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 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 non-zero. 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 $k_B T$ 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 $ZT \sim (\tilde{G}_{th}^{ph})^{-1/2}$, where \tilde{G}_{th}^{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. This interest has been motivated both by the potential for applications in electronics and by the opportunity to study novel transport phenomena such as conductance quantization¹ and Coulomb blockade. Compared to electrical transport, 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 merit⁴ ZT, defined as

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

Here G is the charge conductance, S the thermopower, G^{el}_{th} the electron thermal conductance, and G^{ph}_{th} 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. Increased interest in ZT has given additional motivation to work on the thermal and thermoelectric properties of unusual materials: nanowires^{5,6}, nanostructured materials⁷, strongly correlated materials^{8,9,10}, and molecular junctions^{11,12}. Of these, molecular junctions are particularly promising, as it is hoped that the phonon thermal conductance will be small due to a density of states mismatch between the phonons in the leads and the phonon modes of the molecule. Improvements of standard density functional methods are needed to give unambiguous predictions for the transport properties of molecular systems^{13,14}, especially when correlations between electrons are significant. It is therefore valuable to have a

thorough understanding of transport in simplified models, such as the Anderson model (reviewed below), that describe intramolecular correlations, 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.

In this paper we find the figure of merit of a molecular junction. We start 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 $\tau \ll \hbar/(k_B T)$, it is generally true^{15,16} that $ZT \ll 1$. We concentrate therefore on the regime $\tau \gg \hbar/(k_B T)$. Physically, this corresponds to a wavefunction for the level that is strongly localized at the center of the molecule, so that the state is weakly coupled to the leads. In reference (17) it was shown that for the Anderson model in this limit of weak coupling to the leads, with strong interactions, and 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 electronelectron interactions. We clarify the mechanism in both cases by comparing with the work of Mahan and $Sofo^{18}$ on bulk thermoelectrics. (The mechanism, a violation of the Wiedemann-Franz law, has previously been studied in quantum dots in different parameter regimes in references (19,20,21).) 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 where high ZT might be observed.

The Anderson model is defined by the Hamiltonian

$$H = -t \sum_{j>0,j<-1,\sigma} (c^{\dagger}_{j+1,\sigma}c_{j,\sigma} + hc) - \sum_{\sigma} \left\{ t'_R(c^{\dagger}_{1,\sigma}c_{0,\sigma} + hc) + t'_L(c^{\dagger}_{0,\sigma}c_{-1,\sigma} + hc) \right\}$$
(1)
+ $\varepsilon_d(n_{0\uparrow} + n_{0\downarrow}) + Un_{0\uparrow}n_{0\downarrow}.$

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 to place a single electron on the molecule is ε_d , which can be interpreted as a 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 of $E(k) = -2t \cos ka$, 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

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

where E is the energy of the incident electron, $\Gamma_{L(R)} = 2t'_{L(R)}^2/t$, and $\overline{\Gamma} = (\Gamma_L + \Gamma_R)/2$. For electrons close to the center of the band, and $\Gamma_{L,R} \ll t$, we get the familiar Lorentzian transmission

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

The hybridization energy, $\overline{\Gamma}$, determines the mean lifetime, τ , of an electron on the dot, through $\tau = \hbar/\overline{\Gamma}$. We will assume this form of $\mathcal{T}_{\sigma}(E)$ in the study of the non-interacting case that follows.

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

$$I = -\frac{e}{h} \int_{-2t}^{2t} dE(\mathcal{T}_{\uparrow}(E) + \mathcal{T}_{\downarrow}(E))(f_{L}^{0}(E) - f_{R}^{0}(E)),$$

$$I_{Q}^{el} = \frac{1}{h} \int_{-2t}^{2t} dE(E - \mu)(\mathcal{T}_{\uparrow}(E) + \mathcal{T}_{\downarrow}(E))(f_{L}^{0}(E) - f_{R}^{0}(E)).$$

Here -e is the electron charge, and the function f_L^0 is defined by $f_L^0(E) = (e^{(E-\mu_L)/(k_B T_L)} + 1)^{-1}$, 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 a chemical potential away from the band edges, we have

$$I = -\frac{2e}{h} \frac{\gamma_L \gamma_R}{\overline{\gamma}} \left(\mathcal{F}_0(\overline{\gamma}, \delta) eV + \mathcal{F}_1(\overline{\gamma}, \delta) k_B \Delta T \right), \quad (2)$$

$$I_Q^{el} = \frac{2k_BT}{h} \frac{\gamma_L \gamma_R}{\overline{\gamma}} \left(\mathcal{F}_1(\overline{\gamma}, \delta) eV + \mathcal{F}_2(\overline{\gamma}, \delta) k_B \Delta T \right), \quad (3)$$

where $\gamma_{L(R)} = \Gamma_{L(R)}/(k_B T)$, $\overline{\gamma} = \overline{\Gamma}/(k_B T)$, $\delta = (\varepsilon_d - \mu)/(k_B T)$, $eV = \mu_L - \mu_R$, and $\Delta T = T_L - T_R$. The functions \mathcal{F}_n can be found from equations (2) and (3) by setting $x = (E - \mu)/(k_B T)$; the result is

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



FIG. 1: The Lorenz number (main figure) and the thermopower (inset) plotted as a function of $\overline{\Gamma}/(k_B T)$, with $(\varepsilon_d - \mu)/(k_B T) = 2$ in both cases. Only the electron contribution to the thermal conductance is included in the calculation of the Lorenz number.

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

$$\mathcal{F}_{0} = \frac{1}{4\pi} \left\{ \psi \left(\frac{\pi + w}{2\pi} \right) + \psi \left(\frac{\pi + w^{*}}{2\pi} \right) \right\},$$
$$\mathcal{F}_{1} = \frac{1}{4\pi i} \left\{ w\psi \left(\frac{\pi + w}{2\pi} \right) - w^{*}\psi \left(\frac{\pi + w^{*}}{2\pi} \right) \right\},$$
$$\mathcal{F}_{2} = \overline{\gamma} - \frac{1}{4\pi} \left\{ w^{2}\psi \left(\frac{\pi + w}{2\pi} \right) + w^{*2}\psi \left(\frac{\pi + w^{*}}{2\pi} \right) \right\},$$

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

We define the limit of a long-lived molecular state as $\overline{\Gamma} \ll k_B T$, i.e. $\overline{\gamma} \ll 1$. 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 $\overline{\gamma}$ fixed, ZT is largest when $\delta \simeq \pm 2.4$. If one holds δ fixed, and allows $\overline{\gamma} \to 0$, the figure of merit diverges as

$$ZT = \frac{1}{\overline{\gamma}} \frac{\pi \delta^2}{(2\cosh(\delta/2))^2} + \mathcal{O}(\overline{\gamma}^0)$$

(This follows from expanding \mathcal{F}_n to first order in $\overline{\gamma}$.) As shown in Fig. 1, the thermopower is finite as $\overline{\gamma} \to 0$, and 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 figure of merit of the junction will be limited by the phonon thermal conductance. This can be parametrized in terms of the fraction \tilde{G}_{th}^{ph} of a thermal conductance quantum transmitted by the molecule, i.e. $G_{th}^{ph} = \tilde{G}_{th}^{ph} \frac{\pi^2}{3} \frac{k_B^2}{h} T$. Using

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

we include the phonon contribution to get

$$\frac{1}{ZT} = \frac{G_{th}^e}{GS^2T} + \frac{G_{th}^{ph}}{GS^2T} \simeq \frac{(2\cosh(\delta/2))^2}{\pi\delta^2} \left(\overline{\gamma} + \frac{\pi^2 \tilde{G}_{th}^{ph} \overline{\gamma}}{6\gamma_L \gamma_R}\right)$$



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

Assuming $\gamma_L = \gamma_R = \gamma$ and minimising 1/ZT with respect to γ and δ gives, for small \tilde{G}_{th}^{ph} , an optimal value of

$$ZT \simeq 0.51/(\tilde{G}_{th}^{ph})^{1/2}$$

The figure of merit becomes infinite as \tilde{G}^{ph}_{th} goes to zero, as we found before.

There is a simple physical picture that gives us the correct expressions for \mathcal{F}_0 , \mathcal{F}_1 , and \mathcal{F}_2 to order $\overline{\gamma}^0$, and thus gives $1/ZT = 0 + \mathcal{O}(\overline{\gamma}^0)$. This approximation is known as "sequential tunneling", and has been used to study transport in quantum dots and molecules^{22,23,24,25}. 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 therefore conserved throughout the transport process. This allows for a current proportional to $\Gamma_L \Gamma_R / \overline{\Gamma}$. In quantum-mechanical tunneling by contrast, the intermediate state is virtual; away from resonance, the current is proportional to the probability to tunnel onto the level multiplied by the probability to tunnel off, and thus 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, it is essential to bear in mind that the thermal conductance is defined as 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 is the same as the flux of right-moving electrons; since each left or right moving electrons carries exactly the same amount of heat Q, the thermal current ${\cal I}_Q^{el}$ is also zero. This is the same mechanism that Mahan and Sofo used to model the bulk material with the best thermoelectric figure of merit 18,26 . For long-lived molecular states, unlike bulk materials (except in the atomic $limit^{10}$), the theoretical analysis can be extended to include electron-electron repulsion, as now done.

We now consider whether, once electron-electron repulsion in the molecule is added, the electronic figure of merit ZT still scales like $1/\overline{\gamma}$ in the limit of a long-lived molecular state. Define the probability of the molecular level being empty as P(0), of there being an up spin as $P(\uparrow)$, a down spin as $P(\downarrow)$, and of it being 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 at this point 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, both onto and off of the molecule. For $\delta > 0$, ie. $\varepsilon_d > \mu$, the charge and heat currents at the left junction are then given by

$$I = -e\tau_L^{-1} \left(P(0)2f_L(\varepsilon_d) - P(1)(1 - f_L(\varepsilon_d)) + P(1)f_L(\varepsilon_d + U) - 2P(2)(1 - f_L(\varepsilon_d + U))) \right),$$

$$I_Q^{el} = \tau_L^{-1}k_B T \left(\delta P(0)2f_L(\varepsilon_d) - \delta P(1)(1 - f_L(\varepsilon_d)) + (\delta + u)P(1)f_L(\varepsilon_d + U) - (\delta + u)2P(2)(1 - f_L(\varepsilon_d + U))) \right),$$

where $P(1) = P(\uparrow) + P(\downarrow)$, $u = U/(k_BT)$, and, as before, $\delta = (\varepsilon_d - \mu)/(k_BT)$. The probabilities P(0), $P(\uparrow)$, $P(\downarrow)$, and P(2) are determined from the steady state condition. The final result for the linear response transport coefficients is

$$G = \frac{e^2}{\hbar} \frac{\gamma_L \gamma_R}{\overline{\gamma}} \frac{e^{\delta+u} (1+e^{\delta}(2+e^{\delta+u}))}{(1+e^{\delta})(1+e^{\delta+u})(1+e^{\delta+u}(2+e^{\delta}))},$$

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

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

(It is straight-forward to confirm that this result, with u = 0, agrees with the exact result for the non-interacting case in the limit of $\gamma_{L,R} \ll 1$, if one makes the identification $\tau_{L(R)}^{-1} = \Gamma_{L(R)}/\hbar$. This confirms that only sequential tunneling is important in the limit of a long-lived state.)

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

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

(An approximate version of this formula was derived in 17.) 1/ZT is plotted in Fig. 2 as a function of u for $\delta = 2$ and $\gamma \to 0$. At u = 0, the non-interacting case, ZT is divergent, 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 non-interacting case there are now two levels (of energy ε_d and $\varepsilon_d + U$) 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 thus only an exponentially small probability that there will be an electron in the leads with energy $\varepsilon_d + U$. 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 takes place through just one level on the molecule. Thus, the thermal conductance in this case is also zero. (For convenience, let us consider the symmetric case, with $\gamma_L = \gamma_R = \gamma$.) Since the sequential tunneling model is correct only to first order in γ , we can conclude that the thermal conductance vanishes to first order in γ , and so must be of order γ^2 . For $\delta \simeq 2.4$ and $u \gg 1$, we have $GS^2 \simeq \gamma 0.4 k_B^2/\hbar$, and so GS^2 scales like γ as in the non-interacting case. Adding in once more the phonon contribution to the heat current, we can again conclude that ZT will scale like $(\tilde{G}_{th}^{ph})^{-1/2}$. In the limit of $u \to \infty$, the Green function method^{27,28} can be used to find the transport coefficients to higher order in γ , and so the coefficient in the scaling of ZT. The result is that, including the phonon contribution as before, the optimal value of ZT is $0.42(G_{ph}^{th})^{-1/2}$.

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 longlived (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 opti-

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mal band structures in bulk materials¹⁸, the advantage of molecular systems is that they may have only a small phonon contribution to the thermal conductance, so that their maximum achieved value of ZT once phonons are included may be higher than in bulk materials.

There are some practical challenges in achieving dramatically enhanced ZT in a real device by the mechanism presented here. The wavefunction of the level must be localized at the center of the molecule to give a small overlap with the states in the leads, and so a long lifetime; in addition, the energy of the level must lie a distance of about $2k_BT$ from the Fermi level of the leads. These requirements may be satisfied by the Co(tpy-(CH₂)₅-SH)₂ molecules studied by Park et al^{29,30}. 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 see if indeed the Wiedemann-Franz law is violated in these molecules, as implied by the results in this paper.

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