Three-terminal thermoelectric transport through a molecule placed on an Aharonov-Bohm ring

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The thermoelectric transport through a ring threaded by an Aharonov-Bohm flux, with a molecular bridge on one of its arms, is analyzed. The charge carriers also interact with the vibrational excitations of that molecule. This nano-system is connected to three terminals: two are electronic reservoirs, which supply the charge carriers, and the third is the phonon bath which thermalizes the molecular vibrations. Expressions for the transport coefficients, relating all charge and heat currents to the temperature and chemical potential differences between the terminals, are derived second order in the electron-vibration coupling. At linear response, all these coefficients obey the full Onsager-Casimir relations. When the phonon bath is held at a temperature different from that of the electronic reservoirs, a heat current exchanged between the molecular vibrations and the charge carriers can be converted into electric and/or heat electronic currents. The related transport coefficients, which exist only due to the electron-vibration coupling, change sign under the interchange between the electronic terminals and the sign change of the magnetic flux. It is also demonstrated that the Aharonov-Bohm flux can enhance this type of conversion.

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I. INTRODUCTION

Thermoelectric effects in bulk conductors usually necessitate breaking of particle-hole symmetry. In mesoscopic structures this asymmetry may be fairly high and can be also controlled experimentally, leading to the possibility of realizing a relatively large thermopower coefficient. As a result there is currently much interest in investigations of thermoelectric phenomena in nanoscale devices at low temperatures. Experimental studies have been carried out on point-contacts\textsuperscript{11–15} quantum dots\textsuperscript{1,2} nanotubes\textsuperscript{2,2} silicon nanowires\textsuperscript{2} and more. Very recently, the paramount importance of another symmetry breaking has been pointed out. It has been proposed that the thermal efficiency (defined at steady state as the ratio of the output power to the heat current) can be significantly enhanced once time-reversal symmetry is broken and the thermopower coefficient becomes asymmetrical (as a function of, e.g., a magnetic field).\textsuperscript{16}

Early theoretical studies of thermoelectric transport coefficients of microstructures were based on the Landauer approach\textsuperscript{11–15} and were mainly focused on charge and heat currents between two electronic terminals, without coupling to phonons. Later on, effects of electron-electron processes and electronic correlations (increasingly important at lower temperatures), as well as that of an applied magnetic field, on the thermopower produced in large\textsuperscript{16} and single-level\textsuperscript{12} quantum dots, and also in quantum wires\textsuperscript{18} were considered. The signature of attractive electronic interactions on the thermopower was considered in Ref. \textsuperscript{19} and the dependence of the thermoelectric response on the length of the atomic chain connecting the leads has been recently computed within a density-functional theory.\textsuperscript{20}

The coupling of the charge carriers to vibrational modes of the molecule should play a significant role in thermoelectric transport through molecular bridges, even more so in the nonlinear regime.\textsuperscript{21} Indeed, a density-functional computation of the nonlinear differential conductance of gold wires attributed changes in the I-V characteristics to phonon heating\textsuperscript{20,22} and the thermopower coefficient was proposed as a tool to monitor the excitation spectrum of a molecule forming the junction between two leads.\textsuperscript{20,22} It was suggested that the Seebeck effect in such bridges can be used for converting heat into electric energy\textsuperscript{20} and to determine the location of the Fermi level of the transport electrons relative to the molecular levels, and also the sign of the dominant charge carriers, either for a molecular conductor\textsuperscript{27,28} or for an atomic chain.\textsuperscript{29,31} This was confirmed experimentally: the Seebeck coefficient, as measured by STM on the benzenedithiol family sandwiched between two gold electrodes, showed that the charge carriers are holes passing through the HOMO, whose location with respect to the metal Fermi level was determined from the magnitude of the coefficient.\textsuperscript{22}

Theoretically, when the coupling to the vibrational modes is ignored, the transport coefficients have the same functional form as in bulk conductors, with the energy-dependent transmission coefficient and its derivative replacing the conductivity.\textsuperscript{20,14} Although the corrections to the thermoelectric transport due to the coupling to the vibrational modes is often small, their study is of interest because of fundamental questions related to the symmetries of the conventional transport coefficients, and since they give rise to additional coefficients connecting the
heat transport in-between the electrons and the vibrational modes. In a recent article\textsuperscript{34} (referred to below as I) we have analyzed the thermoelectric phenomena in a molecular bridge, and studied effects induced by the coupling of the charge carriers with molecular vibrational modes. In particular we have considered the situation in which the molecule is strongly coupled to a heat bath of its own and thus may be kept at a temperature different from those of the source and sink of the charge carriers, making the junction a mixed thermal/electronic three-terminal one. Namely, we have assumed that the relaxation time due to the coupling of the molecule to its own heat bath, $\tau_V$, is short on the scale of the coupling of the molecule to the charge carriers. The latter is determined by the electron-vibration coupling, $\gamma$ (and the conductance electrons density of states) which is the small parameter of our theory. Hence, $\hbar/\tau_V$ may still be very small on all other physical scales, such as $\hbar \omega_0$, where $\omega_0$ is the frequency of the vibrations, or the molecular (electronic) level width. The phonon bath may be realized by an electronically insulating substrate or a piece of such material touching the junction, each held at a temperature $T_V$. Similar experimental three-terminal setups, consisting of quantum dots, were discussed in Refs. \textsuperscript{35,36,37}. The effect of thermal probes on the electronic heat conduction have been considered theoretically for tunnel normal-superconducting junctions\textsuperscript{38} and for mesoscopic conductors\textsuperscript{39}.

In this mixed thermal/electronic junction, heat supplied by the phonon baths [to which the electrons and the molecule are (separately) coupled] can be exchanged between the transport electrons and the vibrational modes. Even more intriguing, heat carried from the phonon bath to the vibrations can be converted into a charge current (or an electronic heat current) flowing between the electronic reservoirs. We have found in I that in order for this conversion to take place, one needs to break the spatial symmetry of a molecular bridge, in addition to the broken electron-hole symmetry. Here we examine the outcome of breaking another symmetry, that of time-reversal. To this end, we exploit the Aharonov-Bohm effect, placing the molecular bridge on one arm of a ring threaded by a magnetic flux, $\Phi$, see Fig. 1. As we show, for a non-zero flux the above conversion can also appear in a spatially symmetric bridge, provided that the effective couplings to the leads are energy dependent. The specific quantities we study are the heat and the charge currents in a small mesoscopic (or nanometric) system, depicted schematically in Fig. 1. A molecule (having one electronic level) is placed on an Aharonov-Bohm ring, which is attached to two electronic reservoirs (held in general at different temperatures, $T_{L,R}$, and at different chemical potentials, $\mu_{L,R}$). The vibrational modes of the molecule, with which the charge carriers may exchange energy, are thermalized by a third terminal, kept at the temperature $T_V$.

Since the calculations are rather technical, we organize the paper as follows. After a short analysis of the entropy production in our system (Sec. II), we summarize the main results and in particular discuss the magnetic-flux dependence of the transport coefficients. We then proceed in Sec. III to specify our model, and to derive the explicit expressions for the currents. Section IV details the various transport coefficients of the three-terminal junction in the linear-response regime. In particular, we examine the various symmetries of the coefficients, and verify that they obey the Onsager relations. Section V is devoted to a discussion of our results; we consider the transport coefficients in certain simple cases, in particular their dependence on the spatial and electron-hole symmetries of the junction.

\section{Entropy production and thermoelectric transport coefficients}

The consideration of the entropy production in the linear-response regime, carried out in I, is quite illuminating. Using the thermodynamic identity $TdS = dE - \mu dN - \frac{dW}{T}$ one finds that the entropy production at the left (right) electronic reservoir is

$$\dot{S}_{L(R)} = \frac{1}{T_{L(R)}} \left( \dot{E}_{L(R)} - \mu_{L(R)} \langle N_{L(R)} \rangle \right). \tag{1}$$

Here, $-\dot{E}_{L(R)}$ is the energy current emerging from the left (right) reservoir, while $-\langle N_{L(R)} \rangle$ is the corresponding particle current. Adding to Eqs. (1) the entropy production of the vibrational modes, $\dot{S}_V = \dot{E}_V/T_V$, where $\dot{E}_V$ is the energy current from the phonon bath into the molecule, yields the total dissipation of the system,

$$\dot{S}_V + \dot{S}_L + \dot{S}_R = \dot{E}_V \frac{T_V}{T_L} + \frac{1}{T_L} \left( \dot{E}_L - \mu_L \langle N_L \rangle \right) + \frac{1}{T_R} \left( \dot{E}_R - \mu_R \langle N_R \rangle \right). \tag{2}$$
We demonstrate below that our three-terminal junction conserves charge, i.e., \( \langle \dot{N}_L + \dot{N}_R \rangle = 0 \), and also energy, i.e. \( \dot{E}_L + \dot{E}_R + \dot{E}_V = 0 \). In the linear-response regime all three temperatures (see Fig. 1) are only slightly different from each other,

\[
T_{L(R)} = T \pm \frac{\Delta T}{2}, \\
T_V = T + \Delta T_V,
\]

and the chemical potentials differ by a small amount,

\[
\mu_{L(R)} = \mu \pm \frac{\Delta \mu}{2}.
\]

One then finds

\[
\dot{S}_V + \dot{S}_L + \dot{S}_R = \frac{\Delta T_V}{T^2}(-\dot{E}_V) + \frac{\Delta \mu/e}{T} I + \frac{\Delta T}{T^2} I_Q,
\]

where \( I \) is the net charge current flowing from the left electronic reservoir to the right one,

\[
I = -\frac{e}{2} \langle \dot{N}_L - \dot{N}_R \rangle,
\]

while \( I_Q \) is the net heat current carried by the electrons,

\[
I_Q = I_e - (\mu/e) I, \quad \text{with} \quad I_e = -\frac{1}{2} \left( \dot{E}_L - \dot{E}_R \right).
\]

We keep the notation \(-\dot{E}_V\) for the the energy/current from the phonon bath. Thus, the entropy production of our three-terminal system is a simple example of the general expressions for linear transport, consistent with the Onsager theory.

The calculations in the next two sections yield the relations among the driving fields and the currents. In the linear response limit one has

\[
\begin{bmatrix}
I \\
I_Q \\
-\dot{E}_V
\end{bmatrix} = \mathcal{M} \begin{bmatrix}
\frac{\Delta \mu/e}{T} \\
\frac{\Delta T}{T^2} \\
\frac{\Delta T}{T^2}
\end{bmatrix},
\]

where the matrix of the transport coefficients, \( \mathcal{M} \), is

\[
\mathcal{M} = \begin{bmatrix}
G(\Phi) & K(\Phi) & X^V(\Phi) \\
K(-\Phi) & K_2(\Phi) & X^V(-\Phi) \\
X^V(\Phi) & X^V(-\Phi) & C^V(\Phi)
\end{bmatrix}.
\]

This matrix satisfies the Onsager-Casimir relations. We find below that all three diagonal entries are even functions of the flux \( \Phi \). The off-diagonal entries of \( \mathcal{M} \) consist each of a term even in the flux, and another one, odd in it, obeying altogether \( \mathcal{M}_{ij}(\Phi) = \mathcal{M}_{ji}(-\Phi) \).

The flux dependence of the transport coefficients is very interesting. We find (see Secs. III and IV for details) that there are three types of flux dependencies hiding in those six coefficients. First, there is the one caused by interference. The interference processes modify the self energy of the Green functions pertaining to the Aharonov-Bohm ring, in particular the broadening of the electronic resonance level due to the coupling with the leads. The interference leads to terms involving \( \cos \Phi \). Secondly, there is the flux dependence which appears in the form of \( \cos 2\Phi \) (or alternatively, \( \sin^2 \Phi \)). This reflects the contributions of time-reversed paths. These two dependencies are even in the flux. They yield the full flux dependence of the diagonal entries of the matrix \( \mathcal{M} \), Eq. (9), and the even (in the flux) parts of the off-diagonal elements. Finally, there is the odd dependence in the flux, that appears as \( \sin \Phi \). This dependence characterizes the odd parts of the off-diagonal entries of \( \mathcal{M} \). These terms necessitate the coupling of the electrons to the vibrational modes.

## III. THE CURRENTS

In this section we present our model system, give details of the currents’ calculation, and verify their balance.

### A. The model

In our analysis, the molecular bridge is replaced by a single localized electronic level, representing the lowest available orbital of the molecule; when a transport electron resides on the level, it interacts (linearly) with Einstein vibrations. Our analysis does not include electronic interactions, but focuses on the electron-phonon ones. Thus, the Hamiltonian of the molecular bridge, which includes the coupling with the vibrations, reads

\[
\mathcal{H}_M = \epsilon_0 c_0 \dagger c_0 + \omega_0 (b^\dagger b + \frac{1}{2}) + \gamma (b + b^\dagger) c_0 \dagger c_0,
\]

where \( \epsilon_0 \) is the energy of the localized level, \( \omega_0 \) is the frequency of the harmonic oscillator representing the vibrations, and \( \gamma \) is its coupling to the transport electrons. The Hamiltonian describing the tunneling between the molecule and the leads is

\[
\mathcal{H}_{coup} = \sum_k (V_k c_\dagger k c_0 + \text{H.c.}) + \sum_p (V_p c_\dagger p c_0 + \text{H.c.})
\]

[using \( k(p) \) for the left (right) lead]. The leads’ Hamiltonian is

\[
\mathcal{H}_{\text{lead}} = \mathcal{H}_L + \mathcal{H}_R + \mathcal{H}_{LR}.
\]

Here

\[
\mathcal{H}_{LR} = \sum_{k(p)} \epsilon_{k(p)} c_{k(p)} \dagger c_{k(p)}
\]

is the Hamiltonian of each of the leads and

\[
\mathcal{H}_{LR} = \sum_{k p} V_{k p} e^{i \Phi} c_{k(p)} \dagger c_0 + \text{H.c.}
\]

describes the direct coupling between the two leads (pictorially shown as the lower arm of the ring in Fig. 1). In
the phase factor $e^{i\Phi}$, the flux $\Phi$ is measured in units of the flux quantum, $\hbar c/e$. Since we use units in which $\hbar = 1$, the flux quantum is $2\pi c/e$. Thus, our model Hamiltonian is

$$\mathcal{H} = \mathcal{H}_{\text{lead}} + \mathcal{H}_\text{M} + \mathcal{H}_\text{coup},$$

(15)

where the operators $c_k^\dagger$, $c_k^\dagger$ and $c_p^\dagger$ ($c_0, c_L,$ and $c_R$) create (annihilate) an electron on the level, on the left lead, and on the right lead, respectively, while $b^\dagger (b)$ creates (annihilates) an excitation of frequency $\omega_0$ on the molecule.

In the spirit of the Landauer approach, the various reservoirs connected to the leads are described by the populations of the excitations pertaining to a specific reservoir. The electronic reservoirs on the left and on the right of the bridge are characterized by the electronic reservoirs connected to the leads described by the Green functions.

$$N = \left( \exp[\beta \omega_0] - 1 \right)^{-1},$$

(17)

with $\beta = 1/k_B T_V$.

**B. Formal expressions for the currents**

The charge current leaving the left lead is given by $I_L = -e \langle N_L \rangle$, where $N_L = \sum_k c_k^\dagger c_k$ is the number operator on the left reservoir; $I_L$ is the sum of the currents flowing from the left lead to the bridge and into the lower arm of the ring, see Fig. 1. In terms of the Keldysh Green functions,

$$I_L = -e \int \frac{d\omega}{2\pi} \mathcal{J}_L(\omega),$$

(18)

where

$$\mathcal{J}_L(\omega) = \sum_k V_k \left( G_{k,0}(\omega) - G_{0,k}(\omega) \right) $$

$$\sum_{kp} V_{kp} \left( e^{-i\Phi} G_{k,p}(\omega) - e^{i\Phi} G_{p,k}(\omega) \right).$$

(19)

The subscripts of the Green functions indicate the corresponding operators which form them. The electronic energy rate in the left electronic reservoir is $\dot{E}_L = \langle \mathcal{H}_L \rangle$; the energy current leaving the left reservoir is given by Eqs. 18 and 19, with $e$ replaced by $\omega$ (within the integral). The electronic currents (charge and energy) associated with the right lead are $-e \langle N_R \rangle$ and $-\dot{E}_R = -\langle \mathcal{H}_R \rangle$; they are given by Eqs. 18 and 19 upon interchanging $k$ with $p$, $L$ with $R$, and $\Phi$ with $-\Phi$. (The explicit frequency dependence in some of the following equations is omitted for brevity.)

**C. Details of the currents’ calculation**

Using the Keldysh technique, we express the currents [see Eqs. (13) and (19)] in terms of the Green function of the localized level, denoted $G \equiv G_{0,0}(\omega)$. The latter is calculated up to second order in the coupling to the vibrations, $\gamma$,

$$G^r = \left( |G|^2 \right)^{-1} - \delta \epsilon V - \Sigma_V^r,$$

$$G^< = G^r \left( \Sigma_V^I + \Sigma_V^< \right) G^a,$$

(20)

Here, $G^r$ ($G^a$) is the retarded (advanced) Green function, and $G^<$ is the lesser one (below we also use the greater Green function, $G^>$); $\gamma$ is the Green function in the absence of the coupling with the vibrations,

$$G^r = \frac{1}{\omega - \epsilon_0 - \Sigma^r \gamma},$$

(21)

where $\Sigma^r_\gamma$ is the self-energy due to the coupling with the leads, see Eq. (22) below. Similarly, $\Sigma^< \gamma = G^r \Sigma^< \gamma G^a$. The superscripts on the self energies $\Sigma$ have the same meaning as those indexing the Green functions.

We now discuss the two self energies which appear in Eq. (20). The first, which comes from the coupling to the leads, $\Sigma_\gamma$, is independent of the coupling to the vibronial mode, and is given by

$$\Sigma^r_\gamma = \frac{-i}{2(1 + \lambda)} \left( |\Gamma^r| + |\Gamma^<| \right) \cos \Phi,$$

$$\Sigma^<_\gamma = \frac{i}{(1 + \lambda)^2} \left( f_L(\Gamma^r + \lambda \Gamma^<) + f_R(\Gamma^< + \lambda \Gamma^r) \right.$$ 

$$+ 2 \sqrt{\lambda \Gamma^r \Gamma^<} (f_R - f_L) \sin \Phi \right).$$

(22)

This self energy is determined by the resonance width $|\Gamma^r| [\Gamma^<|$ induced by the coupling with the left (right) lead, dressed by all interference paths. In Eqs. 22, $\lambda$ is the (dimensionless) direct coupling between the leads,

$$\lambda(\omega) = (2\pi)^2 \sum_{k,p} |V_{kp}|^2 \delta(\omega - \epsilon_k) \delta(\omega - \epsilon_p).$$

(23)

In our model, the transmission and reflection amplitudes of the lower arm of the ring alone (see Fig. 1), $t_o$ and $r_o$, respectively, are chosen to be real and are given in terms of $\lambda$,

$$t_o^2(\omega) = \frac{4 \lambda^2(\omega)}{1 + |\lambda(\omega)|^2}, \quad r_o^2(\omega) = 1 - t_o^2(\omega).$$

(24)

The total width of the resonance level caused by the couplings to the leads, $\Gamma$, is given by $-2 \text{Im} \Sigma^r_\gamma$ [see Eqs. 22 and 23],

$$\Gamma(\omega) = \frac{\Gamma_L(\omega) + \Gamma_R(\omega)}{1 + \lambda(\omega)^2},$$

(25)
while the asymmetry in those couplings is characterized by
\[ \alpha^2(\omega) = \frac{4\Gamma_L(\omega)\Gamma_R(\omega)}{\Gamma_L(\omega) + \Gamma_R(\omega)^2}, \]  
(26)
or alternatively
\[ \alpha(\omega) = \frac{\Gamma_L(\omega) - \Gamma_R(\omega)}{\Gamma_L(\omega) + \Gamma_R(\omega)}, \]
(27)
such that \( \alpha^2 + \alpha^2 = 1 \). None of the above details depends on the coupling to the vibrational mode.

The second self energy in Eq. (20), \( \Sigma_V \), comes from the coupling with the vibrations. To second order in \( \gamma \), it is given by
\[ \Sigma_V^\pm(\omega) = \gamma^2\left(NG^\pm(\omega - \omega_0) + (1 + N)G^\pm(\omega + \omega_0)\right) \]
\[ \Sigma_V^\pm(\omega) = \gamma^2\left(NG^\pm(\omega + \omega_0) + (1 + N)G^\pm(\omega - \omega_0)\right), \]
(28)
where \( N \) denotes the population of the vibrational modes [see Eq. (17)]; \( \delta \gamma \) is the polaron shift,
\[ \delta \gamma = \frac{2\Gamma^2}{\omega_0} \int \frac{d\omega}{2\pi} G^\pm(\omega). \]  
(29)

Note that the Green functions here contain \( \Sigma^\pm \) and \( \Sigma^\pm \), and therefore they also depend on the flux \( \Phi \).

In terms of these parameters, the integrand determining the electronic currents running from left to right [see Eqs. (19) and (20), and Fig. 1] is
\[ J_L = \langle f_R - f_L \rangle \left( \frac{\epsilon^2}{2\pi} \left[ -\alpha \Gamma \cos \Phi ReG^a \right] + \alpha t_o \sin \Phi \right) \]
\[ = \frac{\Gamma}{2} \left( (1 + \alpha^2)(G^a - f_L[G^a - G^a]) \right) + \alpha t_o \sin \Phi \left[ G^a - f_R(G^a - G^a) \right]. \]  
(30)

The corresponding integrand determining the currents flowing from right to left, \( J_R \), is obtained from Eq. (30) upon interchanging \( L \) with \( R \) and \( \Phi \) with \( -\Phi \), a transformation which leaves \( G \) invariant.

Let us first consider the sum of the electronic currents, flowing from the left towards the ring and from the right towards the ring. Using Eqs. (22), we find
\[ J_L + J_R = \left( \Sigma^\pm - \Sigma^a \right) G^\pm + \Sigma^\pm(G^a - G^a) \]
\[ = |G^a|^2 \left( \Sigma^\pm \Sigma^\pm - \Sigma^a \Sigma^a \right). \]  
(31)

Therefore, up to second order in the coupling with the vibrations, the sum of the currents is given by
\[ \int \frac{\omega d\omega}{2\pi} \left( J_L + J_R \right) = \int \frac{\omega d\omega}{2\pi} |G^a|^2 \left( \Sigma^\pm \Sigma^\pm - \Sigma^a \Sigma^a \right), \]  
(32)
where \( s = 0 \) for the sum of the two electronic electric currents, and \( s = 1 \) for the sum of the two electronic energy currents. Inserting here Eqs. (22) for the self energy due to the coupling with the vibrations, one obtains that Eq. (32) vanishes for \( s = 0 \), ensuring the electric current conservation,
\[ \langle N_L \rangle + \langle N_R \rangle = 0. \]  
(33)

On the other hand, for \( s = 1 \) one finds
\[ \int \frac{\omega d\omega}{2\pi} \left( J_L(\omega) + J_R(\omega) \right) = \gamma^2 \omega_0 \int \frac{d\omega}{2\pi} |G^a(\omega_0)G^a(\omega_+)|^2 \]
\[ \times \left( N\Sigma^\pm(\omega_+)\Sigma^\pm(\omega_-) - (1 + N)\Sigma^\pm(\omega_-)\Sigma^\pm(\omega_+) \right), \]  
(34)
where we have introduced the abbreviations
\[ \omega_\pm = \omega \pm \frac{\omega_0}{2}. \]  
(35)
The energy current carried by the vibrations, \( \omega_0 \langle b^\dagger b \rangle / dt \) [see Eq. (10)], may be calculated from the Keldysh phonon Green functions\(^{29}\) and it is straightforward to show that it is given by the result \( -\dot{E}_V \), ensuring the total energy conservation of our model,
\[ -\dot{E}_V = \dot{E}_L + \dot{E}_R. \]  
(36)

D. Explicit expressions for the currents

Returning to Eq. (30) and inserting there Eqs. (20), we find that, like the self energies, \( J_L \) can be separated into two contributions, one from the coupling to the leads and the other from the coupling with the vibrations,
\[ J_L(\omega) = [f_R(\omega) - f_L(\omega)]J^L(\omega) + J^L_V(\omega), \]  
(37)
where the ‘bare’ transition probability between the leads is (cf. Ref. [44])

\[
\mathcal{J}^I(\omega) = t_o^2 \left( 1 - \Gamma \text{Im} G^a + \frac{\Gamma^2}{4} (1 - \alpha^2 \cos^2 \Phi) |G^a|^2 \right) \\
+ t_o r_o \Gamma \alpha \cos \Phi \text{Re} G^a + \frac{\Gamma^2 \alpha^2}{4} |G^a|^2 .
\] (38)

The first term here, \(t_o^2\), yields the conductance in the absence of the ring arm carrying the bridge (see Fig. 1), while the last term yields the conductance of that arm alone. All other three terms in Eq. (38) result from various interference processes which do not involve the coupling to the vibrations [apart from their renormalization of the bridge Green function, see Eq. (20)]. This ‘bare’ transition probability is an even function of the flux \(\Phi\).

The contribution of the coupling to the vibrations, i.e. the last term of Eq. (37), is given to order \(\gamma^2\) by

\[
\mathcal{J}^V_L(\omega) = -\frac{\Gamma}{2} |G^a|^2 \left( a_+ \Sigma^y^+ (1 - f_L) + \Sigma^y f_L \right) \\
+ b(\omega) \Sigma^y^+ (1 - f_R) + \Sigma^y f_R \right) ,
\] (39)

where

\[
a_\pm(\omega) = 1 \pm \pi(\omega) r_o(\omega) ,
\]
\[
b(\omega) = \alpha(\omega) t_o(\omega) ,
\] (40)

see Eqs. (24), (26), and (27). (The function \(a_-\) is obtained from the function \(a_+\) upon interchanging L with R.)

We are now in position to present the detailed expressions for the currents, by inserting Eq. (37) [and the analogous one, obtained upon interchanging there L with R and \(\Phi\) with \(-\Phi\) into Eqs. (6), (7), and (26). The electric current is

\[
I = -e \int \frac{d\omega}{2\pi} [f_R(\omega) - f_L(\omega)] \mathcal{J}^I(\omega)
- e \int \frac{d\omega}{4\pi} c(\omega, \Phi) \mathcal{J}^V(\omega) ,
\] (41)

while the energy current carried by the electrons is

\[
I_E = - \int \frac{d\omega d\omega}{2\pi} [f_R(\omega) - f_L(\omega)] \mathcal{J}^I(\omega)
- \int \frac{d\omega}{4\pi} c(\omega, \Phi) \mathcal{J}^V(\omega) .
\] (42)

The function

\[
c(\omega, \Phi) = \gamma^2 \Gamma(\omega_\pm) |G^a(\omega_\pm) G^a(\omega_\pm)|^2
\] (43)

introduced in Eqs. (11) and (12) has a simple meaning. Keeping in mind that \((\Gamma/2)|G^a|^2\) sets the scale for the local density of states on the bridge (to leading order), it is seen that \(c(\omega, \Phi)\) is the product of the local densities of states at the two shifted frequencies \(\omega_\pm\) [see Eq. (35)], multiplied by the coupling to the vibrations, \(\gamma^2\). Note that the broadening of the energy level on the dot resulting from the coupling to the leads depends on the flux \(\Phi\), see Eqs. (22), leading in turn to the flux dependence of \(\mathcal{G}\) and the function \(c\), Eq. (43). This is the cos \(\Phi\) dependence resulting from the usual interference processes, discussed at the end of Sec. II.

The other function introduced above is \(\mathcal{J}^V_s\), where \(s = 0\) in Eq. (11), and \(s = 1\) in Eq. (12).

\[
\mathcal{J}^V_s(\omega) = F_{LL}(\omega) \left( \omega_+^s g_{++}(\omega_+) g_{--}(\omega_-) - \omega_-^s g_{++}(\omega_-) g_{--}(\omega_+) \right)
+ F_{RR}(\omega) \left( -\omega_+^s g_{--}(\omega_+) g_{--}(\omega_-) + \omega_-^s g_{--}(\omega_-) g_{--}(\omega_+) \right)
+ F_{LR}(\omega) \left( \omega_+^s g_{++}(\omega_+) g_{--}(\omega_-) + \omega_-^s g_{++}(\omega_-) g_{--}(\omega_+) \right)
+ F_{RL}(\omega) \left( -\omega_+^s g_{--}(\omega_+) g_{--}(\omega_-) - \omega_-^s g_{++}(\omega_-) g_{--}(\omega_+) \right) .
\] (44)

The various excitation populations characterizing the reservoirs are incorporated into the functions \(F_{nn'}\),

\[
F_{nn'}(\omega) = \left. N(1 - f_n(\omega_+)) f_{n'}(\omega_-) \right|_{-N \to N} ,
\] (45)

[see Eqs. (16) and (17)]. In addition, the four functions \(g_{\pm\pm}\) are given by

\[
g_{\pm\pm}(\omega) = a_\pm(\omega) \mp b(\omega) \sin \Phi
\] (46)

for the equal-sign functions \(g_{\pm}\), and

\[
g_{\pm\mp}(\omega) = a_\pm(\omega) \mp b(\omega) \sin \Phi
\] (47)

for the unequal ones.

Finally, the energy current carried by the vibrations is
given by
\[ -E_V = \omega_0 \int \frac{d\omega}{4\pi} \left( F_{LL}(\omega)g_{+}(\omega+)g_{+}(\omega-) + F_{RR}(\omega)g_{-}(\omega+)g_{+}(\omega-) + F_{LR}(\omega)g_{+}(\omega-)g_{+}(\omega-) \right). \] (48)

These lengthy expressions are significantly simplified when one assumes a symmetrically-coupled bridge, or a perfect bare transmission of the lower arm of the ring (see Fig. 1). In both cases, Eqs. (10) yield \( a_{\pm} = 1 \).

IV. THE LINEAR-RESPONSE REGIME

In the linear-response regime one expands all currents to first order in the driving forces, which in our case are \( \Delta \mu, \Delta T, \) and \( \Delta T_V \) (see discussion in Sec. II). This amounts to expanding the Fermi distributions, Eqs. (16), around the common temperature \( T \) and the common chemical potential \( \mu \) of the device, i.e., around \( f(\omega) = \exp(\beta(\omega - \mu)) + 1 \)^{-1}, and the vibrational mode population, Eq. (17), around the Bose function \( N_T = \exp(\beta\omega_0) - 1 \)^{-1}, where \( \beta = 1/k_BT \).

The electric current in the linear-response regime takes the form
\[ I = G(\Phi)\frac{\Delta \mu}{e} + K(\Phi)\frac{\Delta T}{T} + X^V(\Phi)\frac{\Delta T_V}{T}. \] (49)

As is clear from the discussion in Sec. II, there are two contributions to each of the first two terms of the electric current, one coming from the coupling to the leads [the first term on the right-hand side of Eq. (11)] and the other coming from the coupling to the vibrations. The last term in Eq. (10) arises from the latter coupling alone. Accordingly,
\[ G = G^l + G^V, \]
\[ K = K^l + K^V, \] (50)

with
\[ G^l(\Phi) = e^2 \int \frac{d\omega}{2\pi} T^l(\omega, \Phi), \] (51)

where
\[ T^l(\omega, \Phi) = \beta f(\omega)[1 - f(\omega)]T(\omega, \Phi) \] (52)
is essentially the transition probability, Eq. (38), at the Fermi energy (at low temperatures). Similarly the transport coefficient related to the thermopower is
\[ K^l(\Phi) = e \int \frac{d\omega}{2\pi}(\omega - \mu)T^l(\omega, \Phi). \] (53)

These expressions for the transport coefficients are the standard ones, see for example Ref. 11; both coefficients, \( G^l \) and \( K^l \), are even in the magnetic flux.

Next we examine the contribution of the ‘vibronic’ transitions to the transport coefficients. Introducing the function
\[ T^V(\omega, \Phi) = \beta N_T f(\omega_-)[1 - f(\omega_+)]c(\omega, \Phi), \] (54)
we find
\[ G^V(\Phi) = e^2 \int \frac{d\omega}{\pi} T^V(\omega, \Phi)m_0(\omega, \Phi), \] (55)

where
\[ m_0(\omega, \Phi) = 1 - \pi(\omega_-)\pi(\omega_+)r_o(\omega_-)r_o(\omega_+) + \alpha(\omega_-)\alpha(\omega_+)t_o(\omega_-)t_o(\omega_+) \sin^2 \Phi. \] (56)

[We remind the reader that \( \alpha \) and \( \pi \) characterize the asymmetry of the bridge, see Eqs. (27), while \( t_o \) and \( r_o \) are the transmission and reflection amplitudes of the lower arm of the ring, see Eqs. (24). The frequencies \( \omega \pm \) are given in Eq. (35).] Notice that the full conductance \( G^l + G^V \) is even in the flux. Thus it is seen that the electron-vibration interaction introduces only a modest modification in the conductance, but does not lead to major effects. This is not the case with all other transport coefficients of the ring. The thermopower coefficient \( K^V \) is given by
\[ K^V(\Phi) = e \int \frac{d\omega}{\pi}(\omega - \mu)T^V(\omega, \Phi)m_0(\omega, \Phi) + \frac{\omega_0}{2} \sin \Phi \int \frac{d\omega}{\pi} T^V(\omega, \Phi)m_1(\omega), \] (57)

where
\[ m_1(\omega) = \alpha(\omega_+)t_o(\omega_-)\pi(\omega_+)r_o(\omega_-) - \alpha(\omega_-)t_o(\omega_+)\pi(\omega_+)r_o(\omega_+). \] (58)

While the first term of \( K^V \) is even in the flux, the second term is an odd function of \( \Phi \). In order not to vanish, this odd component necessitates that the bridge will not be coupled symmetrically to the leads, and that the transmission of the lower arm of the ring will not be perfect (to ensure interference). In addition, \( K^V \) is invariant under the transformation \( \Phi \leftrightarrow -\Phi \), see Eq. (27) and \( \Phi \leftrightarrow -\Phi \).

Finally, the coefficient \( X^V \) [see Eq. (40)] is
\[ X^V(\Phi) = \omega_0 \int \frac{d\omega}{\pi} T^V(\omega, \Phi)m_2(\omega, \Phi), \] (59)

with
\[ m_2(\omega, \Phi) = \pi(\omega_-)r_o(\omega_-) + \alpha(\omega_-)t_o(\omega_-) \sin \Phi - \pi(\omega_+)r_o(\omega_+) - \alpha(\omega_+)t_o(\omega_+) \sin \Phi. \] (60)

Note that under the transformation \( \Phi \leftrightarrow -\Phi \), \( X^V \) changes its sign. Also note that, again, the \( \sin \Phi \) dependence of this transport coefficient necessitates the coupling to the vibrational modes.
In an analogous fashion we derive the heat current carried by the electrons, and find

$$I_Q = K(-\Phi)\frac{\Delta\mu}{e} + K_2(\Phi)\frac{\Delta T}{T} + \tilde{X}^V(\Phi)\frac{\Delta T_V}{T}. \quad (61)$$

Here, the transport coefficient related to the thermal conductivity, $K_2$, has again two contributions,

$$K_2 = K_2^l + K_2^V, \quad (62)$$

where

$$K_2^l(\Phi) = \int \frac{d\omega}{2\pi}(\omega - \mu)^2T l(\omega, \Phi)$$

as expected, while the ‘vibronic’ term is

$$K_2^V(\Phi) = \int \frac{d\omega}{\pi}(\omega - \mu)^2T V(\omega, \Phi)m_0(\omega, \Phi)$$

$$+ \frac{\omega_0^2}{4} \int \frac{d\omega}{\pi}V V(\omega, \Phi)m_0(\omega, \Phi), \quad (63)$$

with

$$m_0(\omega, \Phi) = 1 + \alpha(\omega_-)\alpha(\omega_+)r_o(\omega_-)r_o(\omega_+)$$

$$- \alpha(\omega_-)\alpha(\omega_+)t_o(\omega_-)t_o(\omega_+)\sin^2 \Phi. \quad (65)$$

One notes that $K_2$ is even in the flux. The last transport coefficient in Eq. (61) is

$$\tilde{X}^V(\Phi) = \omega_0 \int \frac{d\omega}{\pi}(\omega - \mu)T V(\omega, \Phi)m_2(\omega, \Phi)$$

$$- \frac{\omega_0^2}{2} \int \frac{d\omega}{\pi}V V(\omega, \Phi)m_2(\omega, \Phi), \quad (66)$$

with

$$m_2(\omega, \Phi) = \alpha(\omega_-)r_o(\omega_-) + \alpha(\omega_+)t_o(\omega_-)\sin \Phi$$

$$+ \alpha(\omega_+)r_o(\omega_+) + \alpha(\omega_-)t_o(\omega_+)\sin \Phi. \quad (67)$$

This coefficient changes its sign under the transformation $L \leftrightarrow R$ and $\Phi \leftrightarrow -\Phi$, as expected from the Onsager relations.

The energy current from the thermal bath takes the form

$$-\dot{E}^V = X^V(-\Phi)\frac{\Delta\mu}{e} + \tilde{X}^V(-\Phi)\frac{\Delta T}{T} + C^V\frac{\Delta T_V}{T}, \quad (68)$$

where the third coefficient here is

$$C^V = 2\omega_0^2 \int \frac{d\omega}{\pi}V V(\omega, \Phi), \quad (69)$$

and is an even function of the flux. Collecting all results, we arrive at the matrix form for the relations among the currents and the driving forces, Eqs. (8) and (9).

V. EXAMPLES AND DISCUSSION

As is clear from the results in Sec. IV (and also from Ref. 34, which treated the bridge without the lower branch), the interesting effect induced exclusively by the coupling of the electrons to the vibrational modes is the possibility to create an electric current, or an electronic heat current, by applying a temperature difference $\Delta T_V$ on the phonon bath thermalizing this mode. These new thermoelectric phenomena are specified by the two coefficients $X^V$ and $\tilde{X}^V$, Eqs. (59) and (60), respectively. All other transport coefficients related to the electronic currents are mainly due to the transport of the electrons between the electronic terminals, with slight modifications from the (small) coupling to the vibrations. We therefore confine the main discussion in this section to the coefficients $X^V$ and $\tilde{X}^V$. To make a closer connection with a possible experiment, we introduce the (dimensionless) coefficients

$$S^V = e\beta \frac{X^V}{G}, \quad (70)$$

and

$$\tilde{S}^V = \frac{\tilde{X}^V}{K_2}. \quad (71)$$

The first gives the potential drop across the molecular bridge created by $\Delta T_V$ when the temperature drop there, $\Delta T$, vanishes, and the second yields the temperature difference created by $\Delta T_V$ when $\Delta\mu = 0$ [or the inverse processes, see Eqs. (8) and (9)]. For both the conductance, $G$, and the thermal conductance, $K_2$, we use below their leading terms, resulting from the coupling to the leads alone (the numerators result from the coupling to the vibrations, and hence are already of order $\gamma^2$).

As mentioned above, the transport coefficients of our three-terminal junction obey the Onsager-Casimir relations. They do it though in a somewhat unique way: the “off-diagonal” elements are related to one another by the reversal of the magnetic field. However, they are not a purely odd function of it. A special situation arises when the molecule is connected symmetrically to the two leads. In that case, the anisotropy parameter $\gamma$ vanishes, while $\alpha = 1$ [see Eqs. (28) and (29)]. Then, the two coefficients, $X^V$ and $\tilde{X}^V$, are odd functions of the flux, resembling the thermal Hall effect discussed recently in connection with quantum magnets.\(^{45}\)

$$X^V(\Phi) = e\omega_0 \sin \Phi \int \frac{d\omega}{\pi}V V(\omega, \Phi)(t_o(\omega_-) - t_o(\omega_+)), \quad (72)$$

and

$$\tilde{X}^V(\Phi) = 2e\omega_0 \sin \Phi \int \frac{d\omega}{\pi}V V(\omega, \Phi)$$

$$\times (t_o(\omega_-)(\omega_- - \mu) - t_o(\omega_+)(\omega_+ - \mu)). \quad (73)$$
In other words, the thermoelectric processes described by $X^V(\Phi)$ and $\bar{X}^V(\Phi)$ require a certain symmetry-breaking. In the absence of the magnetic field, that is supplied by the spatial asymmetry of the junction: in the presence of a flux, those processes appear also for a junction symmetrically coupled to the leads, provided that the couplings to the leads depend on the energy.

When the two leads connected to the electronic reservoirs are identical (making the molecular bridge symmetric) the transmission amplitude of the direct bond between the two leads, $t_\omega$ [see Eq. \ref{eq:transfer}], is an even function of $\omega$. The function $T^V(\omega, \Phi)$ given by Eqs. \ref{eq:transmission} and \ref{eq:extended_transmission}, is not entirely even or odd in $\omega$, and therefore \textit{a priori} the integrals which give $X^V(\Phi)$ and $\bar{X}^V(\Phi)$ do not vanish. However, the asymmetry in the $\omega-$dependence of the integrand (which results from the $\omega-$dependence of the Green function) is not significant. As a result, $S^V$ is extremely small, while $\bar{S}^V$ is not (because of the extra $\omega$ factor in the integrand), see Fig. \ref{fig:transport}. These plots are computed using $\Gamma(\omega) = \Gamma^0 \sqrt{1 - (\omega/W)^2}$, and $\lambda(\omega) = \lambda^0 [1 - (\omega/W)^2]$, where $W$ is half the bandwidth, and all energies are measured in units of $\beta = 1/(k_B T)$ (we have set $\Gamma^0 = \lambda^0 = 1$ and $W = 50$).

![Fig. 2: The transport coefficients $S^V$ and $\bar{S}^V$ as functions of the flux (measured in units of the flux quantum) and $\beta\omega_0$, for a symmetric bridge.](image2.png)

The relative magnitudes of $S^V$ and $\bar{S}^V$ are significantly changed when the molecule is coupled \textit{asymmetrically} to the leads, and moreover, the character of the charge carriers on the two reservoirs is different. Let us assume that the left reservoir is represented by an electron band, such that the partial width it causes to the resonant level is given by

$$\Gamma_L(\omega) = \Gamma^0_L \sqrt{\frac{\omega - \omega_c}{\omega_v - \omega_c}}, \quad (74)$$

while the right reservoir is modeled by a hole band, with

$$\Gamma_R(\omega) = \Gamma^0_R \sqrt{\frac{\omega_v - \omega}{\omega_v - \omega_c}}. \quad (75)$$

The corresponding quantity pertaining to the lower arm of the ring in Fig. \ref{fig:ring} is

$$\lambda(\omega) = \lambda^0 \sqrt{\frac{\omega_v - \omega}{\omega_v - \omega_c}} \sqrt{\frac{\omega - \omega_c}{\omega_v - \omega_c}}. \quad (76)$$

Here, $\omega_c$ is the bottom of the conductance band (on the left side of the junction), while $\omega_v$ is the top of the hole band (on the right one). The energy integration determining the various transport coefficients is therefore limited to the region $\omega_c \leq \omega \leq \omega_v$. (For convenience, we normalize the $\Gamma$’s by the full band width, $\omega_v - \omega_c$.) Examplifying results in such a case are shown in Fig. \ref{fig:symmetric} computed with $\Gamma^0_L = \Gamma^0_R = \lambda^0 = 1$ [see Eqs. \ref{eq:gamma_left}, \ref{eq:gamma_right}, and \ref{eq:lambda}], and $\omega_c = -\omega_v = 100$, all in units of $\beta$.

![Fig. 3: Same as Fig. 2 for an asymmetric bridge.](image3.png)
difference on the phonon bath thermalizing the molecular vibrations into a temperature difference across the molecule is not very sensitive to the details of the model, apparently because the term proportional to \( \sin \Phi \) in Eq. (60) is the dominant one. This means that by reversing the direction of the magnetic field, one reverses the sign of the temperature difference or alternatively, the sign of the electronic heat current. On the other hand, the coefficient \( S^\beta \), which sets the scale of the capability to turn a temperature difference across that phonon bath into an electric current, is far more sensitive to the details of the model (as expressed e.g. in our choice for the density of states on the leads) and is less affected by the magnetic field.

We now return to the diagonal charge and heat conductances. Figure 4 shows the flux-dependence of their dimensionless ratio, \( \beta^2 e^2 K_2 / G \), plotted with the same parameters as above. It is interesting to observe that, for both the symmetric and the asymmetric bridges, this ratio remains quite close to the textbook Wiedemann-Franz ratio \( \pi^2 / 3 \), calculated from the Fermi-Dirac distribution of a free electron gas. This is quite surprising, in view of the much richer resonance structure of the transmission through the ring.

In conclusion, we have found that the thermoelectric transport coefficients through a vibrating molecular junction, placed on an Aharonov-Bohm interferometer, have an interesting dependence on the magnetic flux. In particular, the coefficients which relate the temperature difference between the phonon and electron reservoirs to the charge and heat currents carried by the electrons, which exist only due to the electron-vibron coupling, can be enhanced by the magnetic flux.

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FIG. 4: (color online) The Wiedemann-Franz ratio, $\beta^2 e^2 K_2/G$, as a function of the magnetic flux (in units of the flux quantum), for a symmetric (top) and the asymmetric (bottom) bridges. The dotted line is $\pi^2/3$. Parameters are the same as for Figs. 2 and 3.

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