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# Wiedemann–Franz Law for Molecular Hopping Transport

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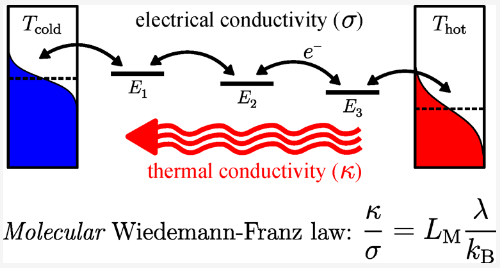

**ABSTRACT:** The Wiedemann–Franz (WF) law is a fundamental result in solid-state physics that relates the thermal and electrical conductivity of a metal. It is derived from the predominant transport mechanism in metals: the motion of quasi-free charge-carrying particles. Here, an equivalent WF relationship is developed for molecular systems in which charge carriers are moving not as free particles but instead hop between redox sites. We derive a concise analytical relationship between the electrical and thermal conductivity generated by electron hopping in molecular systems and find that the linear temperature dependence of their ratio as expressed in the standard WF law is replaced by a linear dependence on the nuclear reorganization energy associated with the electron hopping process. The robustness of the molecular WF relation is confirmed by examining the conductance properties of a paradigmatic molecular junction. This result opens a new way to analyze conductivity in molecular systems, with possible applications advancing the design of molecular technologies that derive their function from electrical and/or thermal conductance.

**KEYWORDS:** *Wiedemann–Franz law, electrical conductivity, thermal conductivity, molecular junction, molecular electronics*

Electrical and thermal conductance are the principal transport mechanisms giving rise to both the functionality and limitations of the majority of devices in the modern technological infrastructure. Because of this importance, understanding the interplay between these mechanisms is paramount in the development of next-generation technologies. In metals, the relation between electrical conductivity $\sigma$ and the electronic contribution to the thermal conductivity $\kappa$ can be described using the Wiedemann–Franz (WF) law[1]

$$\frac{\kappa}{\sigma} = \frac{\pi^2}{3}\left(\frac{k_{\text{B}}}{e}\right)^2 T = LT \tag{1}$$

where $L = \frac{\pi^2}{3}(k_{\text{B}}/e)^2$ is the Lorenz number, $e$ is the electron charge, $k_{\text{B}}$ is the Boltzmann constant, and $T$ is the temperature. The WF law forms the basis for analyzing the conductivity of myriad systems and materials in which the dominant energy transport mechanism is the nearly free motion of charge carriers.[2−8] There is no equivalent law, however, for molecular systems where electron transport is often dominated by inelastic hopping between redox sites, and therefore, the theoretical picture of a possible relationship between the electric and thermal conductivities of such systems is currently lacking.

The analysis of electrical conductance in single-molecule devices is a well-established field that has primarily been motivated by the goal of designing and fabricating new nanoscale molecular electronics.[9−14] In contrast, the examination of thermal conductance that arises from electron transfer (ET) between molecules is a nascent research area. A recent focus on electronic thermal conductance in molecular systems has been brought about by three particular advances: (a) newly developed experimental techniques that allow the measurement of temperature gradients over length scales commensurate with the distances involved in molecular ET processes,[15−17] (b) the development of a theory that describes electron-transfer-induced (ETI) heat transport, a phenomenon in which ET across a thermal gradient between molecules induces a heat current,[18−25] and (c) recent experiments in which the thermal conductivity of a single molecule has been measured for the first time.[26,27] These advances serve as impetus for analyzing the relations between different types of conductivity in molecules.

Here, the ratio between ETI thermal conduction and electrical conduction is derived for purely molecular systems and then numerically validated in a molecular junction—a device that is broadly applied in the development of nanotechnologies. We term this ratio a *molecular* Wiedemann–Franz (MWF) law, in analogy with the WF law for metals. Experimental examination of this MWF relation could be performed using typical molecular junction setups[28−33] by measuring the thermal conductance properties of a junction with suppressed phononic thermal conductivity and/or by taking two different measurements, first using conducting leads and then insulating leads, where the difference between them will be the ETI thermal conductivity.[34,35]

Our focus on a system in which electronic conduction is dominated by hopping (i.e., successive tunneling events) does

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not preclude other contributions to the total heat conduction, namely, phononic and radiative heat conduction mechanisms. Here, we ignore both of these contributions in order to draw a direct analogy with the standard WF law. Calculations comparing ETI and phononic heat transport suggest that the ETI thermal conductivity could be of the order or even greater than the phononic thermal conductivity in properly engineered systems.[23] Moreover, recent experimental and theoretical work suggests that in molecular conduction junctions the radiative thermal conductance could be of the same order as the other contributions (ETI, electronic, and phononic) to the total thermal conductance.[5,27,36]

To derive a MWF law,[37] consider a system consisting of identical molecular charge transfer sites at a density $\rho$ so that the distance between the center of the sites is $d = \rho^{-1/3}$. The electron transfer rate between identical molecular sites is given by the standard Arrhenius form $k = k_0 \mathrm{e}^{-E_A/k_BT}$, where $E_A = 2\lambda/4$ being the site reorganization energy (so that $2\lambda$ is the total reorganization energy, an important physical parameter in condensed-phase ET reactions which parametrizes the electron−phonon coupling).[38,39] In the presence of an applied electric field $E$, the voltage difference between sites in the direction of the field is $V = Ed = E\rho^{-1/3}$. Electrical conductivity $\sigma$ is defined from

$$J_{\mathrm{el}} = \sigma E = \sigma \frac{V}{d} \tag{2}$$

where $J_{\mathrm{el}}$ is the electrical current density. The electric current between a pair of identical hopping sites in the field direction is

$$\mathcal{J}_{\mathrm{el}} = e\chi(1-\chi)k_0(\mathrm{e}^{-E_A/k_BT} - \mathrm{e}^{-(E_A+eV)/k_BT}) \tag{3}$$

where $\chi$ is the probability that a site is occupied by an electron, i.e., the fraction of occupied sites in the system, and the term $\chi(1 - \chi)$ enforces the avoidance of multiple site occupancy. The associated electrical conductivity is obtained as follows: Consider a volume element with unit surface area and thickness $d$. The surface density of sites in this volume element is $\rho_s = \rho d = d^{-2}$, which is also a measure of the number of pairs across a surface in a picture where each site on one side of the dividing surface finds its nearest-neighbor on the other side of the surface. The electric current density in the field direction is

$$\begin{aligned} J_{\mathrm{el}} &= \mathcal{J}_{\mathrm{el}}\rho_s \\ &= e\chi(1-\chi)\rho_s k_0(\mathrm{e}^{-E_A/k_BT} - \mathrm{e}^{-(E_A+eV)/k_BT}) \\ &\approx \frac{e^2\chi(1-\chi)\rho d^2 kE}{k_BT} \end{aligned} \tag{4}$$

where the last approximation is valid in the limit $eV \ll k_BT$. Equation 4 implies that the electrical conductivity of the system is

$$\sigma = \frac{e^2\chi(1-\chi)\rho d^2 k}{k_BT} \tag{5}$$

Equation 5 is derived for bulk systems. The relationship between electron transfer and conduction has also been established in molecular conduction junctions.[40−43]

Next, consider the same system in the absence of an electric field but in the presence of a temperature gradient $\nabla T$. The thermal conductivity $\kappa$ is defined from

$$\mathbf{J}_Q = -\kappa\nabla T \tag{6}$$

where $\mathbf{J}_Q$ is the heat current density. In the direction of the temperature gradient, the heat current density is $J_Q = -\kappa\nabla_x T$, where $\nabla_x T = \Delta T/d$ with $\Delta T$ being the temperature difference between nearest sites. We want to calculate the thermal conductivity in this system due to electron hopping between sites with different temperatures. To this end, consider two neighboring charge transfer sites $a$ and $b$ which are assumed to be at different local equilibrium temperatures $T_a = T + \Delta T/2$ and $T_b = T - \Delta T/2$ but are otherwise identical and thus have the same electron occupation energy $E'$ and reorganization energy $\lambda$. In the absence of a driving electric field, the number of electron hops from site $a$ to site $b$ and from site $b$ to site $a$ per unit time is $\chi(1 - \chi)k$. Each such hop (in any direction) is associated with heat transfer $Q$, the amount of which is given by[19]

$$Q_{a,b} = Q_{b,a} = \lambda\left(\frac{T_b - T_a}{T_a + T_b}\right) = -\frac{\lambda}{2}\frac{\Delta T}{T} \tag{7}$$

Hence, the heat current between sites is

$$\mathcal{J}_Q = \chi(1-\chi)k(Q_{a,b} + Q_{b,a}) = -\frac{\chi(1-\chi)k\lambda\Delta T}{T} \tag{8}$$

The current density in the direction of the gradient is

$$J_Q = \mathcal{J}_Q\rho_s = -\frac{\chi(1-\chi)k\lambda}{Td}\nabla_x T \tag{9}$$

and after using eq 6 we obtain

$$\kappa = \frac{\chi(1-\chi)k\lambda}{Td} \tag{10}$$

which is the ETI thermal conductivity.

Combining the results in eq 5 and eq 10, we arrive at a WF relation for molecular systems

$$\frac{\kappa}{\sigma} = \left(\frac{k_B}{e}\right)^2 \frac{\lambda}{k_B} = L_M T_M \tag{11}$$

where $L_M = (k_B/e)^2$ is the Lorenz number for molecular hopping conductance and the effective temperature $T_M = \lambda/k_B$ is parametrized by the reorganization energy $\lambda$. For site reorganization energies between 0.05 and 0.25 eV, the effective temperature is of the order 500−3000 K. Comparing the MWF result in eq 11 with the WF law for metals in eq 1, we see that the explicit dependence on temperature is replaced by the temperature dependence of the reorganization energy. In most systems, the reorganization energy depends weakly on temperature and the MWF will be approximately temperature-independent. In some situations, however, the electron−phonon coupling and resulting extent of nuclear reorganization arising from ET vary significantly with temperature.[44−47] Moreover, the MWF relation is proportional to $\lambda$, which implies that the strength of electron−phonon coupling and its manifestation through the reorganization energy dictates the relationship between ETI thermal conductivity and electrical conductivity in molecular systems. Note that, while we have drawn analogies between the functional forms of the MWF law and the standard WF law, eq 11 constitutes an entirely new scaling law that is valid for systems in which charge transport is dominated by inelastic electron hopping—dramatically different physics than what is used to derive the standard WF law.

The robustness of the MWF law can be examined by calculating the WF ratio in a model molecular junction and comparing it with the general result in eq 11. Next, we want to numerically calculate the WF ratio in a model molecular junction and compare it with the analytical result in eq 11. Single-molecule junctions have been studied for the electronic transport properties for the past three decades,[11] and phononic heat conduction studies of such systems have very recently appeared.[26,27] Here, we consider a junction where heat conduction is dominated by electron hopping between molecular sites; see, e.g., refs 48 and 49. The specific process we consider is electron hopping transport along a bridge of $N$ charge transfer sites seated between two metal electrodes (see Figure 1), as is often invoked to examine long-range junction transport.[50] Note that electrical conductance $G$ and thermal conductance $\mathcal{K}$ replace the corresponding conductivities as the pertinent transport properties in this model. The respective temperatures of the electrodes are $T_L = T + \Delta T/2$ and $T_R = T - \Delta T/2$, where $\Delta T = T_L - T_R$ is the temperature bias across the device. The biased chemical potentials of the electrodes are $\mu_L = \mu - eV/2$ and $\mu_R = \mu + eV/2$, where $\mu$ is the Fermi level and $V$ is an applied voltage bias across the junction. Each site $s$ in the molecular bridge is associated with an electronic occupation energy $E'_s$ and a local thermal environment at temperature $T_s$. Associated with each site is a set of vibrational modes that participate in the ET process which are in equilibrium at the corresponding local temperature. In order to focus on the ETI contribution to the thermal conductance and to facilitate a direct comparison with standard WF law, we disregard coupling between the sets of vibrational modes and therefore there is no phononic heat transport between sites. The spatial distribution of the energy levels $E'_s$ in the junction, i.e., the electronic structure of the molecular bridge, is termed an *energy landscape*.

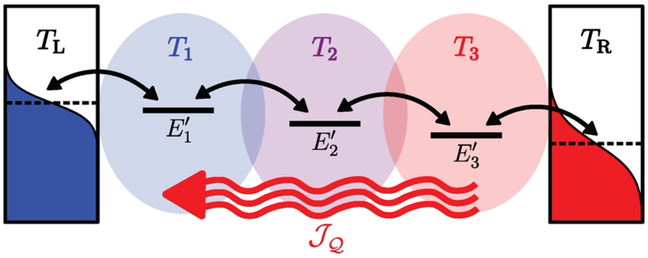

**Figure 1.** Schematic diagram of a representative molecular junction system. The specific model we examine consists of $N$ charge transfer sites seated between two metal electrodes (rectangles). Each site $s$ in the molecular bridge is associated with an electronic occupation energy $E'_s$ and a set of vibrational modes that are in equilibrium with a local thermal environment at temperature $T_s$ (transparent oval). The respective temperatures of the electrodes are $T_L$ and $T_R$. The biased chemical potentials of the electrodes are $\mu_L$ and $\mu_R$ are shown as dashed lines, and the corresponding Fermi–Dirac distribution of each electrode is represented by a colored region.

Electrons move between sites via a hopping mechanism (represented by black arrows in Figure 1), and therefore, the system has $N + 1$ electronic states $a \in \{M, 1, ..., N\}$ where, for example, in state 1 the charge density of the hopping electron is localized on molecular site 1, in state 2 the charge density is localized on molecular site 2, and so forth. The special case of $a = M$ corresponds to the state in which the electron occupies an energy level in one of the metal electrodes. Hopping between molecular sites and across the molecule–metal interfaces is controlled by a nuclear reorganization energy $\lambda$ that is described using the Marcus formalism.[19,38,39,51,52] The temperature profile in the molecular bridge is defined through application of a variant of the self-consistent reservoir method[53−56] that is modified to treat ETI heat transport.[37]

The electronic current through the junction $\mathcal{J}_{el}$ can be derived from the kinetic master equations describing the probability for an electron to localize on each site in the bridge or in the electronic manifold of one of the metals.[37] The electrical conductance in the linear transport regime and under zero temperature bias ($\Delta T = 0$) is

$$G = \lim_{V\to 0} \frac{\mathcal{J}_{el}}{V}\bigg|_{\Delta T=0} \tag{12}$$

where $V$ is the voltage bias across the junction. In the presence of a temperature bias ($\Delta T \neq 0$), ET across the thermal gradient in the molecular junction generates a heat current $\mathcal{J}_Q$ through the

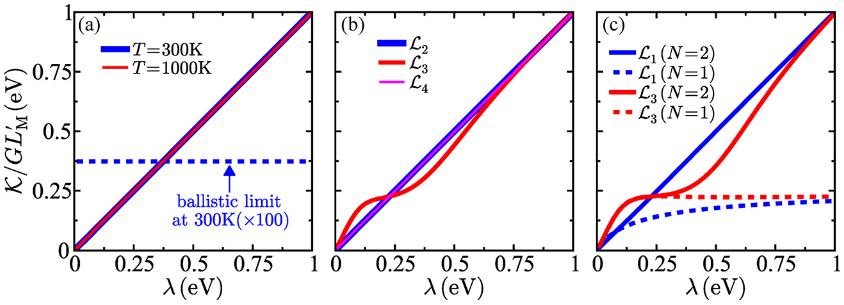

**Figure 2.** Calculated conductance ratio $\mathcal{K}/GL'_M$ with $L'_M = L_M/k_B$ as a function of reorganization energy $\lambda$ in a model molecular junction. (a) Conductance ratios for energy landscape $\mathcal{L}_1 \equiv E'_s = 0\ \forall\ s$ (the energy levels are measured relative to $\mu$) with $N = 5$ sites. The solid blue diagonal line is the hopping result for 300 K, and the solid red diagonal line is the hopping result for 1000 K. Note that the red line aligns over the blue line. The dashed blue horizontal line is the result calculated in the ballistic Landauer limit at 300 K for a junction with $N = 5$ sites and landscape $\mathcal{L}_1$ (full details of this calculation are shown in the Supporting Information). (b) Conductance ratios in a junction with $N = 5$ sites at 300 K for energy landscapes $\mathcal{L}_2 \equiv E'_s = 0.25$ eV $\forall\ s$ (blue), $\mathcal{L}_3 \equiv E'_s = -0.25$ eV $\forall\ s$ (red), and $\mathcal{L}_4$ (magenta) which is a linear ramp of energy levels from 0.15 to −0.15 eV (see, for example, the level spacing in Figure 1). Notice that the magenta line aligns over the blue line. (c) Conductance ratios for energy landscapes $\mathcal{L}_1$ (blue) and $\mathcal{L}_3$ (red) with $N = 2$ (solid) and $N = 1$ (dashed) sites. In all calculations shown in this figure, the electronic coupling between molecular sites corresponding to the off-diagonal elements in the Hamiltonian of the two electronic states is $V_{a,b} = 0.01$ eV and the molecule–metal coupling strength at each electrode is defined by $\Gamma = \frac{2\pi}{\hbar}|V_M|^2\rho_M = 100\ \text{ps}^{-1}$, where $V_M$ is the tunneling coupling for ET between molecule and metal and $\rho_M$ is the density of states—details of both of these properties can be found in section 3 of the Supporting Information.

device (see Figure 1),[37] and the corresponding thermal conductance obtained in the linear response regime under zero electric current conditions is

$$\mathcal{K} = \lim_{\Delta T \to 0} \frac{\mathcal{J}_Q}{\Delta T}\bigg|_{\mathcal{J}_{\mathrm{el}}=0} \tag{13}$$

The conductance ratio $\mathcal{K}/GL'_{\mathrm{M}}$ ($L'_{\mathrm{M}} = L_{\mathrm{M}}/k_{\mathrm{B}}$) calculated in the molecular junction model described above is shown in Figure 2 as a function of $\lambda$. This ratio can be compared with the MWF law which predicts that $\mathcal{K}/GL'_{\mathrm{M}} = \lambda$. Varying the electronic landscape of the molecular bridge, as well other physical properties of the system, such as temperature, can affect the conductance ratio. Figure 2a illustrates the calculated conductance ratios for energy landscape $\mathcal{L}_1 \equiv E'_s = 0\ \forall\ s$ at $T = 300$ K (blue) and $T = 1000$ K (red). At both temperatures, the numerically calculated result almost exactly follows the MWF law. We have confirmed that this agreement persists for temperatures as low as our numerical methods allow sampling ($\approx T = 150$ K) as well. The dashed horizontal line is the conductance ratio calculated in the ballistic transport limit using the Landauer formalism.[37] The ballistic result is independent of $\lambda$ due to the absence of electron−phonon interactions in the Landauer picture and thus does not follow the MWF law. Shown in Figure 2b are the results for several different energy landscapes (see the Figure 2 caption for details) calculated at 300 K. Notice that in all cases the calculated results show either excellent or essentially exact agreement with the MWF law. This illustrates the robustness of eq 11 for describing conductivity in molecules with varying electronic structures. These observations support the suitability of the MWF law for characterizing conductivity relations obtained under both linear and nonlinear response conditions.[21,57−59] We have confirmed that this agreement is observed over a broad range of energy landscapes and temperatures (see Figure S1 in the Supporting Information). Interestingly, the calculated results satisfy the trend predicted by eq 11 even when the energy difference between neighboring redox sites exceeds $k_{\mathrm{B}}T$ (as in landscape $\mathcal{L}_4$), a situation where the approximation used to derive eq 5 is not valid. This indicates that the MWF law has a broader range of validity than indicated by this approximation at least when the reorganization energy is large enough. Figure 2c illustrates how the conductance ratio is affected by changing the number of sites in the molecular bridge. In the case of a one-site bridge ($N = 1$), the MWF law is not obeyed. This is expected because the MWF law is derived for molecule-to-molecule ET processes which are absent in a system with one charge transfer site. In the two-site case ($N = 2$), the results agree with the MWF law. This implies that, for a junction with $N > 1$ sites, the ratio between thermal and electrical conductivity is mostly dominated by intersite hopping processes in the molecular bridge.

A comparison between the temperature dependence of the conductance ratio $\mathcal{K}/GL$ in the molecular junction model and the ratio predicted by the traditional WF law ($\mathcal{K}/GL = T$) is shown in Figure 3. The solid curves illustrate the numerical results for different energy landscapes and reorganization energies. The dashed curve is the result of a ballistic Landauer calculation. Three observations are noteworthy: (a) the calculated results deviate significantly from the WF law, (b) the ballistic result follows the WF law only at very low temperatures, which agrees with previous results,[3] and (c) the hopping results are either approximately temperature-independent (assuming temperature-independent reorganization energies) over all temperature ranges (solid blue curves) or weakly temperature-dependent in the low-temperature regime while becoming temperature-independent at higher temperatures (solid red curve). Note that, for most energy landscapes we have examined, the conductance ratio associated with hopping transport is approximately temperature-independent (see Figure S2 in the Supporting Information), in agreement with the MWF law.

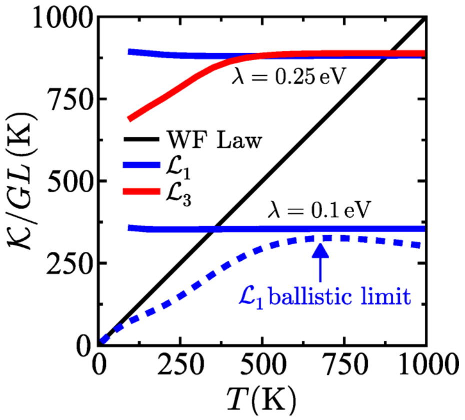

**Figure 3.** Calculated conductance ratio $\mathcal{K}/GL$ ($L$ is the Lorenz number for metals) as a function of temperature $T$ in a model molecular junction with $N = 5$ sites. The two upper solid curves are the hopping results for energy landscapes $\mathcal{L}_1$ (blue) and $\mathcal{L}_3$ (red) with reorganization energy $\lambda = 0.25$ eV. The lower solid curve (blue) is the result for energy landscape $\mathcal{L}_1$ and reorganization energy $\lambda = 0.1$ eV. In all hopping calculations, $V_{a,b} = 0.01$ eV and $\Gamma = 100$ ps$^{-1}$ (see the Figure 2 caption for details). The dashed blue curve is the result for energy landscape $\mathcal{L}_1$ in the ballistic Landauer limit with $V_{a,b} = 0.1$ eV and $\Gamma = 1000$ ps$^{-1}$. The black diagonal line is the result predicted by the WF law.

We have derived a WF law for molecules and confirmed its validity using numerical simulations of a paradigmatic molecular nanostructure. It is significant that the MWF law is able to accurately describe conductivity relations in hybrid molecule−metal systems. We therefore expect that it will describe the relationship between electrical conductivity and ETI thermal conductivity in both purely molecular systems and in systems where electron transfer takes place between heterogeneous structures with molecular components. Experimental examination of the theoretical results presented here could be realized using similar setups to those that are currently applied to probe the thermal, electronic, and thermoelectric properties of molecular junctions.[27−33] The MWF law opens a new way to analyze conductance in molecular systems and could lead to advancements in the design of thermoelectric and photovoltaic devices, computing architectures, and molecular electronics.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.9b04070.

Detailed derivation of the molecular Wiedemann−Franz law and more information about the conductance calculations in the molecular junction model (PDF)

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### Notes

The authors declare no competing financial interest.

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