Validity of Wiedemann Franz law in small molecular wires

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We report our investigations on the finite size effects of Lorenz number in a molecular wire. Using Landauer-Büttiker formalism, we find that for sufficiently long wires there are two validity regimes of Wiedemann-Franz (WF) law, the cotunneling and the sequential tunneling regimes, while in small systems only the first regime survives. We compare our results with standard Kubo formula and explain its failure to detect the WF law in small systems. Furthermore, our studies on exponentially localized disordered wires show that Lorenz number value $L_0$ predicted by WF law is obtained only in the cotunneling regime. Also, Lorenz number $L$ exhibits typical distribution at different temperatures corresponding to different tunneling process. In particular, first order tunneling results in a low value of $L$ whereas second order tunneling recovers the universal value $L_0$.

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I. INTRODUCTION

Thermoelectricity is attracting huge scientific interest on account of its applications in future energy production and utilization\(^1\)\(^-\)\(^6\). Much of the work has focussed on developing efficient thermoelectric materials to convert waste heat energy to electric current and in reverse to perform refrigeration. Compared to bulk materials, low dimensional systems have the potential to achieve improved thermoelectric efficiency owing to their highly peaked density of states and to the high density of interfaces that could be used to reduce parasitic heat flow\(^7\)\(^-\)\(^10\). In this regard, studies related to thermal and electrical transport in nano scaled molecular wires have gained considerable attention.

Thermoelectric conversion efficiency is characterized by the figure of merit \(ZT = TS^2 \sigma / \kappa\), where \(S\) is the thermopower and \(\sigma\) and \(\kappa\) are the electrical and thermal conductivity at temperature \(T\). For practical applications, it is required that \(ZT \gg 1\). However, this is practically hard to achieve as the thermal and electrical conductivity are related by the Wiedemann-Franz (WF) law which states that the Lorenz number \(L = \kappa / \sigma T\) is constant\(^11\). The constant value \(L_0 = (\pi^2/3)(k_B/e)^2\) for non-interacting systems, where \(k_B\) is the Boltzmann constant and \(e\) the charge carried by each electron. WF law follows from the single particle Fermi liquid (FL) theory which assumes that both electric and thermal current are carried by the same Fermi liquid particles at sufficiently low temperatures, so that the Sommerfeld expansion can be applied\(^12\). In a non-interacting system where this FL theory holds WF law is valid even in the presence of arbitrary disorder\(^13\). Studies in interacting systems showed that the law is violated largely due to the non FL behavior\(^14\)\(^-\)\(^16\).

However, studies so far reported are limited to either one or two quantum molecules or in the thermodynamic limit. In mesoscopic physics, the thermodynamic limit is meaningless and one is interested in the transport properties of finite systems. Finite size effects are expected to influence the properties considerably in a one dimensional quantum system. For instance, the thermopower \(S\) does not follow the relation \(S \propto T\) as expected in the thermodynamic limit\(^19\). Also, Lorenz number is shown to diverge in a finite size closed system\(^20\). Above mentioned works follow from Kubo formula, without explicitly considering the connections to the baths. Recently, the transport properties obtained using the Kubo formula were shown to differ significantly from the Redfield Quantum Master Equation approach (QME) that takes into account the effect of baths\(^21\). In practice, it is required that both ends of the molecular wire are in contact with baths, which are able to exchange charges and energy with the wire. The validity regimes of WF law in these finite size molecular wires is still an open question.

Following the seminal work of Anderson\(^22\), disorder has played an important role in understanding the transport properties of mesoscopic systems. Moreover, disorder has interesting effects on the properties of a finite system as the transport properties are affected considerably, depending upon its size. For instance, a disordered system shows ballistic transport if the localization length is very large compared to the system length\(^23\). Conductivities of strongly localized systems decrease exponentially with the system size\(^24\). However, it is not yet clear how the Lorenz number varies with disorder in finite systems. While considering disordered systems, it is worthwhile to study the statistical distribution of observables. Studies in theses directions showed that the conductances of strongly disordered system follow log-normal distribution\(^25\). Hence, it is interesting to explore whether Lorenz number still holds this log-normal distri-
bution.

In this paper, we investigate the validity regimes of WF law in a finite non-interacting molecular wire attached to reservoirs using Landauer-Büttiker formalism for phase-coherent quantum transport from one reservoir to the other. With this approach we obtain conductances rather than conductivities and the Lorenz number is re-defined as \( L = \Xi/GT \), with \( G \) and \( \Xi \) electric and thermal conductances, respectively. We compare our results with two other commonly used formalisms, namely standard Kubo formalism and QME, in exploring the transport properties of finite sized systems. In the latter part of the work, the studies are extended to disordered systems. In particular, our results show that the validity regimes of WF law depend upon the finite size of the system even for a non-interacting system. For long clean wires, there are saturation plateaus of Lorenz number at the universal value of \( (\pi^2/3)(k_B/e)^2 \) at two temperature regimes, corresponding to the cotunneling and the sequential tunneling regime. As the wire length is reduced, one of the plateaus vanishes. We also find that the standard Kubo formalism and QME approach fail, for any system size, to obtain WF law in the cotunneling regime. With disordered localized wires, WF law is valid only in the cotunneling regime. In addition, Lorenz number shows typical distribution at different temperature regimes.

The outline of the paper is as follows. We introduce the model system and discuss the Landauer-Büttiker formalism to calculate conductances and the Lorenz number in Sec. II. Numerical results are discussed for a clean model in Sec. III and for a disordered one in Sec. IV. Finally, we draw our conclusions in Sec. V.

II. MODEL AND FORMALISM

We consider a molecular junction formed by connecting a one dimensional molecular wire between two electrodes. The Hamiltonian of our molecular system is

\[
H = H_W + H_E + H_{WE};
\]

\[
H_W = - \sum_{i=1}^{N-1} (c_i^\dagger c_{i+1} + \text{h.c.}),
\]

\[
H_E = \sum_{j=L,R} \sum_{k} E_{kj} d_{kj}^\dagger d_{kj},
\]

\[
H_{WE} = \sum_{k} (t_{kL} c_{i}^\dagger d_{kL} + t_{kR} c_{N}^\dagger d_{kR} + \text{h.c.}).
\]

The first term \( H_W \) corresponds to a wire of \( N \) sites with nearest neighbor interactions, the second term \( H_E \) to the two electrodes left (L) and right (R) and the last term \( H_{WE} \) to the wire-electrode coupling. The operators \( c_i^\dagger \) and \( d_{kj}^\dagger \) are creation (annihilation) operators of electrons in wire and electrode \( j \), respectively. \( E_{kj} \) is the energy of the \( k \)th electron in the \( j \)th electrode and \( t_{kj} \) is its tunneling amplitude. Here, the electrodes are reservoirs of non-interacting electrons in equilibrium at some temperature \( T \) and electrochemical potential \( \mu \).

Below we outline the calculations of thermoelectric properties in our model using Landauer-Büttiker formalism. The current through the wire is due to the electrons tunneling from one electrode to another. An electron at a given energy \( E \) scatters at the junction and can be transmitted through it or reflected back. The probability to tunnel across the junction is given by the transmission coefficient \( T(E) \). Hence, the electric \( (J_e) \) and thermal \( (J_q) \) current (from left to right reservoir) in the molecular wire are given by

\[
J_e = \frac{e}{h} \int dE T(E) [f_L(E) - f_R(E)],
\]

\[
J_q = \frac{1}{h} \int dE (E - \mu) T(E) [f_L(E) - f_R(E)].
\]

Here, \( e \) is the electronic charge, \( h \) is the Planck’s constant, \( f_L(E) \) and \( f_R(E) \) are the Fermi distribution in the left (L) and right (R) electrodes with temperature \( T_{L,R} \) and electrochemical potential \( \mu_{L,R} \). \( f_L, R(E) = \{\exp(-E - \mu_{L,R})/k_B T_{L,R} + 1\}^{-1} \) where \( k_B \) is the Boltzmann constant. In this work, we are interested in the linear response of the system and hence assume that the differences \( \Delta \mu = \mu_L - \mu_R \) and \( \Delta T = T_L - T_R \) are infinitesimally small. Hence, in Eq. (2), the electrochemical potential \( \mu \approx \mu_L \approx \mu_R \) and the temperature \( T \approx T_L \approx T_R \).

Using the nonequilibrium Green’s function technique, the transmission coefficient can be expressed as

\[
T(E) = \text{Tr}(\Gamma_L(E)G_{sL}(E)\Gamma_R(E)G_{sR}(E)),
\]

where \( \text{Tr} \) is the trace, \( G_{sL}(E) = (E - H_W - \Sigma_L - \Sigma_R)^{-1} \) is the retarded single particle Green’s function operator and \( \Gamma_L,R(E) = i[\Sigma_L,R(E) - \Sigma_L,R_{L,R}(E)] \) are the level broadening functions. \( \Sigma_L \) and \( \Sigma_R \) are the retarded self energies of the left and right electrodes respectively.

We assume wide band limit of the electrodes. Hence the level widths are energy independent and are given by \( \gamma_j = 2\pi \sum_k \vert t_{kj} \vert^2 \delta(E - E_{kj}) \). Furthermore, we take \( \gamma_L = \gamma_R = \gamma \). Thus, \( \Gamma_L = \gamma c_{i}^\dagger c_i, \Gamma_R = \gamma c_{N}^\dagger c_N \) and the Eq. (3) can be rewritten as

\[
T(E) = \gamma^2 \vert \langle 1 | G_{s} | N \rangle \vert^2.
\]

Note that \( \gamma \) is the coupling strength which physically measures the rate at which the electrons tunnel across the junction.

Using the Taylor expansion,

\[
f_L(E) \approx f_R(E) + \frac{\partial f_{L,R}(E)}{\partial \mu} \Delta \mu + \frac{\partial f_{L,R}(E)}{\partial T} \Delta T,
\]

in Eq. (2), the response of the system is given by

\[
\begin{pmatrix}
J_e \\
J_q
\end{pmatrix} =
\begin{pmatrix}
L_{11} & L_{12} \\
L_{21} & L_{22}
\end{pmatrix}
\begin{pmatrix}
\Delta \mu / eT \\
\Delta T / T^2
\end{pmatrix},
\]
where the Onsager coefficients $L_{11}, L_{12}, L_{21}, L_{22}$ are given by

$$L_{11} = \frac{T e^2}{\hbar} \int dE T(E) \left( -\frac{\partial f(E)}{\partial E} \right),$$

$$L_{12} = \frac{T e^2}{\hbar} \int dE T(E) \left( \frac{\partial f(E)}{\partial E} \right) (E - \mu),$$

$$L_{22} = \frac{T}{\hbar} \int dE T(E) \left( -\frac{\partial f(E)}{\partial E} \right) (E - \mu)^2,$$

$$L_{21} = L_{12}.$$  (7)

The (isothermal) conductance $G$, defined as the electric current under the application of the voltage $\Delta \mu/e$ with no temperature gradient, is

$$G = \frac{eJ_e}{\Delta \mu} \bigg|_{\Delta T = 0} = \frac{L_{11}}{T}. \quad (8)$$

The thermal conductance $\Xi$, the heat current per unit temperature gradient for zero electric current, is

$$\Xi = \frac{J_q}{\Delta T} \bigg|_{J_e = 0} = \frac{L_{11}L_{22} - L_{21}L_{12}}{L_{11}T^2}, \quad (9)$$

and the Lorenz number $L$ is

$$L = \frac{\Xi}{GT}. \quad (10)$$

For a smooth function $T(E)$, the Sommerfeld expansion of the integrals in (7) to lowest order in $k_B T/E_F$, with $E_F$ Fermi energy, leads to the Wiedemann Franz law

$$L = L_0 = \frac{\pi^2}{3} \left( \frac{k_B}{e} \right)^2. \quad (11)$$

In the following sections we investigate in detail the dependence of the Lorenz number $L$ on the temperature $T$ and coupling strength $\gamma$ for a clean and disordered molecular wire.

### III. CLEAN WIRE

The transport mechanisms in the molecular system can be understood from the transmission function $T(E)$ of the molecular wire. For a wire of $N$ sites, there are $N$ quantum states with discrete energies. The density of states and $T(E)$ in the limit $\gamma \to 0$ consist of series of delta functions corresponding to these energies. While coupling to electrodes, electrons can enter or leave the wire and hence these delta peaks are broadened due to the finite life time of the electrons. If the coupling is very weak then the density of states remain as delta peaks broadened by a factor proportional to the coupling strength $\gamma$ whereas for a strong coupling all the peaks merge. Depending upon its energy relative to the energy spacing between the different levels in the wire ($\Delta E$), an electron can tunnel the junction mainly in three different ways: 1) Sequential tunneling: At temperature $T \gg \Delta E$, the energy of the electron is very high and hence can tunnel across the junction in a sequential manner by spending a finite life time within the wire. Hence, the current in this regime is proportional to the coupling $\gamma$. 2) Cotunneling: This is a second order tunneling process occurring at temperatures $T \ll \Delta E$. In this regime, the current through the wire varies quadratically with the coupling strength $\gamma$. 3) Resonant tunneling: This occurs when the energy of an electron matches exactly one of the discrete energy levels in the wire. Under these conditions, the electron is transmitted with unit probability and the current through the system increases sharply.

Transmission coefficient $T(E)$ is a smooth function in the sequential and cotunneling regimes. Hence, the Sommerfeld expansion can be applied and we expect to recover WF law in these regimes. To investigate the validity of WF law, we have plotted the variation of Lorenz number with temperature $T$ for a wire of $N = 110$ sites in Fig. II Here we present the results for fixed coupling strength $\gamma = 10^{-4}$. (Throughout this paper we take $\hbar = e = k_B = 1$. Also, we set $\mu = 0$). As shown in Fig. II we found two plateaus where the law is satisfied exactly i.e., when the ratio $L/L_0$ is one. Our numerical analysis shows that these two valid regimes correspond to sequential and cotunneling process. Between these two plateaus, there is a region bounded by the temperatures $T_1$ and $T_2$ where, lowering $T$, the Lorenz number increases initially due to resonance tunneling and thereafter decreases when the mixing of higher order tunneling occurs.
In order to clarify our statement that WF law is satisfied only in sequential and cotunneling regime, we study the variation of \( T_1 \) and \( T_2 \) with the number of sites \( N \). Note that these regimes correspond to cases where the energy level spacing \( \Delta E \ll T \) and \( \Delta E \gg T \) respectively. The mean energy level spacing \( \Delta E \) in the molecular wire decreases with the number of sites \( N \) as \( 1/N \). Thus dependences of temperatures \( T_1, T_2 \propto 1/N \) are expected. This is indeed what we obtain in Fig. 2. Here, the top panel represents the highest temperature \( T_1 \) in the cotunneling regime where the WF law is satisfied. The bottom panel represents the lowest temperature \( T_2 \) in the sequential tunneling regime. Decreasing the temperature below \( T_2 \) results in resonant tunneling and deviation of \( L \) from its constant value of \( L_0 \). The temperatures \( T_1 \) and \( T_2 \) are calculated such that the ratio \( L/L_0 \) is one up to third decimal point.

From Fig. 2 it is clear that the temperature \( T_2 \) is 0.075 for a chain of 40 sites. The decrease \( T_2 \propto 1/N \) suggests that \( T_2 \) for \( N = 10 \) should be \( \approx 0.18 \). In Fig. 3 we have plotted the Lorenz number ratio as a function of temperature for \( N = 10 \) sites. From the figure, it is clear that at \( T = 0.18 \) the ratio \( L/L_0 \) is 0.953. Also, Lorenz number increases linearly with decreasing temperature \( T \) without any saturation in the sequential tunneling regime. Indeed, numerical results showed that the plateau of constant Lorenz number seen in the sequential tunneling regime decreases with decreasing \( N \) and is almost absent below \( N = 40 \). This is justified as it follows from the analytical derivation of WF law that the Lorenz number is obtained only at low temperatures \( T \ll E_F \) where Sommerfeld expansion holds. Note that the conduction band width for our model is \([-2, 2]\). Thus, the Fermi energy, the energy of the highest occupied energy level, \( E_F \) is of the order of 2 (see for instance ref.\textsuperscript{15}).

Another important observation is that the magnitude of violation of the WF law is almost independent of length of the wire.

So far we have discussed only the length dependence of Lorenz number ratio for weak couplings to the electrodes. However, the strength of the coupling also plays an important role in modifying the transmission spectrum. Hence we have investigated the Lorenz number as a function of the coupling strength \( \gamma \) in a wire of length \( N = 100 \) in Fig. 4. As seen from the figure, the large variation of Lorenz number is smoothed for stronger coupling. This is due to the fact that a strong coupling broadens the transmission function such that different resonance peaks overlap. Hence, it is difficult to observe the sharp increase in current due to the delta peaked transmission function.

Our numerical analysis shows that the temperature \( T_Q \) at which \( L \) is maximum and below which mixing regime (mixing of first order and second order tunneling process) occurs linearly increases with \( \gamma \). This is illustrated in Fig. 5 where \( T_Q \) is plotted versus \( \gamma \) for a wire of 10 sites. Thus, for a wire with \( \gamma \to 0 \), the temperature \( T_Q \to 0 \).
Our analytical calculations show that the Lorenz number diverges as $1/T^2$ for $\gamma \to 0$ (Details of the calculations are given in the Appendix). This perturbative (in $\gamma$) result is plotted as a straight line in Fig. 4. Also, $T_Q$ decreases $\propto 1/N$ with increasing length of the wire.

Another approach commonly used in investigating the transport properties of finite systems is the Kubo formalism. Here, details regarding the baths (in our case electrodes) and coupling to the system (wire) are neglected and only the steady state distribution of the system is used. These assumptions are justified for investigating the linear response of an infinite system. However, formulas for finite systems are derived by extrapolating results of $N \to \infty$. The electrical and thermal conductivities, $\sigma$ and $\kappa$, can be calculated using Eqs. (8) and (9) but with $\sigma$ and $\kappa$ instead of the conductances $G$ and $\Xi$, and with the Onsager coefficients given by

$$L_{11} = e^2 T |D_{11}\delta(\omega) + \sigma_{11}(\omega)|,$$
$$L_{12} = e T |D_{12}\delta(\omega) + \sigma_{12}(\omega)|,$$
$$L_{22} = T |D_{22}\delta(\omega) + \sigma_{22}(\omega)|.$$

Here,

$$D_{lm} = \frac{\pi \beta^m}{ZN} \sum_{E_i=E_k} e^{-\beta E_i} \langle i|j|k\rangle \langle k|j_m|i\rangle,$$

$$\sigma_{lm}(\omega) = \frac{\pi \beta^{m-1}}{ZN} \frac{1-e^{-\beta \omega}}{\omega} \sum_{E_i\neq E_k} e^{-\beta E_i} \times \langle i|j|k\rangle \langle k|j_m|i\rangle \delta(\omega - \Delta E).$$

$E_i$ and $|i\rangle$ are the $i$th Eigenenergy and Eigenstate of the system, $\Delta E = E_i - E_k$, $\omega$ is the frequency, $\beta = 1/k_B T$, $Z$ is the partition function and $j_1$ and $j_2$ are the charge and heat currents. Currents $j_1$ and $j_2$ are calculated as $j_1 = J_c$ and $j_2 = J_q - \mu J_c$ where $J_{c|q} = i \sum_{l=1}^{N-1} [h_{l-1}, d_l]$, $d_l$ is the number of electrons in the wire and $d_2 = h_{N-1}$ is the local system Hamiltonian. Note that $H_W = \sum_{l=1}^{N-1} h_l$ where $h_l = c_l^\dagger c_{l+1}^\dagger + h.c.$

Fig. 5 shows the ratio of Lorenz number calculated using the above formula for our model with $N = 200$ sites.
For comparison, results obtained using the Landauer-Büttiker formalism are also plotted. The results were the same till temperature \( T = 0.03 \) after which the ratio decreases by using the Kubo formula. Let \( T_K \) be the temperature at which deviation occurs. We found that the temperature \( T_K \) decreases \( \propto 1/N \) with the increase in the length \( N \) of the wire. This can be understood as follows. Eqs. (12) are exact only for infinite systems for which the partition function \( Z = \sum_i e^{-\beta E_i} \gg 1 \). For small molecular wires, \( Z \) can be large only for high temperature \( T \). Fig. 7 shows the plot of the divergence temperature \( T_K \) with the variation of length of the wire \( N \). It is clear from the Figs. 2 and 7 that the temperature \( T_2 < T_K \). This implies that Kubo formula only gives the results for sequential tunneling regime and hence can predict only one regime of WF law even in arbitrarily long wires.

Finally, we have compared the results obtained by means of the Landauer-Büttiker approach with the Redfield QME\(^{21,27,28} \). By construction QME is first-order perturbative in the coupling \( \gamma \) and hence reproduces the results in the perturbative regime of the Landauer formula. This regime is bounded by the temperature \( T_Q \) from below. Since \( T_1 < T_Q \), QME cannot reproduce WF in the cotunneling regime.

IV. DISORDERED WIRE

In this section, we discuss the validity of WF law in a disordered wire. We model the disorder by introducing on-site energies \( \epsilon_i \) with randomness. The Hamiltonian of such a wire is

\[
H_{\text{dw}} = -\sum_{i=1}^{N-1}(c_i^\dagger c_{i+1} + \text{h.c.}) + \sum_{i=1}^{N} \epsilon_i c_i^\dagger c_i,
\]

where \( \epsilon_i \) are random numbers uniformly distributed in the interval \([-W, W]\). In one dimension, even for arbitrary small disorder strength, the system becomes exponentially localized and exhibits insulating behavior\(^{20} \). Conductances of disordered wires decrease exponentially with the length of the wire as \( G = G_0 e^{-N/\xi} \), \( \Xi = \Xi_0 e^{-N/\xi} \), where \( \xi \) is the localization length. Also, distributions of the conductances are log-normal parameterized solely by its mean value. However, these conclusions are true only at \( T = 0 \) K. At any non-zero temperature, the exponential decrease is not apparent as the electrons can hop from one localized state to another\(^{20} \).

Localization length is related to disorder strength as \( \xi \sim 25/W^2 \). We restrict our analysis to wires with \( \xi \ll N \) so that the system is insulating at all temperatures. For this we consider a wire of length \( N = 100 \) with disorder strength \( W = 5 \) and coupling strength \( \gamma = 10^{-4} \). The straight line corresponds to the case of clean wire. Here regime (1), (2), (3) and (4) corresponds to cotunneling, mixing, resonant tunneling and sequential tunneling respectively. Note that only in the cotunneling regime the results are the same for both wires.

Localization length is related to disorder strength as \( \xi \sim 25/W^2 \). We restrict our analysis to wires with \( \xi \ll N \) so that the system is insulating at all temperatures. For this we consider a wire of length \( N = 100 \) with disorder strength \( W = 5 \). Localization length of the wire is \( \xi \sim 1 \). As the conductivities exhibit giant fluctuations for different samples, we take logarithmic averages. Dependence of logarithm of Lorenz number \( \langle \ln L \rangle \) on temperature \( T \) for this model is depicted in Fig. 8. The values are obtained by taking average over 1500 disorder realizations. Logarithm of Lorenz number \( \ln L = \pi^2/3 \) is equal to 1.1908 (in units where \( e = k_B = 1 \)). From the figure, it is clear that the plateau of constant Lorenz
number $L_0$ is recovered at low temperatures. This corresponds to cotunneling regime as indicated by (1) in the figure. As the temperature is increased, mixing regime (region (2) in Fig. 8) is reached where the Lorenz number decreases with increase in temperature. The decrease is apparent till the temperature where the resonant tunneling occurs (region (3)). Further increasing temperature increases the Lorenz number until the sequential tunneling regime. Finally, in the sequential tunneling regime as shown by (4) in the figure, Lorenz number decreases linearly with temperature.

To better understand the differences in the variation of Lorenz number for the disordered and undisordered wire, we have plotted the variation of logarithm of Lorenz number $L$ for clean wire as a straight line in Fig. 8. Our findings in this regard are summarized as follows: a) The Lorenz number for the disordered wire is always equal to or less than that of the clean wire at all temperatures. b) There is no saturation plateau of constant Lorenz number in the sequential tunneling regime. This is in contrast to the results in ref. 22 where it was pointed out that WF law is violated in the resonant tunneling regime and is valid far away from the resonance in the sequential tunneling regime. We note that due to the finite size of our wire sample to sample deviations from the WF law do not self average to zero in the higher temperature regime. Indeed, we numerically observe that the variance saturates to a constant value and is discussed in the latter part of this section. c) The temperature $T_1$ at which the Lorenz number $L_0$ is recovered is shifted to lower temperature. This follows from the argument that for $\xi \ll N$, disorder reduces the width of the transmission peaks and the transmission function is smooth only at low temperatures compared to the clean case. Therefore, the Sommerfeld expansion substantiating WF law is valid only at lower temperatures than in the clean case.

So far we have focused only on the mean value of the Lorenz number. However, in a disordered system with localization length much smaller than the system length i.e., $\xi \ll N$, fluctuations can be as large as the average value. Under these conditions, only a statistical distribution provides meaningful information about the system properties. It is well known that in these highly localized systems, conductance distribution is log-normal i.e., ln$G$ (or ln$\Xi$) follows normal distribution at $T = 0$ K. In the latter part of this section, we analyze in detail the distribution followed by Lorenz number in the different tunneling regimes.

1) Cotunneling regime: It is clear from Fig. 8 that in this regime we reproduce the WF law. From our numerical analysis we found that fluctuations of the conductances are almost twice as that of the average value. This has been advocated as the evidence for insulating behavior in one dimensional systems and thus we ensure that disordered wire is indeed localized. We find that the fluctuations of both conductances are almost perfectly correlated and hence the Lorenz number $L_0$ with almost zero variance is obtained. This is clear from Fig. 9 (a) where the distribution at temperature $T = 0.00001$ is shown. A delta peak around the value $\pi^2/3 = 3.2898$ is obtained at all temperatures in this regime.

2) Mixing regime: In this regime we found that the logarithms of conductances still follow normal like distribution with variance almost twice as that of average. However, the skewness is non-zero. Moreover, the fluctuations of both conductances are not perfectly correlated and therefore the constant value of Lorenz number $L_0$ is not recovered. Interestingly, we obtain a bimodal distribution for the Lorenz number. This is shown in Fig. 9 (b) for temperature $T = 0.001$. One of the two peaks corresponds to the value $\pi^2/3$ while the other corresponds to a value near to zero. The peak around $\pi^2/3$ is largely populated at low temperatures. By increasing the temperature, this peak is reduced while the peak with small Lorenz number is populated. This continues till the resonant tunneling regime is reached where there is only one peak. Indeed, our results suggest that the two peaks correspond to first and second order tunneling process. For disordered wires, second order tunneling favors WF law with Lorenz number $L_0$ whereas first order tunneling favors a small value of Lorenz number.

3) Resonant tunneling regime: Here, similarly to the mixing regime case, the logarithm of conductances has a skew normal distribution (a normal distribution but with non zero skewness). In contrast to the mixing regime, the variances of the conductances decrease faster with temperature compared to their mean values and are almost of the order of the mean values. The distribution of the
distribution in this regime at temperature $T$ plotted the distribution of the logarithm of value with long tails towards the large value and can be in the sequential tunneling regime.

The Lorenz number distribution at different temperatures $T_2$ and $T_3$ with strengths $W_1$ and $W_2$ for a wire of length $N = 100$ with disorder $W = 5$ in the sequential tunneling regime at temperature $T = 20$ and $T = 1000$ c). The bottom panel represents c) the variance ($\Sigma^2$) and d) the skewness ($m_3/\Sigma^3$) of the Lorenz number distribution at different temperatures in the sequential tunneling regime.

Lorenz number in this regime is always peaked near zero value with long tails towards the large value and can be approximated to a log-normal distribution. Hence, we plotted the distribution of the logarithm of $L$. A typical distribution in this regime at temperature $T = 0.01$ is shown in Fig. 9 (c) and is in accordance with our expectation.

4) Sequential tunneling regime: Our results in this regime indicate that the logarithm of the conductances has a distribution similar to that of resonant tunneling regime. However, the variance initially decreases with increasing temperature and thereafter saturates. The distribution of the Lorenz number is still peaked around very small value. Hence, similarly to the case of resonant tunneling regime, we plotted the logarithmic distribution in Fig. 10 (d). Here, a skew normal distribution of increasing variance and decreasing skewness is obtained as the temperature is initially increased. However, after the initial change, both the variance and the skewness saturate to a constant value as the fluctuations of the conductances also saturate. Thus, a distribution invariant with temperature emerges and is demonstrated in the top panel of Fig. 10. Here the panels (a) and (b) correspond to temperature $T = 20$ and 1000 respectively. In order to better clarify the emergence of the invariant distribution, we have plotted the variance ($\Sigma^2$) and the skewness ($m_3/\Sigma^3$, where $m_3$ is the third moment about the mean) of the distributions in the bottom panel. It is clear from the figure that the variance saturates around the value 15 whereas the skewness fluctuates around $-0.85$ at high temperatures, indicating a temperature invariant distribution.

V. CONCLUSIONS

Using the Landauer-Büttiker formalism, we investigated the validity of WF law in finite sized molecular wires with and without disorder. For a clean system, we found that the validity regimes of WF law depend upon how an electron tunnels across the wire. In particular, Lorenz number $L_0 = (\pi^2/3)(k_B/e)^2$ is obtained in the cotunneling and the sequential tunneling regime as long as the temperature in these regimes is much less than Fermi energy $E_F$. For wires with length $N \lesssim 40$, the resonant tunneling occurs for temperatures larger than the Fermi energy $E_F$ and hence WF law is valid only in cotunneling regime. We further compared our results with standard Kubo formula and with Redfield quantum master equation and found that the two approaches diverge from the Landauer formula at particular temperatures $T_K$ and $T_Q$ that decrease with the increase in the length of the wire $N$. The temperatures $T_K$ and $T_Q$ are always larger than the temperature at which cotunneling occurs and hence it follows from our results that Kubo formula and QME will differ from the Landauer-Büttiker formalism even in the limit of infinite length of the wire.

Furthermore, we explored an exponentially localized disordered wire using the Landauer-Büttiker formalism. Here, even for wires of length $N = 100$, WF law is valid only at very low temperatures corresponding to the cotunneling regime. In contrast to an infinitely long wire, there is no self averaging of the sample to sample deviations from the WF law at higher temperatures in small wires. Moreover, Lorenz number shows typical distributions at different temperatures corresponding to different tunneling processes. A delta distribution peaked around the value $L_0$ is obtained in the cotunneling regime while a bimodal distribution is obtained in the regime where the mixing of first and second order tunneling processes occurs. Logarithm of Lorenz number shows skew normal distribution in the resonant and sequential tunneling regime. In particular, we find that a distribution with constant variance and skewness emerges in high temperature regime. We infer from our results that first order tunneling favors a small Lorenz number whereas second order tunneling favors the universal value $L_0$ in a disordered wire.

Finally, we point out that we have not addressed the effects of interaction between the electrons in our model. Commonly used approaches in investigating the transport properties of interacting finite sized systems are standard Kubo formalism and QME. We have discussed numerically in detail the failure of Kubo formalism in determining the WF law in finite sized systems. Furthermore, it follows from our numerical analysis that standard QME approach also fails. Standard QME is derived by taking second order perturbative expansion of tunneling amplitudes $t_{kj}$ and is only linear in coupling
strength $\gamma$. Hence, the currents calculated using this formalism is always of first order in $\gamma$. However, in the cotunneling regime currents varies quadratically with $\gamma$. A fourth order perturbative expansion of tunneling amplitudes in QME indeed explains this regime\cite{31}. Thus, we note that to investigate the Lorenz number in finite sized strongly interacting systems the standard QME has to be extended to include terms of $i\hbar\beta$.

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**Appendix A: ANALYTICAL DERIVATION**

In this section, we analytically derive the electric ($J_e$) and thermal ($J_q$) currents for a wire weakly coupled to the electrodes ($\gamma \to 0$).

From the definition of the single particle Green’s function operator $G_s$, it follows that $G_s$ is the inverse of the matrix

$$
\begin{pmatrix}
E - i\frac{\gamma}{2} & -1 & \cdots & 0 \\
-1 & E & \cdots & 0 \\
\vdots & \vdots & \ddots & \vdots \\
0 & \cdots & E & -1 \\
\cdots & \cdots & \cdots & -1 & E + i\frac{\gamma}{2}
\end{pmatrix}
$$

(A1)

Thus, $\langle 1|G_s|N\rangle$ is the $(1, N)$ element of the inverse of the above matrix.

Consider a wire with $N=1$ coupled to both left and right reservoirs. Here, $\langle 1|G_s|N\rangle = 1/(E - i\gamma)$ and hence

$$
J_e = \frac{\gamma^2}{2\pi\hbar} \int dE \frac{1}{E^2 + \gamma^2} [f_L(E) - f_R(E)].
$$

(A2)

Apart from the constant factor, the first integral is of the form

$$
I = \int dE \frac{1}{E^2 + \gamma^2} f(E) = \int dE g(E),
$$

(A3)

which can be evaluated using residue theorem. The first part of the integrand has two poles namely $E_{\pm} = \pm i\gamma$ whereas the second part has infinite number of poles namely Mastubara frequencies at $E_n = \mu + \frac{1}{\beta}(2n + 1)\pi$ with $n \in \mathbb{Z}$ and $\beta = 1/T$ (we set $k_B = 1$).

To evaluate the integral, we consider two distinct contours, one on the upper half plane ($C_1$) and the other on the lower half plane ($C_2$). Each contour runs from $-R$ to $R$ on the real axis and then comes back following semicircle of radius $R$. Thus, the integration domain is the sum of the following two parts:

$$
\int_{C_1} = \int_{-R}^{R} + \int_{C_R} : \int_{C_2} = \int_{-R}^{R} + \int_{C_R}^{R}
$$

(A4)

where $C_R$ ($C_R^t$) denotes the upper (lower) semicircle. Since the integrand function satisfies the ‘big circle lemma’ (Jordan’s lemma), the contribution of the integrals on the semicircles is zero when $R \to \infty$ and thus only the contribution from the real axis integration survives. Applying the residue theorem, we get

$$
I = \frac{1}{2} 2\pi i \left[ \text{res} g(E_+) - \text{res} g(E_-) \right] + \sum_{n=0}^{\infty} \text{res} g(E_n) - \sum_{n=-\infty}^{\infty} \text{res} g(E_n).
$$

(A5)

The factor $1/2$ follows from the fact that integrating on two contours real axis integration is encountered twice. Now the first two terms in Eq. (A5) are

$$
\text{res} g(E_+) = \lim_{E \to E_+} g(E)(E - E_+) = 0,
$$

$$
\text{res} g(E_-) = \lim_{E \to E_-} g(E)(E - E_-) = \frac{f(E_-)}{(E_+ - E_-)}.
$$

(A6)

and

$$
\text{res} g(E_+) - \text{res} g(E_-) = \frac{1}{(E_+ - E_-)} [f(E_+) - f(E_-)] = 2\text{Re} [f(E_+)]
$$

$$
= \frac{1}{i\gamma} \text{Re} [(fi\gamma)].
$$

(A7)

Thus, their differences is

$$
\text{res} g(E_+) - \text{res} g(E_-) = \frac{1}{(E_+ - E_-)} [f(E_+) - f(E_-)] = 2\text{Re} [f(E_+)]
$$

$$
= \frac{1}{i\gamma} \text{Re} [(fi\gamma)].
$$

(A8)

The residue corresponding to the $n$th Mastubara frequency $E_n$ is

$$
\text{res} g(E_n) = \frac{1}{E_n^2 + \gamma^2} \frac{1}{\beta} \left[ \exp[\beta(E - \mu)] + 1 \right] |_{E = E_n}
$$

$$
= \frac{1}{E_n^2 + \gamma^2} \frac{1}{\beta} \left[ \exp[\beta(E - \mu)] + 1 \right] |_{-1} = \frac{1}{E_n^2 + \gamma^2}
$$

(A9)

Here we point out that

$$
E_{n-1} = \mu + \frac{1}{\beta} (-2(n + 1) + 1)i\pi
$$

$$
\mu + \frac{1}{\beta} (-2n - 1)i\pi = E_n^*.
$$

(A10)

Also,

$$
\sum_{n=-\infty}^{\infty} \text{res} g(E_n) = \sum_{m=0}^{\infty} \text{res} g(E_{-m-1}) \quad (n = -m - 1)
$$

$$
= \sum_{n=0}^{\infty} \text{res} g(E_n^*).
$$

(A11)
Therefore, the difference between the residues is

\[
\text{res } g(E_n) - \text{res } g(E_{n-1}) = -\frac{1}{\beta} \left[ \frac{1}{E_n^2 + \gamma^2} - \frac{1}{E_{n-1}^2 + \gamma^2} \right] = -\frac{i}{\beta} 2 \text{Im} \left[ \frac{1}{E_n^2 + \gamma^2} \right]. \tag{A12}
\]

Substituting all these results in Eq. (A2) we get,

\[
J_e = \frac{e \gamma^2}{2\pi h} \left\{ \frac{\pi}{\gamma} \text{Re}[f_L(i\gamma)] - \text{Re}[f_R(i\gamma)] \right. \\
+ \frac{2\pi}{\beta L} \sum_{n=0}^{\infty} \text{Im} \left( \frac{1}{E_n^2 L + \gamma^2} \right) \\
- \frac{2\pi}{\beta R} \sum_{n=0}^{\infty} \text{Im} \left( \frac{1}{E_n^2 R + \gamma^2} \right) \right\}, \tag{A13}
\]

where \(E_{nL,R} = \mu_{L,R} + \beta_{L,R}^{-1}(2n+1)i\pi\) with \(n \in \mathbb{Z}\). In the limit of weak coupling i.e., \(\gamma \ll T\), the above equation reduces to

\[
J_e \simeq \frac{e \gamma}{2h} [f_L(E = 0) - f_R(E = 0)]. \tag{A14}
\]

Note that in the last formula \(E = 0\) should be substituted by the dot’s energy \(E = \epsilon_0\) in the case the single dot Hamiltonian \(H_W = \epsilon_0 c^2 c\).

For a wire with \(N = 2\),

\[
\langle 1 | G_s | N \rangle = \frac{1}{(E - E_1 + i\frac{\gamma}{2})(E - E_2 + i\frac{\gamma}{2})}, \tag{A15}
\]

where \(E_j = 2 \cosh\{\pi/(N + 1)\}j\) \((j = 1, 2)\). Thus, the current \(J_e\) is given by

\[
J_e = \frac{e \gamma^2}{2\pi h} \int dE \frac{f_L(E) - f_R(E)}{[(E - E_1 + i\frac{\gamma}{2})(E - E_2 + i\frac{\gamma}{2})]^2}. \tag{A16}
\]

Following the same steps of \(N = 1\), we obtain

\[
J_e = \frac{\gamma^2}{2\pi h} \frac{1}{2\pi i} \left\{ \frac{2\text{Re}[f_L(E_1 + i\frac{\gamma}{2})] - \text{Re}[f_R(E_1 + i\frac{\gamma}{2})]}{i\gamma(E_1 - E_2 + i\gamma)(E_1 - E_2)} \\
+ \frac{2\text{Re}[f_L(E_2 + i\frac{\gamma}{2})] - \text{Re}[f_R(E_2 + i\frac{\gamma}{2})]}{i\gamma(E_2 - E_1 + i\gamma)(E_2 - E_1)} \right\}. \tag{A17}
\]

In the limit of \(\gamma \to 0\), the current \(J_e\) is

\[
J_e \simeq \frac{e \gamma}{\hbar} \left[ \frac{f_L(E_1) - f_R(E_1)}{(E_1 - E_2)^2} \right. \\
+ \left. \frac{f_L(E_2) - f_R(E_2)}{(E_2 - E_1)^2} \right]. \tag{A18}
\]

Similarly, for wire of length \(N\) we get

\[
J_e \simeq \frac{e \gamma}{\hbar} \sum_{k=1}^{N} \frac{f_L(E_k) - f_R(E_k)}{\prod_{j \neq k}(E_k - E_j)^2}, \tag{A19}
\]

for the electric current and

\[
J_q \simeq \frac{e \gamma}{\hbar} \sum_{k=1}^{N} \frac{(E_k - \mu)[f_L(E_k) - f_R(E_k)]}{\prod_{j \neq k}(E_k - E_j^2)}, \tag{A20}
\]

for the thermal current, with \(E_j = 2 \cos\{\pi/(N + 1)\}j\) \((j = 1, ..., N)\). Using the Taylor expansion in Eq. (3), the difference of the Fermi functions reads,

\[
f_L(E_k) - f_R(E_k) = \frac{e^3(E_k - \mu)}{(e^3(E_k - \mu) + 1)^2} [\Delta T T^2 + \Delta \mu T] \]

\[
= -\frac{1}{4} \cosh^2 \left( \sqrt{\frac{3}{2}} \frac{\Delta T}{T^2} \right) \times [(E_k - \mu) \frac{\Delta T}{T^2} + \frac{\Delta \mu}{T}]. \tag{A21}
\]

The above expressions are used in Eqs. (3), (9) and (10) for calculating conductances \(G\) and \(\Xi\) and the Lorenz number \(L\) in Fig. 4. It is clear from the above analytical calculations that conductances \(G \propto 1/T\) and \(\Xi \propto 1/T^2\) and thus the Lorenz number \(L = \frac{\Xi}{G^2} \propto 1/T^2\).
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