Pair tunnelling through a molecule: linear thermopower

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Abstract. We present the calculations of the linear thermopower in single electron molecular transistors. The molecule with its vibrational internal degrees of freedom used as central object in a single electron transistor can in some cases be characterised by negative effective charging energy. This allows to model the system by Anderson Hamiltonian with negative U. Here we extend the previous calculations of the conductance of such system and study the linear thermopower of a dot characterised by negative value of the on-dot interaction $U$. We focus on the weak tunnelling limit, for which a rate equation approach is valid.

1. Introduction
The quantum transport in nanostructures has recently become an active field of theoretical and experimental research. This is due to the unprecedented accuracy of the measurements, degree of control over the various artificial structures and potential application of devices [1]. The most studied geometry consists of a quantum dot coupled to two external electrodes. (In this work we shall use the notion quantum dot (QD) in a loose sense describing small central region of the structure, whether metallic, semiconducting, molecular, etc., usually characterised by the single energy level.) Due to the small dimensions of the central region its capacitance is small and the charging energy large, meaning that addition of another electron to the dot requires energy at least as large as charging energy. This introduces many body aspect to the problem and is responsible for interesting physics one observes in such systems.

On the experimental side the highlights comprise such important discoveries as observation of Kondo effect in systems with normal electrodes [2, 3, 4, 5, 6, 7], the splitting of the Kondo resonance due to the ferromagnetism in the leads [8], the interplay between the Kondo effect and superconductivity in carbon nanotube quantum dots [9], the recent measurements of Kondo signatures in Andreev scattering in InAs nanowire [10] or carbon nanotube [11] quantum dot coupled to superconducting electrodes.

In the studies of quantum transport through quantum dots one distinguishes few important regimes [12]. In the weak tunnelling regime the dot is relatively isolated and can be characterised by the non-equilibrium distribution function. In this regime one observes Coulomb blockade phenomena and the transport is incoherent as the time spent on the dot is long enough to destroy any coherence. The system can be described by the rate (or master) equation approach [13, 14]. In the co-tunnelling regime the coupling between the central region and electrodes is increased and the contributions of higher order tunnelling processes to transport can not be
neglected. The most intriguing, however, is the appearance of the so called Abrikosov-Suhl or Kondo resonance in the transport. It is due to spin flip processes and appears if the average occupancy of the dot is close to odd integer (for a theoretical review on the subject see [15, 16]). The appearance of the Kondo effect has important influence on the transport [17] characteristics (conductance, thermopower) of the system.

Recently the increased interest is observed in using single molecules as working elements of devices [18], as such systems are believed to set ultimate limits on the miniaturisation. On the other hand the study of electron transport via single molecules allows observation of the interplay between local energy levels and the intra-molecular vibrational degrees of freedom. Koch et al. [19] have studied the conductance through a single molecule coupled to two external electrodes in the weak tunnelling regime. They assumed that the polaron shift induced by molecular vibrations is strong enough to lead to "potential inversion" scenario and effectively negative charging energy (c.f. Eq. (6) below). It is the purpose of this work to present the extension of that paper to the study of nonequilibrium thermoelectric power. In order to obtain analytical results we limit discussion to the linear regime in the voltage and temperature difference.

In the next section we review the Koch’s et al. work [19]. The analytical calculations and numerical results on the linear thermopower will be presented in Section 3. We end up with a summary of main findings.

2. The linear conductance
The aim of this section is to recall the main results obtained by Koch et.al [19] and to establish notation. One starts with general system consisting of external leads and central molecule coupled with them by tunnelling processes. The electron subsystem on a molecule interacts with bosonic degrees of freedom (phonons)

\[ H = H_{\text{mol}} + H_{\text{vib}} + H_{\text{leads}} + H_i, \]

where

\[ H_{\text{mol}} = \varepsilon_n d_n + U n_d^\dagger n_d^\dagger, \]

\[ H_{\text{vib}} = \hbar \omega b^\dagger b + \lambda \hbar \omega (b^\dagger + b) n_d, \]

\[ H_{\text{leads}} = \sum_{a=L,R} \sum_{p,\sigma} \varepsilon_p c_{a p \sigma}^\dagger c_{a p \sigma}, \]

\[ H_i = \sum_{a=L,R} \sum_{p,\sigma} (t_a c_{a p \sigma}^\dagger d_\sigma + h.c.), \]

describing interacting electrons on the dot. Here \( n_d = \sum_{\sigma} n_{d\sigma} = \sum_{\sigma} d_{\sigma}^\dagger d_{\sigma} \) is the number operator, and \( d_{\sigma}^\dagger (d_{\sigma}) \) denotes creation (annihilation) operator of a spin \( \sigma \) electron on the molecule. \( U \) denotes (positive) charging energy.

stands for the energy of bosonic system of frequency \( \omega \) (the first term) and the coupling between electron and boson subsystems (the second term) on a molecule. Bosonic creation (annihilation) operators are denoted by \( b^\dagger (b) \). The spectrum of bosons is assumed to be dispersion less. The external leads (left-L and right-R) are described by free electron models with energy \( \varepsilon_p \) measured from the Fermi level \( \mu \) and the corresponding term in the Hamiltonian is given by

while the coupling between the molecule and leads is governed by the Hamiltonian

\[ H_i = \sum_{a=L,R} \sum_{p,\sigma} (t_a c_{a p \sigma}^\dagger d_\sigma + h.c.), \]

describing the tunnelling of electrons between leads and the dot.
To proceed one eliminates electron-boson coupling via canonical transformation $\tilde{H} = e^{S}H e^{-S}$ with $S = -\lambda n_{d}(b^{\dagger} - b)$ and gets transformed Hamiltonian with

$$\tilde{t}_{a} = t_{a}e^{-\lambda(b^{\dagger} - b)},$$
$$\tilde{\varepsilon}_{d} = \varepsilon_{d} - \lambda^{2}\hbar\omega,$$
$$\tilde{U} = U - 2\lambda^{2}\hbar\omega.$$  \hspace{1cm} (6)

Due to the coupling to phonons the on-dot electron energy, the interaction energy and the coupling to electrodes are renormalised. Under appropriate conditions the effective interaction $U_{\text{eff}} = U - 2\lambda^{2}\hbar\omega$ can be negative. In the following we shall assume that $U_{\text{eff}}$ is negative and we shall call it simply $U$. It is interesting to note that after the transformation the (renormalised) effective hopping parameters depend on bosonic operators and have to be evaluated for each bosonic state independently. It is this dependence which is responsible for phonon-induced side bands in conductance [20] and has been found inter alia to renormalise the Kondo coupling [21] and Fano factor [22]. Here we evaluate the hopping in the bosonic ground state and get $\tilde{t}_{a} = t_{a}e^{-\lambda^{2}/2}$ to be denoted $t_{a}$ in the following.

With help of Schrieffer-Wolff [23] transformation we eliminate $H_{i}$ and get [19] the effective low energy Hamiltonian in the form

$$\tilde{H} = H_{\text{mol}} + H_{\text{leads}} + H_{\text{dir,ex}} + H_{\text{pair}}.$$  \hspace{1cm} (7)

The direct and exchange $H_{\text{dir,ex}}$ interactions between dot and the leads are most important for positive $U$ and read

$$H_{\text{dir,ex}} = \frac{1}{2} \sum_{aa'pp'} \left[ \frac{t_{a}t_{a'}^{*}}{\varepsilon_{ap} - \varepsilon_{d}} c_{ap\sigma}^{\dagger} c_{a'p'\sigma}^{\dagger} + t_{a}t_{a'}^{*} M(\varepsilon_{ap}) \cdot (d_{\sigma}^{\dagger}d_{\sigma}c_{ap\sigma}c_{a'p'\sigma}) + H.c. \right],$$  \hspace{1cm} (8)

where $M(\varepsilon) = [\varepsilon - \varepsilon_{d}]^{-1} - [\varepsilon - \varepsilon_{d} - U]^{-1}$. It turns out that the processes described by $H_{\text{dir,ex}}$ do also play a role in the present case of ‘negative $U$ quantum dot’. However, for negative $U$ the pair tunnelling terms $H_{\text{pair}}$ have to be retained as they play a main role [19] for in this case the double occupancy of the dot is favourable

$$H_{\text{pair}} = \sum_{aa'pp'} t_{a}t_{a'}^{*} M(\varepsilon_{ap})d_{p}^{\dagger}d_{p'}^{\dagger}c_{ap\sigma}^{\dagger}c_{a'p'\sigma}^{\dagger} + H.c.$$  \hspace{1cm} (9)

One uses Fermi’s golden rule [12] to calculate rates of tunnelling of electron pairs from electrodes $a$ and $a'$ to the dot or from the dot to electrodes. For the system with constant temperature across the system they have been obtained by Koch et. al [19] and read

$$W_{2\rightarrow 0} = \frac{\Gamma_{a}\Gamma_{a'}}{\hbar} \int d\varepsilon M^{2}(\varepsilon)f(\varepsilon - \varepsilon_{d})f(2\varepsilon_{d} + U - \varepsilon - eV_{a'})$$  \hspace{1cm} (10)

for tunnelling of 2 electrons onto the dot (spin up electron hops on the dot from electrode $a$ and spin down from electrode $a'$), where $\Gamma_{a} = 2\pi\rho_{a}|t_{a}|^{2}$, and $\rho_{a}$ is density of the states at the Fermi level on electrode $a$ and $f_{a}(x)$ is corresponding Fermi function. Similar expressions can be derived for all other rates. The rates of single electron co-tunnellings from left to right electrode, without changing the occupancy of the dot i.e for processes $0 \rightarrow 0$ and $2 \rightarrow 2$, are obtained from $H_{\text{dir,ex}}$ and have also to be taken into account [19]. Obviously Eq. (10) is also valid for system
Figure 1. The dependence of linear conductance (a) and the thermopower (b) calculated on the basis of Mott’s formula (see text for explanation) on the parameter \( x = 2\varepsilon_d + U \), for different temperatures \( k_B T / |U| = 0.01, 0.005, 0.001 \). The energies are measured in units of \(|U|\), while conductance \( G \) in units of \( G_0 = \frac{2e^2}{h} \frac{\Gamma_L \Gamma_R}{|U|} \) and thermopower in units of \( S_0 = \frac{\pi^2 k_B^2}{3e} \).

in which left lead is characterised by temperature \( T_L \) different from that of the right lead \( T_R \). In this case, however, no general analytical solution is possible.

The linear conductance has been found in closed form by Koch et al. and reads

\[
G = \frac{2e^2 \Gamma_L \Gamma_R}{h} \left( \frac{U^2}{\varepsilon_d^2(\varepsilon_d + U)^2} \frac{\beta(2\varepsilon_d + U)}{2\sinh[\beta(2\varepsilon_d + U)]} + \frac{f(-2\varepsilon_d - U)}{\varepsilon_d^2} + \frac{f(2\varepsilon_d + U)}{(\varepsilon_d + U)^2} \right) \tag{11}
\]

It is easy to verify that, in the limit \( x = 2\varepsilon_d + U = 0 \) the linear conductance takes on the value \( G = 12\frac{e^2}{h} \frac{\Gamma_L \Gamma_R}{|U|} \) independent on the temperature. It is the width of the resulting curve which is governed by temperature as it can be seen in Fig. (1a). The contribution of cotunnelling processes is only weakly temperature dependent (dotted curve in Fig. (2b)).

In the next subsection we present our study of linear thermopower of this system.

3. Linear thermopower

To calculate linear thermopower at low temperatures the Mott’s formula [24]

\[
S(T) = -\frac{\pi^2}{3} \frac{k_B^2}{e} \frac{T}{h} \frac{\partial \ln G(\mu)}{\partial \mu} \tag{12}
\]

has often been used. As it has been discussed previously [17] it reproduces the low temperature thermopower quite well, provided there are no very narrow features in the spectrum, like e.g. the Kondo resonance. However, here we are interested in obtaining the exact analytic expression for the linear thermopower valid at arbitrary temperature \( T \). We assume that left and right leads are large enough to remain in a equilibrium state during the current flow. Let denote their temperatures and voltages by \((T_{aL}, V_{aL})\) and \((T_{aR}, V_{aR})\), respectively. The linear thermopower may be calculated by expanding the Fermi functions of the \( a \) and \( a' \) leads for small \( \delta T_a \) and \( \delta T_{a'} \) around \( T \). Specifically we use

\[
f_\beta(\omega) = f \left( \frac{\omega - \mu + eV_\beta}{k_B T_\beta} \right) = f(\omega) + \frac{\partial f(\omega)}{\partial \omega} \left( eV_\beta - \frac{\omega - \mu}{T} \delta T_\beta \right). \tag{13}
\]
Figure 2. The total thermopower (solid line) and the pair hopping contribution to it (left panel). Both calculated on the basis of Mott’s formula temperature $k_B T/|U|=0.01$. The right panel shows the total conductance for the same temperature and the cotunnelling contribution. The energies are measured in units of $|U|$, while conductance $G$ in units of $G_0 = \frac{2e^2}{h} \frac{\Gamma_L}{\Gamma_R}$ and thermopower in units of $S_0 = \frac{\pi}{3} k_B \frac{e}{|U|}$.

The thermopower is defined as the ratio of voltage induced to the temperature difference with the condition that no current flows in the system. Thus

$$S(T) = -\left(\frac{V}{\delta T}\right)_{I(T,V,\delta T)=0},$$

and to calculate $S$ in the linear regime it is enough to calculate the current $I(V,\delta T)$ to linear order in $V$ and $\delta T$. If $I(T,V,\delta T) = I_V V + I_T \delta T$ then $S = \frac{I_T}{I_V}$. To this end we require all the transition probabilities $W_{a,a'}^{n,n'}$ (c.f. eq. (10)) to be written in the general form

$$F(T,V,\delta T) = F(T,0,0) + F_V(T)V + F_T(T)\delta T.$$  

In calculating the transition rates and probabilities of we assume that the function $M(\varepsilon)$ can be replaced by $M(0)$. In particular we get

$$W_{a,a'}^{0,2} = \frac{\Gamma_a \Gamma_{a'}}{h} M^2(0) \left[ I_0(x) + I_V(x)(eV_a + eV_{a'}) + I_T(x)\left(\frac{\delta T_a}{T} + \frac{\delta T_{a'}}{T}\right) \right],$$

where $x = 2\varepsilon_d + U$ and the coefficients read

$$I_0(x) = \int_{-\infty}^{+\infty} d\varepsilon f(\varepsilon)f(x - \varepsilon) = \frac{x}{e^{\beta x} - 1},$$  

$$I_V(x) = \int_{-\infty}^{+\infty} d\varepsilon \frac{\partial f(\varepsilon)}{\partial \varepsilon}f(x - \varepsilon) = \frac{1}{e^{\beta x} - 1} - \frac{\beta x e^{\beta x}}{(e^{\beta x} - 1)^2},$$

and

$$I_T(x) = \int_{-\infty}^{+\infty} d\varepsilon \frac{\partial f(\varepsilon)}{\partial \varepsilon}f(x - \varepsilon).$$
The last integral, in principle, can also be evaluated in closed form with help of Polylogarithmic functions, but we choose to evaluate it numerically for each temperature $T$ and the value of $x$.

With help of the above integrals and the Fermi function the linear thermopower can be written in a closed form as

$$S = -k_B \frac{\beta \frac{U^2}{e^2(\epsilon_d+U)^2} [f(x)I_T(-x) - f(-x)I_T(x)]}{e \frac{1}{\epsilon_d^2(\epsilon_d+U)^2} \tanh(\beta \epsilon_d) + \frac{1}{\epsilon_d^2(\epsilon_d+U)^2} f(x)}$$

(20)

Few comments are in order. The denominator entering the formula of thermopower is up to the normalisation factor given by the linear conductance (c.f. Eq. (11)). The linear thermopower $S$ is an odd function with respect to pair degeneracy point $x = 2\epsilon_d + U = 0$. It is not obvious from the equation above, but up to linear order there is no contribution to the nominator of the thermopower from cotunnelling processes. The total contribution to the current from cotunnelling processes is proportional to $W_{LR}^{0 \rightarrow 0} (2 \rightarrow 2) - W_{RL}^{0 \rightarrow 0} (2 \rightarrow 2)$ and vanishes to linear order in $\delta T_L + \delta T_R$. As mentioned earlier they contribute to denominator of $S$ only. This is in contrast to the result obtained on the basis of Mott’s formula, which contains (however small) the contribution from cotunnelling processes. It is shown in figure (2). In figure (2a) we plot total and pair contribution to $S_{Mott}$, while in figure (2b) total linear conductance and cotunnelling contribution. In both cases temperature $k_B T = 0.010|U|$. The results of numerical calculations of linear thermopower (20) are presented in figure (3) for temperatures $k_B T / |U| = 0.010, 0.005, 0.002$. With increasing temperature the maxima of $S$ move outwards of degeneracy $x = 2\epsilon_d + U = 0$ point. The maximum value of $S$ is very weakly $T$ dependent. The overall dependence of linear thermopower is very much similar to what one obtains from the Mott’s formula. The detailed comparison (cf. Fig. (4)), however, reveals subtle differences. The most str S takes on large and essentially temperature independent values at $x = x_{\text{max}}$ signalling potential cryogenic applicability of the device. This aspect, however, will be discussed elsewhere in the context of nonlinear thermopower.
4. Summary

We have calculated the linear thermopower of the single electron molecular transistor in the limit of large on molecule electron-phonon coupling leading to negative effective charging energy. In this limit it is the pair tunnelling processes which mainly contribute to the thermopower. The detailed comparison shows that Mott’s formula leads to overall qualitatively correct picture of linear thermopower. The numerical values, however may differ by a factor as big as $\pi^2/3$.

Acknowledgments

This work has been partially supported by the Ministry of Science and Education under the grant No. N202 1878 33. KIW would like to thank Max-Planck-Institut für Physik Komplexer Systeme, Dresden for hospitality. The authors thank T Domański for discussions and J Krzyszczak for technical help.

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