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Vladimir N. Ermakov*, Sergei P. Kruchinin*, Thomas Pruschke†, and J.K. Freericks‡

*Bogolyubov Institute for Theoretical Physics, NASU, Kiev 03680, Ukraine

†Institut für Theoretische Physik, Georg-August-Universität

Göttingen, Friedrich-Hund-Platz 1, 37077 Göttingen, Germany

and

‡Department of Physics, Georgetown University, Washington D.C., 20057, USA*

(Dated:)

We employ a simple analyic model to calculate the thermopower of low transparency molecular nanosystems. It turns out that the sign of the thermovoltage for this model depends sensitively on the participating molecular orbital, and one finds a sign change when the transport channel switches from the highest occupied molecular orbital to the lowest unoccupied molecular orbital. Comparing our results to recent experimental data obtained for a BDT molecule contacted with an STM tip, we observe good agreement.

I. INTRODUCTION

Studies of the origin of a voltage or current in nanosystems in the presence of a temperature gradient are an extremely interesting and promising area in the field of nanotechnologies [1–3]. There are several important possible future applications in several areas of devices, among them the development of nanothermosensors (see, e.g., [4]), which is especially urgent for a number of technological processes and for research in biology concerning the functioning of life.

However, different from the classical description of thermoelectric phenomena, which is already challenging enough, the necessity to apply strictly quantum-mechanical methods in the realm of nano-objects makes the whole problem an extremely difficult one, and a proper theory for studying transport phenomena in the most general setup does not yet exist. However, for the description of most experimental realizations of thermoelectric transport through nano-structures, one can fortunately make some simplifying assumptions. Usually, one can consider the system to consist of two metallic structures, which are typically very good conductors and which we will call leads, that are spatially separated. Hence, there will be no current flowing between the leads. Placing an active element like a molecule between these leads will thus induce a transport path and, when voltage or temperature differences between the leads are imposed, thermoelectric phenomena [5–10]. The coupling of the molecule and the leads will be quantum mechanical, i.e., one can usually assume that the coupling that gives rise to a transfer of mobile electrons from the leads onto the molecule is governed by tunneling processes. For example, if one uses gold leads and the molecule has thiol groups on it, so that the contact is formed via a covalent bond, one can nevertheless still have situations where the electron transport across that interface is described via a tunneling process because the charge in the covalent bond remains localized in the bond region. This is similar to the well-known phenomena in Nb-based Josephson junctions, where the Nb superconductor has a thin layer of aluminum evaporated on top of it which is exposed to oxygen forming a disordered aluminum-oxide barrier. Then more Nb superconductor is deposited on the other side. Even though Al_2O_3 is a covalent insulator, quantum-mechanical tunneling between the Nb superconductors occurs due to the exponentially decaying wavefunctions of the Nb metal leads through the insulating barrier. The same type of exponentially decaying connection between metallic leads and molecules should exist regardless of how the molecule bonds to the leads.

Although this setup seems rather straightforward, its actual experimental realization is by no means trivial. In particular, a good control over whether a molecule is even attached to one (or both) leads and a reliable characterization of the coupling of electrons in the leads to the quantum states of the molecule is difficult to obtain [2]. Furthermore, when using two extended leads on a common substrate, it is not easy to set up a temperature gradient across the molecule. An interesting technical solution to this problem has been achieved recently by using a scanning tunneling microscope (STM) tip to contact individual molecules on a metal surface in a controlled manner, thereby generating well-defined break junctions [2]. In this way, control over the tunneling between electrons in the molecule and in the leads can be achieved by moving the STM tip, and a temperature gradient can easily be applied by heating the metal while keeping the tip at a fixed temperature [2]. The voltage between the tip and the metal can then be adjusted as well to arrive at the case where no charge current flows through the molecule. This then is the experimental setup for mea-

suring the Seebeck coefficient: the system has no charge current flowing, but has heat current flowing through it. The ratio of the voltage difference to the temperature difference yields the Seebeck coefficient of the device.

In the present paper, we develop a simple nonequilibrium model to describe the stationary thermotransport through such a nanostructure, using a Green's-function-based approach that is capable of describing sequential tunneling (the electron tunnels without maintaining phase coherence between the tunneling onto and off of the molecule), co-tunneling (the electron tunnels coherently through the molecule by virtually occupying an off-resonant molecular energy eigenstate), and resonant tunneling (which is similar to co-tunneling, but the virtual state is energetically close to the chemical potential). Guided by the experimental findings, we argue that one can actually restrict the theory to the lowest nonzero order in the tunneling. The resulting model is rather simple, but can be solved analytically, and the theoretical results can be directly compared with experimental data by adjusting just a few parameters. We generically find good agreement between experiment and the simple model.

The reason why such a model might be important to the community is that it can serve as a means to try to characterize some of the parameters related to how the leads couple to the molecule. In this sense, it is similar to the Simmons model [11], which is widely used to estimate the tunnel barrier strength and width in a tunnel junction, and is often used by experimentalists as a unifying means to describe experimental data that is independent of the detailed properties of the materials. The Simmons model simply assumes that the electron tunnels through a barrier described by a simple square well potential. It has proved to be quite useful in describing many devices. We believe the model we develop here will share a similar status when we examine experiments that have thermoelectric effects in molecules.

What this model cannot do is determine where the chemical potential of the leads lies relative to the lead-broadened molecular levels of the attached molecule. The reason why is that once we take the limit of no broadening of the molecular levels (which is required for the analytic solution), we must have the chemical potential pinned near (on the order of $k_B T$ or less) one of the levels to be able to model the charge transfer associated with the (perhaps small) ionicity of the bonds with the leads. In the absence of the leads, the chemical potential for the molecule is very sensitive to small perturbations (including temperature) and can be easily forced to move close to one or the other molecular levels. When the leads cause significant broadening of these levels, the chemical potential becomes much more robust and does not change signifiantly with small perturbations. But, because we maintain the sharp levels in the analytic model presented here, the chemical potential has a strong dependence on perturbations and must lie close to one of the molecular levels. It turns out that even though the precise location of the chemical potential is not well determined by this model, one can still accurately calculate the thermopower. We will discuss this effect further below.

The remainder of the paper is organized follows. The model Hamiltonian and observables of interest are described in Sec. II. Sec. III describes the thermoelectricity in tunneling nanostructures. Sec. IV concludes.

II. ANALYTIC MODELING OF ELECTRON TUNNELING WITH AN APPLIED TEMPERATURE GRADIENT

Electron tunneling through a quantum system consisting of double potential barriers is sensitive to the position of the electronic states in the constricted quantum structure [12]. This circumstance can be used for an effective control over the tunneling process. While it is usually challenging to contact molecules via standard leads, using an STM tip to create break junctions with molecules immersed on a metal surface allows for a controlled way to generate reliable contacts. This has been used recently for benzenedithiol (BDT), dibenzenedithiol (DBDT) and tribenzenedithiol (TBDT) to study thermoelectric effects in the transport through such molecules [2].

Based on the setup of the experiment in Ref. 2 and depicted schematically in Fig. 1A, we model the device with a double-barrier tunneling system that has an energy profile shown schematically in Fig. 1 [13–17]. In the following, we identify the substrate with the label "L" and the STM tip with "R". The Hamiltonian describing the tunneling of electrons through such a structure is of the form

$$H = H_0 + H_W + H_T. \tag{1}$$

The first term of this Hamiltonian

$$H_0 = \sum_{k\sigma} \varepsilon_L(k) a^\dagger_{k,L,\sigma} a_{k,L,\sigma} + \sum_{k\sigma} \varepsilon_R(k) a^\dagger_{k,R,\sigma} a_{k,R,\sigma}. \tag{2}$$

describes electrons in the left lead (metal surface) and in the right one (STM tip). Because we are not interested in the detailed properties of the leads, we assume that these charge carriers can be taken to be noninteracting quasiparticles, and $a^\dagger_{k,L,\sigma}(a_{k,L,\sigma})$ and $a^\dagger_{k,R,\sigma}(a_{k,R,\sigma})$ are the creation (annihilation) operators for these quasiparticles in the surface and, respectively, tip. The dispersions are, in the same spirit, given by $\varepsilon_{L/R}(k) = \hbar^2 k^2 / 2m_{L/R}$, where $m_{L/R}$ denote the effective masses for the left and right leads. We will assume $m_L = m_R = m$ in the following for simplicity.

The Hamiltonian H_W describes the electronic states on the molecule. It can be written in the form

$$H_W = \sum_\alpha E_\alpha a^\dagger_\alpha a_\alpha + H_I , \tag{3}$$

where α labels the single-particle levels of the molecule, and H_I denotes possible interactions. The single-particle
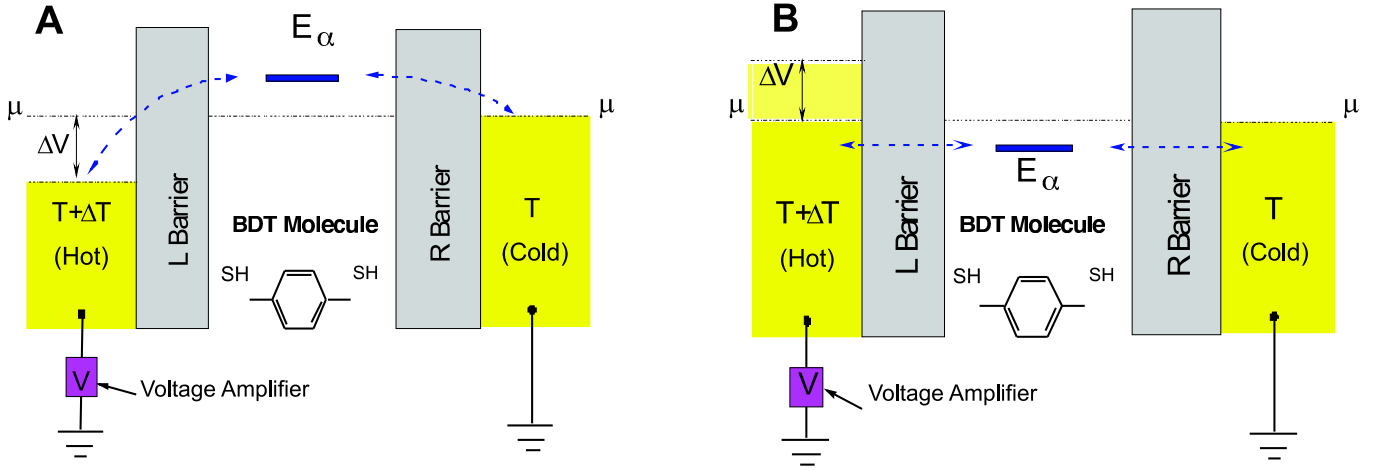
FIG. 1: Schematic model to study thermoelectric phenomena for a BDT molecule attached to leads. **A** shows the case where the LUMO provides the nearby molecular level, and **B** corresponds to the HOMO as the nearby molecular level. The energies of the orbitals, the bias ΔV and the temperature difference ΔT are chosen to provide a setup for the thermopower measurement, i.e., no electrical current is flowing, but heat current is.

energies in the well depend on the applied bias ΔV across the molecule and can be written as $E_\alpha = \epsilon_\alpha - e_0\,\beta\,\Delta V$, where ϵ_α is the bare energy of the molecular state in the quantum well (that is, the energy with no field applied across the molecule), ΔV is the potential drop across the molecule, $e_0 > 0$ is the elementary charge, and β is a factor depending on the profile of the potential barriers (for identical barriers, $\beta = 0.5$). Note that the bare molecular energy levels need not be the levels of the isolated molecule if they shift due to the bonding of the molecule to the leads. What we require in our theory is that the levels will not be significantly broadened due to the coupling of the molecule to the leads, which is expected in cases where the tunneling connection corresponds to a low transparency coupling. Finally, the Hamiltonian H_T describing the tunneling of electrons through the contact barriers with the leads has the conventional form

$$H_T = \sum_{k\alpha,\delta=L,R} \left(T_{\alpha\sigma\delta}(k)\, a_{k,\delta,\sigma}^\dagger a_\alpha + \mathrm{H.c.} \right). \quad (4)$$

Here, $T_{\alpha\sigma\delta}(k)$ is the matrix element of tunneling from the surface (respectively, the tip) to and from the molecule.

When we apply a constant external bias across the system, a nonequilibrium steady-state electron distribution will result. We assume that the electron distribution functions in the electrodes (source, drain) are equilibrium ones, i.e., Fermi functions, due to the large volumes of these reservoirs, but their chemical potentials and temperatures can be different. The chemical potentials in each lead then encode the voltage drop across the nanoregion where the molecule is. Hence, in our model, $\mu_L = \mu + \Delta\mu$, $\mu_R = \mu$, and $\Delta\mu = -e_0\Delta V$.

The setup of the system in Fig. 1 makes the evaluation of nonequilibrium properties comparatively simple. The important quantity entering all formulas is the density of states (DOS) $\rho_\alpha(E)$ for the local level in the presence

of the leads [18]. To calculate it, we need the retarded Green's function $G_{\alpha,\alpha}(E)$ [19], which is defined via

$$G_{\alpha,\alpha}(t,t') = -i\mathrm{Tr}\,e^{-\beta H(\Delta V=0)}\{a_\alpha(t), a_\alpha^\dagger(t')\}/\mathcal{Z} \quad (5)$$

where $\mathcal{Z} = \mathrm{Tr}\exp[-\beta H(\Delta V = 0)]$ is the initial equilibrium partition function when there is no voltage or temperature difference over the molecule. The fermionic creation and annihilation operators of the molecular eigenstates are in the Heisenberg representation. We apply the voltage difference and temperature difference at time $t = 0$ and take the limit where $t + t' \to \infty$ but $t - t'$ remains finite. The steady state Green's function in the energy representation, then arises as the Fourier transform of the Green's function in the long-time limit with respect to the relative time $t - t'$ and is denoted $G_{\alpha,\alpha}(E + i\eta)$. From this we can obtain the DOS as

$$\rho_\alpha(E) = -\frac{1}{\pi}\mathrm{Im}\,G_{\alpha,\alpha}(E + i\eta).$$

The electron distribution function $f_W^\alpha(E)$ in the quantum well is essentially nonequilibrium. It can be determined from the condition of equality of the tunneling currents through the source and the drain. The resulting distribution function has the form [18]

$$f_W^\alpha(E) = \frac{1}{\Gamma_\alpha(E)}[\Gamma_L^\alpha(E)f_L(E) + \Gamma_R^\alpha(E)f_R(E)], \quad (6)$$

$$\Gamma_\alpha(E) = \Gamma_L^\alpha(E) + \Gamma_R^\alpha(E), \quad (7)$$

where $\Gamma_L^\alpha(E)$ and $\Gamma_R^\alpha(E)$ are the tunneling rates for source (L) and drain (R), given by the expressions

$$\Gamma_L^\alpha(E) = \sum_{k\sigma} |T_{\alpha\sigma L}(k)|^2 \delta(E - \varepsilon_L(k)), \quad (8)$$

$$\Gamma_R^\alpha(E) = \sum_{k\sigma} |T_{\alpha\sigma R}(k)|^2 \delta(E - \varepsilon_R(k)), \quad (9)$$

and $f_L(E)$ and $f_R(E)$ are the quasiparticle distribution functions in the source and the drain, respectively. They have the Fermi–Dirac form, and their temperature dependences read

$$f_{L/R}(E) = \left\{ 1 + \exp\left[\frac{E - \mu_{L/R}}{k_\mathrm{B} T_{L/R}}\right] \right\}^{-1}, \qquad (10)$$

where k_B is the Boltzmann constant, and $T_{L/R}$ are temperatures in the source and the drain, respectively.

III. DOUBLE BARRIER THERMOSTRUCTURES FOR ELECTRON TUNNELING

With the above formula for the distribution function, one can straightforwardly evaluate physical quantities. For example, the occupancy of the molecule can be determined with the help of the expression [13]

$$n_\alpha = -\frac{1}{\pi} \int dE \, f_W^\alpha(E) \, \mathrm{Im} G_{\alpha,\alpha}(E).$$

Note that when the chemical potential is far from one of the molecular levels, the density depends exponentially weakly on the chemical potential, hence it always will be pinned to lie close to one of the molecular levels. Moreover, the net current J_{sd} between the source and the drain through the molecule is given by the equation [15, 18]

$$J_{sd} = -\frac{e_0}{\hbar} \sum_\alpha \int \Upsilon_\alpha(E) \left[f_L(E) - f_R(E)\right] \rho_\alpha(E) \, dE, \qquad (11)$$

where $\Upsilon_\alpha(E) = \Gamma_L^\alpha(E) \Gamma_R^\alpha(E) / \Gamma_\alpha(E)$. Since we assume tunneling contacts, the transition rates Γ_R^α, Γ_L^α are exponentially dependent on the barrier widths and heights. Correlation effects between the electrons in a nanostructure encoded in H_I can be taken into account by means of $\rho_\alpha(E)$, too [18], and will in general dramatically modify the properties [20, 21]. Unfortunately, a complete theoretical solution of this more realistic model is at present possible in the linear response regime only (see for example Ref. 22 for an overview). In particular, treating thermoelectric effects is a significant challenge as the temperature gradient across the dot cannot be simply included into the Hamiltonian of the leads.

Fortunately, the situation for the experiment conducted in Ref. 2 appears to be such that further approximations become possible. To this end, we refer to Fig. 3A in Ref. 2, where an estimate [1] of the transmission function through the molecule as a function of energy is shown. From this figure, one can infer that the system is indeed in the weak-coupling regime, with a rather good separation between the HOMO and LUMO of several eV. (Weak coupling here refers to a low transparency tunneling connection between the leads and the molecule for the electrons being transported through the molecule.) Note that, to lowest order, the width of transmission function

is directly related to the effective coupling $\Gamma_\alpha(E)$ defined in Eq. (9) [18]. This observation motivates us to assume a low transparency of the barriers, i.e. $\Gamma(E) \ll |\Delta E|$ with ΔE being the difference in energy between LUMO and HOMO. This assmption implies that structures in the transmission function will be quite sharp, and not be significantly broadened due to the attachment of the molecule to the leads.

While it is possible to examine these results numerically, as many other researchers do, we next take an extreme limit, which allows for the system to be analyzed analytically. This limit is an important one to take, as it also provides a benchmark for numerics, in a regime where the numerics can become difficult to carry out. In particular, we use the limit $\Gamma \to 0$, i.e. we approximate the local Green's function by its atomic limit[1]

$$\rho_\alpha(E) \approx C_\alpha \, \delta(E - E_\alpha), \qquad (12)$$

where the weights C_α encode the effect of interactions on the molecule and we take into account only the pole with the strongest weight. In other words, we neglect the influence of the leads on the molecule's states, in particular also renormalizations due to nonequilibrium. This is, admittedly, a rather severe approximation, but it is consistent with the above interpretation of the particular experimental setup: The experimental results do not indicate a significant change in the observed dependencies down to the smallest distances between surface and tip. As with increasing distance the tunnel coupling becomes exponentially small, we expect our approximation to be valid in the intermediate to large distance regime and, with the previous observation, therefore also down to the smallest distances covered in the experiment. It is important to note that according to standard many-body theory, the temperature does not enter into the broadening of the molecule's levels, i.e. although the actual working temperature of the device at 300 K is rather high, it will not alter our above argument or conclusion. This limit is the opposite limit to the one considered by Paulsson and Datta [1], where the molecular levels are broadened sufficiently that one can determine the themopower via a Mott-like formula that involves the derivative of the transmittance with respect to the energy.

Inserting the approximation (12) into the expression for the charge current, we finally obtain the formula

$$J_{sd} = -\frac{e_0}{\hbar} \sum_\alpha C_\alpha \, \Upsilon_\alpha(E_\alpha) \left(f_L(E_\alpha) - f_R(E_\alpha)\right). \qquad (13)$$

The distribution functions $f_{L/R}(E_\alpha)$ are exponentially dependent on the energy E_α (note that these energies are

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[1] One could in principle also use a Lorentian form with width $\propto \Gamma_\alpha(E)$ here, but we would then lose the analytical solution. Furthermore, this approach would at the present level only introduce a further unknown parameter into the calculations.

the electronic energies of the molecule; we are ignoring vibrational excitations). Thus, when $|E_\alpha - E_{\alpha'}| \gg k_B T$, where $E_{\alpha'}$ denotes a neighboring molecular orbital, there will be one particular energy E_α for which $|E_\alpha - \mu|$ is minimal. As discussed previously, we can assume a weak tunneling coupling and a reasonably strong energetic separation of the molecular orbitals, and hence the transport through all other orbitals will be exponentially suppressed compared to this orbital and can be neglected. Within this approximation, Eq. (13) can thus be reduced to the simple form $\Upsilon_\alpha(E_\alpha)[f_L(E_\alpha) - f_R(E_\alpha)] = 0$, respectively, for small but finite $\Gamma_{L/R}^\alpha(E)$,

$$f_L(E_\alpha) - f_R(E_\alpha) = 0, \qquad (14)$$

since a thermoelectric measurement is made with an open circuit that has no charge current flow, only heat current flow.

According to our definition, E_α is the energy level of the molecule which has the smallest distance to the chemical potential. This will either be the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO). That molecular level is, as noted before, shifted by the voltage ΔV as $\Delta E = E_\alpha - \epsilon_\alpha = -e_0 \beta \Delta V = \beta \Delta \mu$. For asymmetric barriers we have $\beta = a_L/(a_L + a_R)$, where a_L and a_R are the widths of the left and right barriers, respectively. With the explicit form for Fermi's function (10) the solution of Eq. (14) becomes

$$e_0 \Delta V = \frac{(\epsilon_\alpha - \mu)}{T + \beta \Delta T} \Delta T. \qquad (15)$$

This is the condition relating the voltage across the molecule to the temperature gradient to ensure that no charge current flows (given the aforementioned approximations). Equation (15) has a rather interesting implication. Assuming a positive temperature gradient, $\Delta T > 0$, the sign of the thermovoltage depends solely on the relative position of the level contributing to the electron tunneling and the chemical potential. In the case $\epsilon_\alpha > \mu$ we would observe a positive thermovoltage, while a negative one will occur for $\epsilon_\alpha < \mu$. Note that this scenario is valid only when $|\epsilon_\alpha - \mu| \ll |\epsilon_\beta - \mu|$ for all other orbitals $\beta \neq \alpha$. However, for $|E_{LUMO} - \mu| \approx |E_{HOMO} - \mu|$, i.e. close to a particle-hole symmetric situation, the two transmission channels would contribute with opposite sign, and we would expect thermoelectric effects to be strongly suppressed, presumably below the noise level of the experiment. (Indeed, just by continuity, if one goes from HOMO dominated to LUMO dominated, the thermoelectric voltage must vanish somewhere during the transition because it is positive for one limit and negative for the other.) Since the experiment shows a clear thermoelectric signal, we infer that there is only one orbital dominating the tunneling contribution to the transport. Note that this conjecture is also in agreement with the general discussion in Ref. 2 following their Eq. (4).

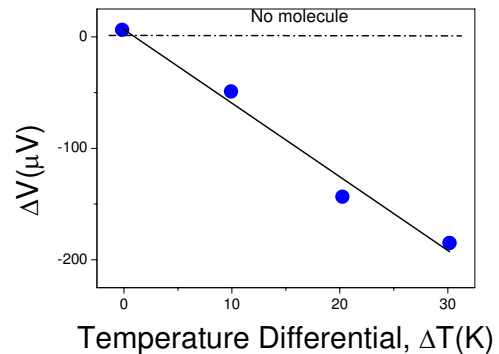Our result in Eq. (15) can now be used to interpret the

FIG. 2: Comparison of experimental data (blue circles [2]) with the theoretical curve (from Eq. (15)).

experimental data. To this end, we take the results from Fig. 2D in Ref. 2 to estimate our parameters for BDT.

The first observation is that the experiment gives $\Delta V < 0$, i.e. according to our result we must have $\epsilon_\alpha < \mu$. Thus, the energy level ϵ_α seen in experiment is a HOMO, i.e. we have realised the condition shown in Fig. 1B. In fact, the conductivity of the tunneling structure is determined by electron holes. The detailed comparison of the thermovoltage ΔV as a function of ΔT is shown in Fig. 2. Since $\Delta T \ll T \approx 300$ K, Eq. (15) can be approximated by a linear relation

$$e_0 \Delta V = (\epsilon_\alpha - \mu)\Delta T/T. \qquad (16)$$

From the comparison with the experiment, we get an average value of $(\mu - \epsilon_{HOMO})/e_0 T \approx 7$ μV/K. While this may seem like a close pinning of the chemical potential to the molecular level, if we examine the distance of the chemical potential relative to the width of the molecular level (which is zero) it is an "infinite" distance away. The point is that once we have chosen to neglect broadening of the molecular level, the chemical potential must lie close to one of the molecular levels to properly handle the charge balance.

To study the dependence of thermoelectric effects on the distance d between the substrate surface (source) and the STM tip (drain), let us consider our double-barrier system as a simple resistor network. In this case, Eqs. (14) and (13) can be reduced to

$$-\frac{e_0}{\hbar} C_\alpha \Upsilon(E_\alpha)[f_L(E_\alpha) - f_R(E_\alpha)] = J_{sd}, \qquad (17)$$

with an *externally imposed current* $J_{sd} = \Delta V/R_0$, where R_0 is the external impedance of the whole network. We note that if the conditions $e_0|\Delta V| \ll k_B T$ and $|\epsilon_\alpha - \mu| \ll k_B T$ are valid, Eq. (17) can be rewritten as

$$(\epsilon_\alpha - \mu)\Delta T/T + e_0 \Delta V = -e_0 \, p \Delta V, \qquad (18)$$

where

$$p^{-1} = \frac{e_0^2 R_0 C_\alpha \Upsilon(\epsilon_\alpha)}{\hbar} \frac{\partial f_R(\epsilon_\alpha)}{\partial \mu}.$$
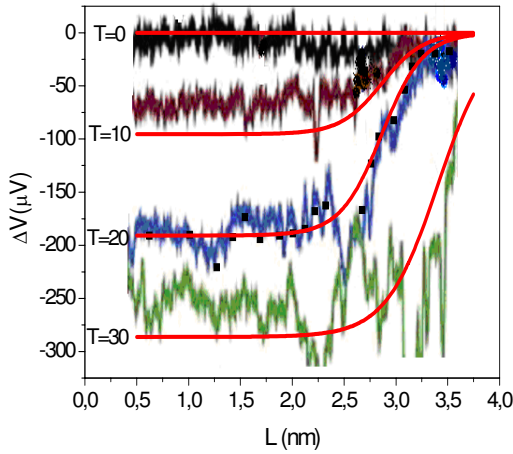
FIG. 3: Dependence of ΔV on the distance Au-BDT-Au for different temperatures. The full lines are the results of our model. For simplicity we assumed that a_L was fixed and the movement of the tip only increased a_R.
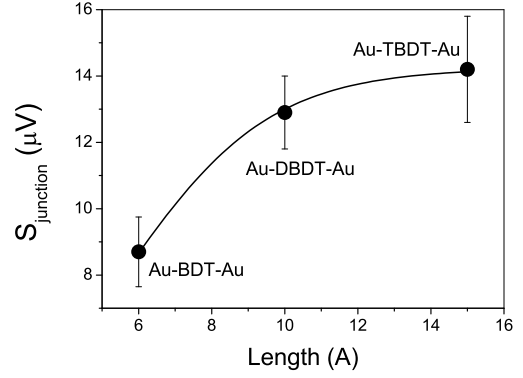

FIG. 4: Seebeck coefficient as a function of the molecular length for BDT, DBDT, and TBDT. The circles are the experimental data from Ref. 2. The results of our calculation are given by the solid line obtained from Eq. (21) using the results for $B(d)$ from Fig. 3 with a_R and ϵ_{HOMO} as fit parameters.

In the case of an open circuit, $R_0 = \infty$, we have $p = 0$, and Eqs. (16) and (18) are the same. The quantities Γ_L and Γ_R entering $\Upsilon(E)$ are exponentially dependent on the barrier widths, i.e. we can approximate them as

$$\Gamma_{L/R} = \Gamma_0 \exp(-\gamma a_{L/R}), \qquad (19)$$

where $a_{L/R}$ are the widths of the left and right barriers, respectively, and γ depends on the barrier height. The barrier lengths can be controlled in the experimental setup by moving the STM tip [2]. Finally, relation (18) can be written in the form

$$e_0 \Delta V = \frac{(\epsilon_\alpha - \mu)}{1 + B(d)} \frac{\Delta T}{T}, \qquad (20)$$

where

$$B(d) = B_0 [\exp(\gamma a_L) + \exp(\gamma a_R)], \quad B_0 = p\, \Upsilon(\epsilon_\alpha)/\Gamma_0.$$

Note that the total distance between the source and the drain is $d = a_L + a_R + a_{\mathrm{BDT}}$, where a_{BDT} is the BDT molecule diameter.

This theoretical length dependence of the thermoelectric voltage can be compared with experimental data [2]. The result is shown in Fig. 3. In our calculations, we fixed the parameters by obtaining the best fit for $\Delta T = 20$ K and $a_{\mathrm{BDT}} = 0.6$ nm [2], resulting in $a_L \approx 0.2$ nm, $\gamma = 5$ nm^{-1}, $B_0 = 2 \times 10^{-5}$, $(\mu - \epsilon_{\mathrm{HOMO}})/e_0 T = 9.54$ μV/K. The remaining curves for the other temperatures were then calculated using these parameters. Let us emphasize that in contrast to the data from Fig. 2, we deal with measurements performed on a single molecule here, i.e. the individual results for the parameters of the molecule will in general differ from the average extracted from Fig. 2.

Relation (20) together with Eq. (2) from Ref. 2 allows us to determine the Seebeck coefficient as a function of

parameters of the nanostructure as

$$S_{junction} = S_{\mathrm{Au}} - \frac{(\epsilon_\alpha - \mu)}{1 + B(d)} \frac{1}{T e_0}, \qquad (21)$$

where S_{AU} is the Seebeck coefficient for the gold surface [2]. In particular, at a fixed distance between the electrodes, it follows from Eq. (21) that the Seebeck coefficient depends on the size of the molecule, through which the electron tunneling is realized and the orbital which dominates the tunneling. Again, because $S_{\mathrm{Au}} > 0$ [2], we expect $S > 0$ if the HOMO dominates the transport, while the second term becomes negative and hence $S < 0$ can become possible when the LUMO is the relevant orbital. As we already know that for BDT the HOMO is the important orbital, we can use the Seebeck coefficient for this molecule as reference and draw conclusions about others depending on their absolute values of S.

The resulting dependence of $S_{junction}$ on the different molecules is shown in Fig. 4 using $S_{\mathrm{Au}} = 2$ μV/K, $d = 2.93$ nm and the other junction parameters as in Fig. 3. Again, the experimental data are averaged over 1000 individual measurements. As before, the Seebeck coefficient of the junction is predominantly determined by the width of the right barrier. All Seebeck coefficients are positive, and their value increases for DBDT and TBDT. This means, that as for BDT, the thermovoltage is negative and hence the HOMO is the orbital dominating the transport process. We also note that in contrast to the fit in Ref. 2, we do not obtain a linear relation, but a strongly non-linear one due to the presence of $B(d)$. Our result obviously gives a better account of the data.

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[2] A derivation for this expression can be found in the supplementary material to Ref. 2.

The particularly interesting observation is that the comparison of theory and experiment results in a constant value of $(\mu - \epsilon_{\text{HOMO}})/e_0 T \approx 12 \ \mu\text{V/K}$ for all molecules. At first glance, this is a strange result. We however think it can be explained in a simple way. Both the substrate, on which the molecules are located, and the STM tip consist of gold, which, as is well known, forms a strong (localized) covalent bond with the thiol groups. The HOMO and LUMO levels will shift with the electric field, as discussed above, and there can be charge transfer onto or off of the molecule due to the electrical contact with the leads which are at fixed chemical potentials. The chemical potential of a free molecule is usually positioned in the middle between HOMO and LUMO levels. When the molecule and electrode form a contact, the chemical potentials become leveled. This is accompanied by a change in the population of the molecular levels. Two cases can now be realized. If the chemical potential of the free molecule is larger than the chemical potential of the electrodes, their leveling requires that some portion of the electronic charge on the molecule must be transferred to the contacts, and the chemical potential will lie close to the HOMO. In the second case, electrons will be injected into the molecule, and the gap between the chemical potential and the LUMO level decreases. Thus, the electrostatic potentials due to the formation of the junction will cause a shift of either the HOMO or LUMO level of the molecule closer to the chemical potential, which further enhances the dominance of that particular level in the transport process.

At some point, the equilibrium with the external potential is reached, which determines the difference $(\epsilon_\alpha - \mu)$. This final distance between the chemical potential of the system and the position of the closest molecular level is in lowest order determined by the level width Γ_α and temperature T. Within the approximation that $\Gamma_\alpha \ll k_{\text{B}}T$, we may expect that the position is mainly determined by the temperature. It is thus reasonable, that the resulting *average* level position for all molecules BDT, DBDT, and TBDT is similar within the error bars of the statistics.

IV. SUMMARY

A theoretical calculation of the transport through nanostructures makes a full quantum-mechanical description of the system mandatory. In contrast to bulk materials, one cannot even adopt some semiclassical approach based on, e.g., the Boltzmann equation here. Since one also needs to take into account the inherent nonequilibrium situation in many cases, solving this problem has become one of the most challenging tasks in modern condensed matter theory. A certain simplification arises when one can use the concept of electron tunneling with low-transparency barriers. This is usually possible in weakly contacted nano-objects like molecules, and allows one to quite accurately describe the thermoelectric phenomena in these systems.

We have presented here the calculation of thermotransport through a BDT molecule contacted with a metal substrate and a STM tip via the generation of a break junction [2]. In the limit of only weakly transparent barriers, we were able to obtain an explicit formula for the voltage drop across the molecule as a function of the temperature difference between the substrate and the tip. We found that the experimental data are described rather accurately by our simple model involving only one tunneling process through the HOMO of the molecule.

Modelling the dependence of tunneling rates between the molecule and substrate/tip with a simple exponential ansatz, we were furthermore able to give a closed expression for the dependence of the thermoelectric effect on the distance between tip and substrate. The comparison to experiment could be done by extracting the relevant model parameters from one set of data for a fixed $\Delta T = 20$ K only, reproducing the remaining curves with good accuracy. Furthermore, using the parameters for the dependence of the thermovoltage on the length of the Au-molecule-Au junction, we were able to provide an accurate description of the dependence of the Seebeck coefficient on the size of the molecule. As an interesting by product, we found that apparently the molecular level position is only weakly dependent on the molecule. This rather odd observation could be explained by including the electrostatic fields due to the formation of the break junction, nicely explaining why the appearance of the HOMO in the thermopower measurements is so robust.

Thus, our formula accurately describes the transport through such a nano-object, provided the tunneling coupling to the leads is of sufficiently low transparency and the initial separation of the molecular levels around the Fermi energy is sufficiently large. There are, of course, several severe simplifications in the model. The most relevant is of course the neglect of the influence of the tunneling on the electronic structure of the molecule. In connection with interaction effects on the molecule, as well as molecular vibrations and also vibrations of the whole molecule between the contacts this can lead to severe modification. These additional features can be taken into account in the linear-response regime [22, 24] and, under very simplifying assumptions, also analytically under nonequilibrium conditions [24]. For the present experimental setup we however think that our simplified theory is at least qualitatively valid and can be used to understand several features of the experiment using only a limited set of input data.

Given the complexity and in particular nonavailability of full-featured theoretical calculations off thermal equilibrium, we believe that such analytical results – even if they appear simple or straightforward – are nevertheless important steps to enhance our knowledge about the transport through nanostructures and can actually also serve as benchmarks to test more elaborate theoretical tools to be developed.

In addition, similar to the simplifying assumptions of the Simmons model [11], which has been used for decades

to characterize the tunneling behavior of normal-state tunnel junctions, the present model provides a simple framework, with a few parameters, that can characterize the transport, especially the thermal transport, across a molecule. We hope that it can then be used to characterize a range of new experimental systems and help understand the tunneling behavior through individual molecules. Unfortunately, we have not been able to find other experiments that have low transparency junctions that we can compare the theory to, but we anticipate such systems will be available to apply this theory to in the future.

Acknowledgments

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