mathcal{F}_1(\bar{\gamma},\delta)k_B\Delta T], \tag{7}$$

$$I_Q^{\mathrm{el}}=\frac{2k_BT}{h}\frac{\gamma_L\gamma_R}{\bar{\gamma}}[\mathcal{F}_1(\bar{\gamma},\delta)eV+\mathcal{F}_2(\bar{\gamma},\delta)k_B\Delta T], \tag{8}$$

where $\gamma_{L(R)}=\Gamma_{L(R)}/(k_BT)$, $\bar{\gamma}=\bar{\Gamma}/(k_BT)$, $\delta=(\varepsilon_d-\mu)/(k_BT)$, $eV=\mu_L-\mu_R$, and $\Delta T=T_L-T_R$. The functions $\mathcal{F}_n$ can be found from Eqs. (7) and (8) by setting $x=(E-\mu)/(k_BT)$; the result is

$$\mathcal{F}_n(\bar{\gamma},\delta)=\int_{-\infty}^{\infty}dx\frac{x^n}{4\cosh^2(x/2)}\frac{\bar{\gamma}}{\bar{\gamma}^2+(x-\delta)^2}. \tag{9}$$

$\mathcal{F}_0$, $\mathcal{F}_1$, and $\mathcal{F}_2$ can then be expressed as

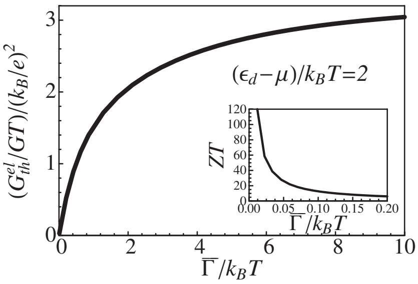

FIG. 1. The Lorenz number (main figure) and electronic ZT (inset) plotted as functions of $\bar{\Gamma}/(k_BT)$, with $(\varepsilon_d-\mu)/(k_BT)=2$ in both cases. Only the electron contribution to the thermal conductance is included. Note that the Lorenz number attains the Sommerfeld value of $\pi^2/3$ for $\Gamma\gg k_BT$.

$$\mathcal{F}_0=\frac{1}{4\pi}\left[\psi\left(\frac{\pi+w}{2\pi}\right)+\psi\left(\frac{\pi+w^*}{2\pi}\right)\right], \tag{10}$$

$$\mathcal{F}_1=\frac{1}{4\pi i}\left[w\psi\left(\frac{\pi+w}{2\pi}\right)-w^*\psi\left(\frac{\pi+w^*}{2\pi}\right)\right], \tag{11}$$

$$\mathcal{F}_2=\bar{\gamma}-\frac{1}{4\pi}\left[w^2\psi\left(\frac{\pi+w}{2\pi}\right)+w^{*2}\psi\left(\frac{\pi+w^*}{2\pi}\right)\right], \tag{12}$$

where $w=\bar{\gamma}+i\delta$. The function ψ is the trigamma function $\psi(z)=\Sigma_{n=0}^{\infty}(z+n)^{-2}$.

We define the limit of a long-lived molecular state as $\bar{\Gamma}\ll k_BT$, i.e., $\bar{\gamma}\ll 1$. Ignoring the phonon contribution to the heat current (to be restored below), the figure of merit is given by $ZT=(\mathcal{F}_0\mathcal{F}_2/\mathcal{F}_1^2-1)^{-1}$. For $\bar{\gamma}$ fixed, ZT is largest when $\delta\simeq\pm 2.4$. If one holds δ fixed, and allows $\bar{\gamma}\to 0$, the figure of merit diverges as

$$ZT=\frac{1}{\bar{\gamma}}\frac{\pi\delta^2}{4\cosh^2(\delta/2)}+\mathcal{O}(\bar{\gamma}^0). \tag{13}$$

(This follows from expanding $\mathcal{F}_n$ to first order in $\bar{\gamma}$.) The thermopower is finite as $\bar{\gamma}\to 0$, and (as shown in Fig. 1) the divergence in ZT is due to a violation of the Wiedemann-Franz law, with the thermal conductance vanishing faster than the electrical conductance.

In practice, the junction figure of merit will be limited by the phonon thermal conductance $G_{\mathrm{th}}^{\mathrm{ph}}=\tilde{G}_{\mathrm{th}}^{\mathrm{ph}}G_0$, with $G_0=\frac{\pi^2}{3}\frac{k_B^2}{h}T$ and $\tilde{G}_{\mathrm{th}}^{\mathrm{ph}}$ dimensionless. Using

$$GS^2=\frac{\gamma_L\gamma_R}{\bar{\gamma}}\frac{2k_B^2}{h}\frac{\pi\delta^2}{4\cosh^2(\delta/2)}, \tag{14}$$

we include the phonon contribution to get

$$\frac{1}{ZT}=\frac{G_{\mathrm{th}}^{\mathrm{el}}}{GS^2T}+\frac{G_{\mathrm{th}}^{\mathrm{ph}}}{GS^2T}\simeq\frac{4\cosh^2(\delta/2)}{\pi\delta^2}\left(\bar{\gamma}+\frac{\pi^2\tilde{G}_{\mathrm{th}}^{\mathrm{ph}}\bar{\gamma}}{6\gamma_L\gamma_R}\right). \tag{15}$$

Assuming $\gamma_L=\gamma_R=\gamma$ and minimizing $1/ZT$ with respect to γ and δ gives, for small $\tilde{G}_{\mathrm{th}}^{\mathrm{ph}}$, an optimal value of $ZT\simeq 0.51/(\tilde{G}_{\mathrm{th}}^{\mathrm{ph}})^{1/2}$, which diverges when $\tilde{G}_{\mathrm{th}}^{\mathrm{ph}}\to 0$.

There is a simple physical picture that gives the correct expressions for $\mathcal{F}_0$, $\mathcal{F}_1$, and $\mathcal{F}_2$ to the order of $\bar{\gamma}^0$, and thus, gives $1/ZT=0+\mathcal{O}(\bar{\gamma}^0)$. This approximation is known as "sequential tunneling" and has been used to study transport in quantum dots and molecules.[23–26] Suppose the molecular level has energy ε_d; then, in this approximation, an electron in the leads can tunnel onto the level only if it too has energy ε_d. Energy is conserved throughout the transport process. This allows for a current proportional to $\Gamma_L\Gamma_R/\bar{\Gamma}$. In contrast, in tunneling through a virtual intermediate state, away from resonance the current is proportional to the probability to tunnel onto the level and the probability to tunnel off, i.e., to $\Gamma_L\Gamma_R$.

In the sequential tunneling limit, each electron passing through the junction carries the same amount of heat, $Q=\varepsilon_d-\mu$. To understand why the Wiedemann-Franz law is violated, recall that the thermal conductance is the heat current divided by the temperature difference *under the condition of zero charge current*. The condition $I=0$ implies that the flux of left-moving electrons equals the flux of right-moving electrons; since each left- or right-moving electron carries exactly the same amount of heat Q, the thermal current I_Q^{el} is also zero. A similar mechanism was used by Mahan and Sofo[19,27] to search for the bulk material with the best thermoelectric figure of merit. For long-lived molecular states, unlike bulk materials (except in the atomic limit[11]), the theory can be extended to include electron-electron repulsion.

We now study whether, once electronic repulsion in the molecule is added, the electronic figure of merit ZT still scales like $1/\bar{\gamma}$ in the limit of a long-lived molecular state. Define the probability of the molecular level being empty as $P(0)$, occupied by an up spin as $P(\uparrow)$, occupied by a down spin as $P(\downarrow)$, and doubly occupied as $P(2)$. We consider the currents where the molecule meets the left lead. An example of a process that contributes to the currents is the tunneling of an up electron with energy ε_d from the left lead onto the empty level. To find the total currents, we consider all possible tunneling processes onto and off of the molecule. For $\delta>0$, i.e., $\varepsilon_d>\mu$, the charge and heat currents at the left junction are then given by

$$I=-e\tau_L^{-1}\{P(0)2f_L(\varepsilon_d)-P(1)[1-f_L(\varepsilon_d)]+P(1)f_L(\varepsilon_d+U)-2P(2)[1-f_L(\varepsilon_d+U)]\}, \qquad (16)$$

$$I_Q^{\mathrm{el}}=\tau_L^{-1}k_BT\{\delta P(0)2f_L(\varepsilon_d)-\delta P(1)[1-f_L(\varepsilon_d)]+(\delta+u)P(1)f_L(\varepsilon_d+U)-(\delta+u)2P(2)[1-f_L(\varepsilon_d+U)]\}, \qquad (17)$$

where $P(1)=P(\uparrow)+P(\downarrow)$, $u=U/(k_BT)$, and, as before, $\delta=(\varepsilon_d-\mu)/(k_BT)$. Similar formulas can be written for the time derivatives of the probabilities $\partial_tP(0)$, etc. The probabilities $P(0)$, $P(\uparrow)$, $P(\downarrow)$, and $P(2)$ are then determined by requiring a steady state. These are inserted into the equations for the currents to determine the linear-response transport coefficients. The final result is[28]

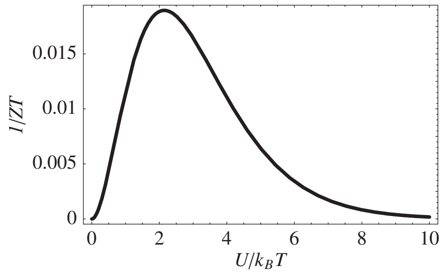

FIG. 2. $1/ZT$ without the phonon contribution to the thermal conductance for $\Gamma/(k_BT)\to 0$ and $(\varepsilon_d-\mu)/(k_BT)=2$.

$$G=\frac{e^2}{\hbar}\frac{\gamma_L\gamma_R}{\bar{\gamma}}\frac{e^{\delta+u}[1+e^{\delta}(2+e^{\delta+u})]}{(1+e^{\delta})(1+e^{\delta+u})[1+e^{\delta+u}(2+e^{\delta})]}, \qquad (18)$$

$$S=-\frac{k_B}{e}\frac{\delta[1+e^{\delta}(2+e^{\delta+u})]+u(1+e^{\delta})}{1+e^{\delta}(2+e^{\delta+u})}, \qquad (19)$$

$$\frac{G_{\mathrm{th}}^{\mathrm{el}}}{T}=\frac{k_B^2}{\hbar}\frac{\gamma_L\gamma_R}{\bar{\gamma}}\frac{u^2e^{2\delta+u}}{(1+2e^{\delta+u}+e^{2\delta+u})(1+2e^{\delta}+e^{2\delta+u})}. \qquad (20)$$

The figure of merit in the sequential tunneling approximation (again ignoring phonons) is given by

$$ZT=\frac{e^{-\delta}}{u^2}\frac{[\delta(1+2e^{\delta}+e^{2\delta+u})+u(1+e^{\delta})]^2}{(1+e^{\delta})(1+e^{\delta+u})}. \qquad (21)$$

(An approximate version of this formula was derived in Ref. 18.) $1/ZT$ is plotted versus u in Fig. 2 for $\delta=2$ and $\gamma\to 0$. ZT diverges for $u=0$ as before.

For $u\gg 1$, $1/ZT$ goes to zero like e^{-u}. This can be understood within the picture presented earlier. Even though, in contrast to the noninteracting case, there are now two levels (of energy ε_d and ε_d+U) on the molecule through which transport can occur, the relative probability of electrons in the leads having the corresponding energies goes as e^{-u}. As U becomes large there is only an exponentially small probability to have an electron in the leads with energy ε_d+U. In this case, each electron that passes through the junction carries heat $(\varepsilon_d-\mu)$ and the situation is similar to the noninteracting case where transport is through a single level; thus, the thermal conductance in this case is also zero. (For convenience, we consider the symmetric case with $\gamma_L=\gamma_R=\gamma$.) Since the sequential tunneling model is correct to first order in γ, the thermal conductance must be nonzero only at order γ^2. For $\delta\simeq 2.4$ and $u\gg 1$, we have $GS^2\simeq\gamma 0.4k_B^2/\hbar$, and so GS^2 scales like γ as in the noninteracting case. Adding in the phonon contribution to the heat current, we again conclude that ZT will scale like $(\tilde{G}_{\mathrm{th}}^{\mathrm{ph}})^{-1/2}$. In the limit of $u\to\infty$, the Green's function method[29,30] was used to find the transport coefficients to higher order in γ. The result is that, including the phonon contribution, the maximum ZT is $0.42(G_{\mathrm{ph}}^{\mathrm{th}})^{-1/2}$.[31]

We have shown that transport through a single molecular level can lead to large values of the thermoelectric figure of merit ZT. Within the Anderson model for the level, this occurs if the molecular state is long lived (i.e., for the case of a symmetric junction, $\gamma\to 0$) and the energy scale U of the electron-electron interactions within the molecule satisfies either $U \ll k_B T$ or $U \gg k_B T$. The increase in ZT is due to a violation of the Wiedemann-Franz law—the charge conductance scales like γ, whereas the electron thermal conductance divided by the temperature scales like γ^2. While similarly large figures of merit may be achieved for optimal band structures in bulk materials,[19] the advantage of molecular systems is that they can have only a small phonon contribution to the thermal conductance, so that the maximum achieved value of ZT including phonons may be higher than in bulk materials. A phonon thermal conductance of $0.1G_0$ would lead to ZT of 1.6 for $U \ll kT$ and 1.3 for $U \gg kT$.

There are some practical challenges in achieving dramatically enhanced ZT in a real device by the mechanism presented here. The wave function of the level must be localized at the center of the molecule to reduce overlap with states in the leads; in addition, the energy of the level must lie about $2k_B T$ from the Fermi level of the leads. These requirements may be satisfied by the $\mathrm{Co[tpy\text{-}(CH_2)_5\text{-}SH]_2}$ molecules studied by Park *et al.*[32,33] The electronic transport in these systems is through a cobalt atom that sits at the center of the molecule; the alkyl chains separate the cobalt from the gold leads, creating a state localized away from the leads. It would be of great interest to confirm that the Wiedemann-Franz law is indeed violated in these molecules.

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