Thermal conductance of a molecule

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Abstract. The effect of the electron-phonon coupling on the thermal conductance of a molecule has been calculated in the regime of weak coupling with two electrode leads within a linear response theory. The molecule is modelled in terms of the relevant electronic orbitals coupled to phonons corresponding to both internal phonon modes (vibrations) and to oscillations of the molecule as a whole. The thermal conductance is calculated using the rate-equation approach as a function of the gate voltage, temperature and electron-phonon coupling. The peak behaviour of the conductance and the thermal conductance are analyzed as a function of the strength of the electron-phonon coupling and of the thermal energy. Sequential tunnelling contributions have been included to the thermal conductance because they dominate at the Coulomb peaks at low temperatures. The electron-phonon coupling causes an increase of the thermal conductance that is more important at low temperatures.

1. Introduction
The electronic transport through single molecules has attracted the research interest in an effort to realize molecular electronics and it is currently a very active research area. Recently, there is growing interest in studying the thermal properties and the heat transfer in nanostructures and molecules (e.g. [1-3]). The present study aims to contribute to this research area.

The electron thermal conductance of a molecule in the regime of weak coupling with two electrode leads is calculated within a linear response theory in the sequential tunneling regime. The theoretical model is briefly described in section 2 and characteristic results are presented in section 3. A conclusion is drawn in section 4.

2. Theoretical model
We consider a molecule that is weakly coupled to two electrodes via tunnel barriers. Each electrode is assumed to be in thermal equilibrium and there are a voltage difference $V$ and a temperature difference $\Delta T$ between the two electrodes. We restrict ourselves to the linear regime assuming small $V$ and $\Delta T$ to ensure that the symmetry and the structure of the molecule itself are not affected. A continuum of electron states is assumed in the electrodes that are occupied according to the Fermi-Dirac distribution.

The molecule is characterized by discrete energy levels (orbitals) $E_p (p=1,2,\ldots)$. It is assumed that the energy spectrum does not change by the number of electrons in the molecule. The energy levels are assumed to be weakly coupled to the states in the electrodes so that the charge of the molecule is well defined. We adopt the common assumption in the Coulomb blockade problems for the electrostatic energy $U(N)$ of the molecule charged with $N$ electrons: $U(N) = (Ne)^2 / 2C - N\phi_{\text{ext}}$, where $C$ is the effective capacitance between the molecule and the reservoirs and $\phi_{\text{ext}}$ is the external potential (e.g. the gate bias in the transistor configuration). The transport through the molecule is described by rate equations [4,5].

Due to the voltage difference $V$ and the temperature difference $\Delta T$ between the two reservoirs, electric and thermal currents pass through the dot. The stationary current $I$ and the heat flux $Q$ through the left barrier are respectively given by the following equations [4,5]:

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Journal of Physics: Conference Series 92 (2007) 012058 doi:10.1088/1742-6596/92/1/012058

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\[
I = -e \sum_{p=1}^{\infty} \sum \sum P^q(\{\eta_i\}) \left( \delta_{n_p,0} \Gamma_{q \rightarrow q',l}^N f(E_{l+1}^l(N) - E_F) - \delta_{n_p,1} \Gamma_{q \rightarrow q',l}^N f(E_{l+1}^l(N) - E_F) \right)[1 - f(E_{l+1}^l(N) - E_F)]
\]

\[
Q = \sum_{p=1}^{\infty} \sum \sum P^q(\{\eta_i\}) \left( \delta_{n_p,0} \Gamma_{q \rightarrow q',l}^N f(E_{l+1}^l(N) - E_F) - \right)
\]

\[
\delta_{n_p,1} \Gamma_{q \rightarrow q',l}^N f(E_{l+1}^l(N) - E_F)\right][1 - f(E_{l+1}^l(N) - E_F)]
\]

where the second summation is over all possible combinations of occupation numbers \(\{n_1, n_2, \ldots\} \equiv \{n_i\}\) of the energy levels in the quantum dot, each with stationary probability \(P^q(\{\eta_i\})\). The numbers \(n_i\) can take on only the values 0 and 1 and it holds: \(N \equiv \sum_i n_i\). The non-equilibrium probability distribution \(P\) is a stationary solution of a kinetic equation. In the linear regime, the equilibrium stationary probability appears in the currents. \(P^q_{eq}(\{\eta_i\})\) is the Gibbs distribution in the grand canonical ensemble. The third summation is over the phonon states. Two phonon types are taken into account in the transition rates \(\Gamma\) [6]: (i) vibrations, that are internal phonon modes of the molecule, for which the center of mass is at rest, and (ii) oscillations, that involve movement of the molecule as a whole. The arguments of the Fermi functions are transition energies imposed by the conservation of energy upon tunneling [4,5].

The thermal conductance is defined as [4]:

\[
\kappa \equiv -\frac{Q}{\Delta T}_{I=0} = -K \left( 1 + \frac{S^2 G T}{G} \right),
\]

where \(G\) is the conductance, \(K\) is the thermal coefficient and \(S\) is the thermopower.

### 3. Calculated thermal conductance

#### 3.1. No electron-phonon coupling

Coulomb effects are important in the transport coefficients when the charging energy dominates over the thermal energy \(k_B T\) and the electron confinement (measured by the energy level spacing \(\Delta E\)). In the quantum regime, where \(\Delta E >> k_B T\), the discreteness of the energy spectrum of the quantum dot plays a predominant role. For non-degenerate energy levels, equidistant energy levels spectrum \((E_p = p \Delta E)\) and level-independent tunneling rates, \(\Gamma^{l,r}\), simplified expressions can be obtained for the transport coefficients [5]:

\[
G = \frac{e^2}{k_B T} \gamma \frac{1}{1 + 4 \cosh^2 (\Delta/2k_B T)} e^{-\Delta E/k_B T},
\]

\[
\kappa = k_B T \gamma \left( \frac{\Delta E}{k_B T} \right)^2 \frac{1}{1 + 4 \cosh^2 (\Delta/2k_B T)} e^{-\Delta E/k_B T},
\]

where \(\gamma \equiv \Gamma^{l,r} / (\Gamma^{l} + \Gamma^{r})\), \(\Delta(N) = E_N + U(N) - U(N-1) - E_F\) with \(N=N_{min}\) is the integer that minimizes the absolute value of \(\Delta \equiv \Delta(N_{min})\).
The calculated conductance and the thermal conductance exhibit periodic Coulomb-blockade oscillations \[4,5\]. The peaks (at the values of \(E_F\) for which it holds: \(\Delta = 0\)) occur each time an extra electron enters in the dot and they are separated by intervals \(\Delta E_F = \Delta E + \frac{e^2}{C}\).

In the thermal conductance behaviour dominates the effect of quantum confinement through the dependence on the ratio of the energy level spacing over the thermal energy, \(\Delta E / k_B T\). The electron thermal conductance decreases nearly exponentially with decreasing temperature and increasing \(\Delta E\). This behaviour agrees with the observation that the thermal conductivity of a quantum dot is very small compared to that of bulk. However, for a realistic description and an understanding of the thermal transport properties of dots and molecules the effect of the electron-phonon coupling must be considered.

3.2. The effect of electron-phonon coupling

3.2.1. Oscillations. In figures 1a and 1b are shown the calculated thermal conductance when electrons are coupled with oscillations of the molecule for two values of temperatures. The parameter \(\xi\) is inversely proportional to the coupling strength \[6\]. The plotted results for \(\xi = 50\) are identical to the case when electron-phonon coupling is neglected and they are here shown for reference. The thermal conductance is enhanced considerably because new channels of conduction are provided through the electron-phonon coupling. The additional conductance channels are far more important at low temperatures. At higher temperatures, thermal broadening offers additional conduction channels and it is mainly responsible for the increase of \(\kappa\).

**Figure 1a.** Calculated thermal conductance \(\kappa\), as a function of the gate voltage \((E_F)\), for \(\Delta E = 0.05 \, e^2/2C\) for \(T = 0.05 \, e^2/2C\) for oscillations. For \(\xi = 50\) dots have been used to make the plot more visible because of the small values of \(\kappa\).

**Figure 1b.** As in figure 1a, for \(T = 0.1 \, e^2/2C\).

3.2.2. Vibrations. Calculated thermal conductance values when electrons are coupled to vibrational phonons are shown in figure 2 for two values of the coupling parameter \(\lambda\) and at two temperatures. It should be noted that the parameters have been chosen taking into account that: \(\lambda = (h/M_0)^{1/2}\) \[6\]. It is found that electron-phonon coupling causes a nearly two orders of magnitude increase of the thermal conductance at low temperatures. The thermal conductance increases with increasing \(\lambda\). At higher temperatures, conduction is governed by the role of thermal broadening that ‘screens’ the role of electron-phonon coupling in providing new channels of conduction. Small increase in \(\kappa\) has been
found for $\lambda=0.2$ relative to $\lambda=0$ whereas for $\lambda=2$ the increase is bigger. However, it should be noted that for strong electron-phonon coupling a reduction of $\kappa$ is found with temperature due to electron-phonon scattering.

Figure 2. Calculated thermal conductance $\kappa$, as a function of the gate voltage ($E_F$), for $\Delta E=0.05$ $e^2/2C$ for vibrations. The solid lines are for $T=0.05$ $e^2/2C$ and the lines with squares are for $T=0.1$ $e^2/2C$. The line with triangles is for $\lambda=0$ and $T=0.1$ $e^2/2C$.

4. Conclusion
The important role of the electron-phonon coupling in determining the magnitude of the thermal conductance of a molecule has become evident. The dependence of the behaviour of $\kappa$ on the electron-phonon coupling parameters has been indicated, that makes interesting the study of the thermal conductance of real molecules.

Acknowledgments
The present work has been co-funded by European Community funds and by National funds (E.P.E.A.E.K.), under the ‘Archimides’ programme.

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