Possible origin of thermoelectric response fluctuations in single-molecule junctions

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New Journal of Physics 15 (2013) 105004 (14pp)
Received 2 April 2013
Published 8 October 2013
Online at http://www.njp.org/
doi:10.1088/1367-2630/15/10/105004

Abstract. The thermoelectric response of molecular junctions exhibits large fluctuations, as observed in recent experiments (e.g. Malen J A et al 2009 Nano Lett. 10 3406). These were attributed to fluctuations in the energy alignment between the highest occupied molecular orbital (HOMO) and the Fermi level at the electrodes. By analyzing these fluctuations assuming resonant transport through the HOMO level, we demonstrate that fluctuations in the HOMO level alone cannot account for the observed fluctuations in the thermopower, and that the thermo-voltage distributions obtained using the non-equilibrium Green’s function method, arguably the most common method at practice, are qualitatively different than those observed experimentally. We suggest that this inconsistency between theory and experiment is due to the level broadening that is inherently built-in to the calculation method, and smears out any variations of the transmission on energy scales smaller than the level broadening. We show that although this smearing only weakly affects the transmission, it has a large effect on the calculated thermopower. To amend this discrepancy, we introduce the method of open quantum systems and use it to calculate the thermopower and its fluctuations. We account for both the magnitude of the variations in the thermopower and the qualitative form of the distributions, and show that they arise not only from variations in the HOMO-Fermi level offset, but also from variations of the local density of states at the contact point between the molecule and the electrode.
1. Introduction

Improving the thermo-electric (TE) energy conversion efficiency relies on increasing the TE response (Seebeck coefficient) and reducing the thermal conductance of the device [1, 2]. Metal–single molecule–metal junctions (molecular junctions) seem promising in both aspects: their thermal conductance is small due to the mismatch between the vibrations of the electrodes and the molecule, and their TE response should be large due to the well-defined resonant structure of the electron transport (via the molecular highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO) levels) [3]. This observation, along with the notion that TE response can shed light on transport mechanisms in molecular junctions [4–6], have initiated in large number of experimental [8–14] and theoretical studies [15–28] on TE effects in molecular junctions.

Most notable are a series of impressive experiments in which TE conversion using a single-molecule junction was demonstrated [3, 8–11]. In these experiments, a single molecule (usually Benzene rings with various end groups) is trapped between an Au substrate and an Au scanning tunneling microscope (STM) tip, which are held at a constant temperature difference $\Delta T$. A voltage bias $\Delta V$ (here called ‘thermo-voltage’) is then applied between the tip and substrate to reach a state of zero current flowing through the molecule. The Seebeck coefficient is defined as (minus) the slope of $\Delta V(\Delta T)$ as a function of $\Delta T$ in the linear response regime (i.e. $\Delta T \rightarrow 0$). In the experiments the value of $\Delta V$ is strongly fluctuating, and repeating the experiment many times results in a broad distribution of $\Delta V$, as can be seen in [10, figure 3] (and inset of figure 2(b) here). Using the typical $\Delta V$ (where the voltage distribution displays a maximum), the authors of [8, 10] find typical Seebeck coefficients of the order of $\sim 10 \mu V K^{-1}$ for single molecule junctions. Naturally, in order to find a pathway for increasing the TE response of molecular junctions, full understanding of the TE conversion process is required. Since fluctuations of the kind described above appear in all of the reported experiments, it is clear that understanding them is an important step in understanding the electronic and TE properties of molecular junctions.

The observed variations in the TE response do not seem to be simple (Gaussian) noise, and the distributions of the thermo-voltage $\Delta V$ may have a well-defined double-peak structure [8, 10]. Malen et al [10] concluded that the fluctuations (also reported in TE measurements of metal–fullerene–metal junctions [13]) are caused by variations of the position of the HOMO level, which are translated into variations in the energy offset between the HOMO level and the Fermi energy of the contacts, $E = E_{\text{HOMO}} - E_F$, as the junction reconstructs.
Assuming that the transport is dominated by a single resonant level and using the Landauer formula for TE transport (see e.g. [2, 29]) they quantified the variations $\delta E$ in $E$ and found them to be $\delta E \sim 2.5$ eV, of the order of the average offset $E$ itself.

In this paper we suggest that besides the variations in the offset energy between the HOMO level and the Fermi energy, there is an additional contribution to the fluctuations in the thermopower, which is the strong variations of the local density of states LDOS as a function of energy, at the point of contact between the molecule and the electrodes. We use a toy model to verify this effect. The main results are (i) within the non-equilibrium Green’s function (NEGF) formalism (in conjunction with the Landauer formula) for TE transport, with the wide-band approximation (which is the most popular approximation used in the literature), any variations in the transmission function which are smaller than the self-energy (or level broadening) are suppressed. The result is a smooth transmission function and a smooth thermopower (as a function of energy). (ii) The thermopower is extremely sensitive to small fluctuations of the transmission function. As a result, the suppression of fluctuations in the transmission function, inherent to the Green’s function method, strongly affects on the calculated thermopower, and results in an over-estimation in the HOMO level-Fermi level energy offset fluctuations. (iii) The thermo-voltage histogram obtained using the Green’s function method is qualitatively different from the histograms obtained experimentally, and (iv) all of the above draw-backs of the Green’s function formalism can be overcome by using the open quantum system approach to calculating the TE response in molecular junctions.

The paper is organized as follows. In section 2 we derive the estimation for the fluctuations in the HOMO-Fermi level energy offset from the experimental values of thermopower for typical molecular junctions, using a simple description of the molecular junction as a resonant level and using the Landauer formula. In section 3 we present the open quantum systems (OQS) approach, and using a simple model for the molecular junction we show that this approach for calculation of thermopower yields results which are in qualitative agreement with the experimental results. In section 4 we show that, for the same model, the Green’s function approach gives very different results, due to the inherent suppression of fluctuations built in to the method (due to the presence of a self-energy of level broadening). We demonstrate that the thermopower is very sensitive to fluctuations, and thus the suppression of (small) fluctuations in the transmission strongly affects the calculation of thermo-power. Section 5 is devoted to summary and discussion.

2. Analysis of thermopower fluctuations using the Landauer formula for a resonant level

As a starting point, we consider the data presented in [10, figure 3] (also inset of figure 2 here), where the thermo-voltage histograms of a 2′,5′-dimethyl-4, 4′-tribenzenedithiol (DMTBDT) molecular junction are presented. We observe several notable features: (i) noise is present in the measurement: even at $\Delta T \approx 0$ there is a finite thermo-voltage distribution, with an average signal offset of a few tens of microvolts, (ii) the typical form of the thermo-voltage distribution seems Gaussian and (iii) a double-peak structure of the distribution emerges, indicating two dominant values of the Seebeck coefficient, $S_1 \sim 4.6$ and $S_2 \sim 15 \mu V K^{-1}$.

In order to estimate the variation in the molecular HOMO required to obtain these values, we use the standard Landauer formalism. Within this formalism, the conductance is given by $G = \frac{2e^2}{h} \tau(E_F) = G_0 \tau(E_F)$, and the Seebeck coefficient at low temperature can be
approximated as
\[
S \approx -\frac{\pi^2 k_B^2 T}{3e} \frac{\partial \log(\tau(\epsilon))}{\partial \epsilon} \bigg|_{\epsilon=E_F},
\]
where \( \epsilon \) is the electron energy, \( \tau(\epsilon) \) is the electron transmission function, \( e \) is the proton charge, \( k_B \) the Boltzmann constant and \( T \) is the average temperature.

Note that the Landauer approximation by itself cannot say much about the nature of the fluctuations in this regard without some form of approximation for the transmission function itself. To evaluate the transmission function, we proceed by assuming that the transport through the molecule is characterized by a transmission through a resonant level. To justify this, as well as the toy model considered in the next section, we briefly review the literature on theoretical calculations of thermopower in molecular junctions. The most common theoretical tool to calculate the transmission (and from it the thermopower) is the combination of NEGF and density-functional theory (DFT) [29], where the transmission function is evaluated using the Green’s function as obtained from DFT. Within this approach, the transmission function is calculated as a function of the Fermi energy position (or equivalently an applied gate voltage, which induces an energy shift to the molecular levels), and from it the thermopower is calculated, also as a function of the Fermi energy position (see e.g. [12, 17, 25, 26, 30]).

In transport experiments gating of a molecule can be achieved [31–33], such a dependence of the thermopower on the gate voltage was never studied experimentally, and experiments always carry a statistical nature as discussed above. However, to our knowledge the statistical nature of thermopower in molecular junctions has never been addressed (although it has been addressed in the context of transmission [34] or thermopower of atomic wires [35]). Nevertheless, to justify our model we observe that in the theoretical calculations, the transmission function seems always to resemble a resonant level, at least close to the HOMO or LUMO levels [12, 17, 25, 26, 30]. Thus, considering a resonant level model is a common description even of realistic molecules with electron interactions.

For a given resonant molecular level with energy \( E_{\text{HOMO}} \) and contact Fermi energy \( E_F \), the typical form of the transmission function is a resonant Lorentzian, \( \tau(E) = \frac{1}{1+\frac{(E-E_{\text{HOMO}})^2}{\Gamma^2}} \), where \( E = E_{\text{HOMO}} - E_F \) is the energy offset and \( \Gamma \) is the contact-induced effective level broadening. The resulting Seebeck coefficient is of the form
\[
S \approx -\frac{\pi^2 k_B^2 T}{3e} \frac{2E}{E^2 + \Gamma^2}.
\]

Noting the double-peak structure of the voltage distribution, we thus consider that there is a typical shift in the HOMO level \( \delta \epsilon \). Taking the conductance value to be \( G \sim 0.01 G_0 \), one needs to solve simultaneously \( \frac{1}{E^2 + \Gamma^2} = 0.01 \), \( -\frac{\pi^2 k_B^2 T}{3e} \frac{2E}{E^2 + \Gamma^2} = 4.6 \), \( -\frac{\pi^2 k_B^2 T}{3e} \frac{2(E+\delta \epsilon)}{(E+\delta \epsilon)^2 + \Gamma^2} = 15 \mu \text{V} \text{K}^{-1} \). These equations yield (at ambient temperature) \( \Gamma \sim 0.31 \text{ eV} \), \( E \sim 3.1 \text{ eV} \) and \( \delta \epsilon \sim 2.2 \text{ eV} \), such that \( \delta \epsilon / E \approx 0.7 \), similar to the value obtained in [10]. This means that the molecular level alignment with the contact Fermi level is changing by \( \sim 2 \) electron-volts at every reconstruction of the junction. This large variation (of the order of \( E \) itself) was attributed to variations in the junction contact geometry and intermolecular interactions. However, a recent study of transition voltage spectroscopy in molecular junctions (see [36] for description of the method) demonstrated that the variation of \( E \) are of the order of \( \sim 1 \text{ eV} \) [37], much smaller than the variation required to generate the value above. This discrepancy suggests that there is an additional factor contributing to the variations in thermopower. We point again that the
discrepancy is not due to the Landauer formula only, but due to the resonant level model used within the Landauer formalism.

The discrepancy describes above hints that there is a flaw in the analysis of the thermopower fluctuations using the Landauer formula with the resonant level model. As we will show in the following sections, the flaw is that this model inherently suppresses any variations in the transmission function (as a function of molecular level energy $E$) which are on an energy scale smaller than the level broadening (or electron self-energy), and since the thermopower is very sensitive to variations in the transmission, this suppression strongly affects the thermopower. Thus, fluctuations in $E$ sample a thermopower function $S(E)$ which is ‘too smooth’, resulting in the over-estimate of $\delta E$.

3. Open quantum system approach to thermopower

In order to identify the origin of variations in the thermopower, we study a toy model of a molecular junction. We use the method of OQS (which was described in detail in previous publications [16, 38]) to show that the thermopower $S(E)$ exhibits variations as a function of $E$ which are on the same energy scale as the variations in the LDOS at the molecule-lead point of contact, and show that the thermo-voltage histogram resulting in fluctuations in $E$ is qualitatively similar to the experimental ones. In the next section we will compare the result obtained from the OQS method to those obtained by using NEGF method.

Our toy model consists of two finite electrodes with a molecular bridge between them (upper panel of figure 1), attached to reservoirs with different temperatures $T_L$ and $T_R$ for the left and right edges respectively. The molecule is described by a simple chain with four atomic orbitals. The OQS method enables one to calculate the electronic density in this non-equilibrium situation (a finite temperature difference between the electrodes). From the electronic density, one can calculate (via the Poisson equation) the voltage difference $\Delta V$ between the electrodes as a function of the temperature difference $\Delta T = T_R - T_L$. Repeating the calculation for different values of $\Delta T$ we then find a curve $\Delta V(\Delta T)$, and the linear slope is the thermopower (or Seebeck coefficient) $S = -\frac{\partial \Delta V}{\partial \Delta T}$.

Essentially, OQS theory is a mapping of the system Hamiltonian $H$ (which in general includes all electronic degrees of freedom, electron interactions, junction geometry, etc) onto a master equation for the single-particle density matrix of the Lindblad form $[38]$

$$\dot{\rho} = -i[H, \rho] + \mathcal{L}[\rho].$$

We consider a non-interacting tight-binding Hamiltonian of the form $H = H_L + H_R + H_d + H_c$, where

$$H_{L,R} = -t \sum_{\langle i, j \rangle \in L,R} (c_i^\dagger c_j + h.c.)$$

(4)

are the tight-binding Hamiltonians of the left and right leads, respectively ($t$ is the hopping integral, which is taken as the unit energy, $t = 1$ eV from here on), and

$$H_d = -t \sum_{\langle i, j \rangle \in d} (c_i^\dagger c_j + h.c.) + \sum_{i \in d} (E - \mu) c_i^\dagger c_i$$

(5)

is the Hamiltonian for the wire, which includes the usual hopping integral and an energy $E$ which can be tuned (for instance using a gate electrode experimentally). The energy is measured with respect to the electrodes’ Fermi energy $\mu$ which is set as the zero energy ($\mu = 0$).
Figure 1. Upper panel: schematic representation of the molecular junction. (a) Seebeck coefficient $S$ (solid blue line) and electron occupation of the molecular chain (dashed orange line) as a function energy $E$ (see text for numerical parameters). As the molecular levels cross the electrode Fermi energy (which is set as the zero energy) the occupancy of the dot change, and correspondingly the Seebeck coefficient changes sign. Oscillations of the Seebeck coefficients between the changes of sign are observed. (b) Same as (a) for different values of the electrode–molecule coupling, 200, 100 and 10 meV. The coupling has little effect on the Seebeck coefficient. (c) Temperature dependence of the Seebeck coefficient (at $E = 0$) for various molecular chain lengths, exhibiting a non-monotonic temperature dependence.

The coupling between the electrodes and the molecular wire is given by

$$
\mathcal{H}_c = (g_L c_{L,d,0}^\dagger + g_R c_{R,d,L_d}^\dagger) c_{d,0} + h.c.,
$$

(6)

describing the coupling between the left (right) lead to the wire, with $c_{L(R),d}^\dagger$ being the creation operator for an electron at the point of contact between the left (right) lead and the wire, and $c_{d,0}$ ($c_{d,L_d}$) destroys an electron at the left-most (right-most) sites of the wire (we take here $g_L = g_R = g$). The external environment(s) are accounted for in equation (3) by the second term, which has the form

$$
\mathcal{L}[\rho] = -\frac{1}{2}(V^\dagger V\rho + \rho V^\dagger V) + V\rho V^\dagger,
$$

(7)
where $V$ are the Lindblad $V$-operators which encode the properties of the environment, i.e. its temperatures and position (i.e. left or right electrode). An appropriate form for the $V$-operators is

$$V_{kk'}^{(L,R)} = \sqrt{\gamma_{kk'}^{(L,R)}} \frac{f_D^{(L,R)}(\epsilon_k)}{\sqrt{f_D^{(L,R)}(\epsilon_k)}} |k\rangle \langle k'|, \tag{8}$$

where $f_D^{(L,R)}(\epsilon_k) = 1/(\exp(\frac{\epsilon_k}{k_B T_{L,R}}) + 1)$ are the Fermi distributions of the left and right leads (with the corresponding temperature), $\mu$ the chemical potential and $\gamma_{kk'}^{(L,R)}$ are the overlap integrals between the $k$ and $k'$ states on the left (L) and right (R) edges of the electrodes. This form for the $V$-operators guarantees that at equilibrium (i.e. $T_L = T_R$) the diagonal elements of the density matrix are described by a Fermi function.

The Lindblad equation assumes a Markov approximation for the environment, which is reasonable since we are considering a system at room temperature (where quantum memory effect of the environment should not be important), and since we are interested in the steady state (and not the dynamics). The numerical calculation is performed in the following way: (i) from the tight-binding Hamiltonian the single-particle states and energies are calculated, and the $V$-operators are constructed according to equation (8) for different electrode temperatures $T_L$ and $T_R$. (ii) The $V$-operators are inserted to equations (3) and (7), which are then solved in the steady-state (i.e. for $\dot{\rho} = 0$). (iii) From the diagonal elements steady-state solution for $\rho$ and the wave functions, the electron density is calculated. (iv) By solving the Poisson equation, the voltage at the center of the electrodes is calculated. The voltage difference between the electrodes is the thermo-voltage, as it is induced by the temperature difference. The slope of the thermo-voltage as a function of the temperature difference is the thermopower.

We stress that the OQS formalism presented here deals with a finite electronic system which is open to thermal baths (but not to external electron reservoirs), which is the essential difference between OQS and the NEGF formalism. As a result, the OQS method does not require calculation of the electronic self-energy and is not subjected to the wide-band approximation. The only level broadening applied is due to the numerical procedure and is of the order of the level spacing (which is a very small energy scale in the systems considered here, three orders of magnitude smaller than the HOMO-Fermi level energy separation).

In figure 1 we plot the Seebeck coefficient (solid blue line) and the electron occupation of the molecular chain (dashed orange line) of a model molecular junction as a function of a gate potential applied to the junction, i.e. as a function of the molecular energy level with respect to the Fermi level (which is set as the zero energy). The junction is composed of a series of four atomic orbitals connected to square two dimensional electrodes (upper panel). Numerical parameters are: electrode size $L^2 = 25 \times 25$, tight-binding hopping integral $t = 1$ eV (corresponding to a band-width of $W = 8$ eV), electrode–molecule coupling is $g = 0.1$ eV, temperature is room temperature, $T = 300$ K and the electrodes are kept at half filling.

The first thing to be noted is that whenever a molecular orbital crosses the Fermi energy, the molecular occupation changes by one, and the thermopower changes sign. This is in accord with the known results from the Landauer formula for thermopower, and is due to the change from electron-dominated to hole-dominated transport every time the Fermi level is crossed (which also corresponds to a transmission resonance). The second important feature is that, in contrast to the result expected from the regular Landauer formula [2, 4], the Seebeck coefficient exhibits strong variations with energy (i.e. with the position of the Fermi energy with respect to the molecular levels).
Before we proceed to discussing the origin of these variations, it is useful to compare the properties of the Seebeck coefficient as obtained from the OQS method to those known from the Landauer formalism. In figure 1(b) the Seebeck coefficient as a function of energy (same as in figure 1(a)) is plotted for different values of the coupling between the electrode and the molecule, $g = 200, 100$ and $10$ meV. As expected from the Landauer formalism [25], there is little effect to the coupling on the magnitude of the Seebeck coefficient. In figure 1(c) the Seebeck coefficient is plotted as a function of temperature for various molecular chain lengths. An inhomogeneous temperature dependence is found, originating from a crossover from coherent to incoherent transport, again in agreement with results obtained from the Landauer formalism (e.g. [6, 7]). These results demonstrate that the main physical features of the thermopower which are present in the Landauer formalism, also appear within the framework of the OQS theory.

We now turn to calculating the distribution of the thermo-voltage $\Delta V$ across the molecular junction. To obtain the distribution, we calculate the temperature-difference induced voltage $\Delta V = S(E) \Delta T$, taking the HOMO-Fermi energy offset $E$ to be a random variable, normally distributed around $E_0 = 0.3$ eV with a width $\Gamma_E = 0.2$ eV. While these values are rather different then experimental values (probably $E_0$ is bigger in experiments) we point that we are aiming at qualitative similarity to experiment, to point the origin of the variations, rather than to analyze realistic junctions. To mimic the experiment, we also apply a small variation (2 k) to the electrode temperatures (note that in the experiments, a finite thermo-voltage distribution was observed even at $\Delta T \approx 0$, see inset of figure 2(b), indicating the existence of a small temperature difference, probably due to Johnson noise [39]. This does not affect our results or conclusions).

In figure 2(a) the distribution of thermo-voltage is plotted for temperature differences $\Delta T = 0, 5, 10, 20$ and $30$ K. The distributions qualitatively resemble the experimental distributions, exhibiting a broad double-peak structure. To understand the origin of the distribution shapes, in the right panel of figure 2(a) the Seebeck coefficient is again plotted (solid line). Due to the strong sensitivity of $S$ on $E$, even a relatively small variation in $E$ (of the order of $\Gamma_E \sim 0.2$ eV) can include several maxima of $S$, giving rise to the different peaks in the distributions.

To understand the origin of the sensitivity of $S$, in the right panel of figure 2(a) we plot the local density of states at the point of contact between the electrode and the molecular chain (dashed line). One can see that the variations of $S(E)$ and the LDOS vary on the same energy scale. Note that these variations are a surface effect, and are not due to the electrode level spacing (the average level spacing is $\sim 0.01$ eV). We thus conclude that it is the variations in the LDOS (which are on an energy scale much smaller than the energy difference between the molecular levels) that give rise to the sensitivity of $S$ (we note that the total DOS of the electrodes is a much smoother function with no observed variations on these energy scales). We point that the LDOS variations are not a finite-size effect, but rather are a surface effect. Calculating the LDOS to systems as large as $200 \times 200$ (where the level spacing is $\sim 0.0005$ eV), we found that local variations in the LDOS persist with roughly the same energy scale of $\sim 0.1$ eV (although their magnitude somewhat changes).

On the other hand, when considering the thermopower as obtained by the resonant level model with the Landauer formula (section 2), the local variations in the LDOS are not taken into account, or rather they are smeared by the electron self-energy which is reflected through the level broadening $\Gamma$ in equation (2). The resulting $S(E)$ is a much smoother function. As a first demonstration of this effect, here we use the formula for transport and thermopower

New Journal of Physics 15 (2013) 105004 (http://www.njp.org/)
Figure 2. Thermo-voltage $\Delta V$ histograms for different temperature differences $\Delta T = 0, 5, 10, 20, 30$ K, obtained by taking $\Delta V = S(E) \Delta T$ with $E$ normally distributed around $E = 0.3$ eV with width $\Gamma_E = 0.2$ eV. (a) Histograms obtained from the thermopower $S(E)$ obtained using OQS theory (right panel solid line). The LDOS at the point of contact between the molecular chain and the electrode is also plotted (right panel solid line). (b) Same as (a), but for the Seebeck coefficient $S(E)$ obtained using the Landauer formula, which does not exhibit strong local fluctuations. Inset: experimental histograms of $\Delta V$ for a DMTBDT molecular junctions, reproduced from [10] with permission of The Royal Society of Chemistry.

through a resonant level, equation (1). The positions of the levels and the level broadenings are obtained by fitting the data of figure 1(a). In the right panel of figure 2(b) $S(E)$ is plotted using equation (2) and the parameters of the junction (i.e. resonances and widths fitted to figure 1(a)). For comparison, $S(E)$ obtained from OQS theory is plotted as a bright line in the background. The resulting $\Delta V$ distributions are plotted in figure 2(b) for different $\Delta T$. The distributions obtained using equation (2) are quite different from the experimental results (inset of figure 2(b)), both in terms of shape and in the lack of the double-peak structure.

4. Green’s function analysis of the toy model

Let us now examine the same model within the Green’s function formalism, taking the same Hamiltonian for the chain and electrodes. In this formalism, and for our non-interacting toy
model, the transmission function $\tau(E)$ is given by [29, 40]

$$\tau(E) = \text{Tr} (\Gamma_L G^r(E) \Gamma_R G^a(E))$$

(9)

where $G^{r,a}(E) = (E - \mathcal{H} + \Sigma^{r,a})$ are the retarded and advanced Green’s functions, and $\mathcal{H}$ is the same Hamiltonian as studied in section 3, described by equations (4) and (5). $\Gamma_{L,R}$ represent the level broadening due to the electrodes, typically a few hundreds meVs [18, 28]. In the basis of atomic orbitals (as the Hamiltonian is written) $\Gamma_{L,R}$ are diagonal matrices, with $\Gamma_{L,R}(n, n) = \Gamma$.

Figure 3. (a) Transmission function $\tau(E)$ and thermopower $S(E)$ as a function of energy offset for the tight-binding toy model. The transmission and the thermopower are perfectly smooth and disregard any variations due to the DOS. Upper inset: the local density of states at the point of contact between the wire and the electrode (solid line), and the same LDOS broadened by $\Gamma$ (dashed line). (b) Same as (a) for the artificial transmission function $\tilde{\tau}(E) = \tau(E) \left(1 + 0.1 \cos(E/E_0)\right)$. The oscillations in the transmission function are hardly visible, yet they induce large variations in the thermopower $S(E)$. Inset: $\tilde{\tau}(E)$ on a log-scale, only there the oscillations are visible.
if $n$ is in the left or right edges of the electrodes, and zero otherwise. We take $\Gamma = 0.3\,\text{eV}$ in the numerical example below. $\Sigma$ is the self-energy, which in the non-interacting case is only due to the electrodes, and hence $\Sigma^{\text{el}} = i(\Gamma_L + \Gamma_R)$. It is important to stress that the Green’s function treatment described here requires the self-energy, while the OQS approach does not, and hence although the Hamiltonian is the same, the resulting thermopower may differ due to these different approximations.

Once the transmission is calculated, the thermopower can be calculated directly using equation (1). In figure 3(a) the transmission function $\tau(E)$ and the its logarithmic derivative (proportional to the thermopower $S(E)$) of the toy model are plotted (as a function of the energy). For comparison, the local density of states at the point of contact between the wire and the electrode is plotted in the upper inset (the dashed line in the inset is the DOS when broadened by $\Gamma = 0.3\,\text{eV}$). As seen, the oscillations in the LDOS are completely smeared in the transmission (plotted as a function of the energy). For comparison, the local density of states is plotted in the upper inset (the dashed line in the inset is the DOS when broadened by $\Gamma = 0.3\,\text{eV}$). As seen, the oscillations in the LDOS are completely smeared in the transmission function and hence in the thermopower. The lower inset shows the transmission function on a log scale, verifying that the variations are really smeared out.

To demonstrate that this smearing due to the self-energy has a large effect on the thermopower, we consider an artificial transmission function $\tilde{\tau}(E) = \tau(E) \left(1 + 0.1 \cos(E/E_0)\right)$ with $E_0 = 0.02\,\text{eV}$. This transmission exhibits oscillations on an energy scale $E_0$. Such a transmission function cannot be obtained within the wide-band approximation, as all variations on the scale $E_0$ would be flattened out. The amplitude of the oscillations is chosen in such a way that they are hardly visible if the transmission is observed in its full scale, as seen from figure 3(b), where $\tilde{\tau}(E)$ is plotted. In the inset the transmission is plotted on a log scale, and only there the oscillations are visible. On the other hand, the thermopower exhibits very strong oscillations of considerable size even if the oscillations are hardly observed in the transmission functions. This is due to the extreme sensitivity of $S(E)$ to local variations of $\tau(E)$, reflecting its derivative structure.

5. Summary and discussion

In summary, we have analyzed the variations in the TE response of a metal–single molecule–metal junctions, based on detailed examination of experimental results. The experimental results, namely the width of the thermo-voltage variations and the shape of the thermo-voltage distributions, cannot be accounted for by only assuming variations in the misalignment between the molecular HOMO and the electrode Fermi energy. Using the theory of OQS we qualitatively reproduce the experimental results, and show that they may originate in a combination of the level misalignment variations and variations of the local density of states at the point of contact between the molecule and the electrode, specifically the STM tip in typical molecular junction experiments.

To put it differently, we found that in order to explain the thermopower variations in molecular junctions the electronic transmission function cannot have a simple Lorentzian form, but rather should have a more complicated form which includes variations on a scale smaller than the HOMO–LUMO gap. Such variations may be induced by the variations in the LDOS at the tip–molecule point of contact, originating from the STM tip structure, impurities or trapped states, etc. The use of the Green function formula smears out all variations on energy scale
smaller than the level broadening (typically a few hundred meVs). This smearing has a very small effect on the transmission and hence on the conductance of the molecular junction, but have a strong effect on the thermopower. Thus, caution needs to be taken when using the NEGF method for calculation of thermopower. We note a recent paper [41] arguing that the NEGF method has limitations even when calculating the conductance of a molecular junction, although the argument is different then presented in this paper.

In light of the results presented above, we conclude that the use of NEGF–DFT method for calculating realistic TE properties of molecular junctions needs to be improved, since it fails to capture the most common hallmark of the experiments: the fluctuations in the thermopower, observed in all experiments to date. Understanding the role of the self-energy in smearing such fluctuations is critical. Improvement can be achieved by either inserting fluctuations into the NEGF–DFT calculations (for instance by using it in conjunction with molecular dynamics), or by resorting to other methods such as the OQS approach described above, which do not use a self-energy induced broadening, but require a more computationally demanding calculation.

Acknowledgment

The author wishes to thank J Malen for valuable comments on the manuscript.

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