

Tuning the Thermoelectric Properties of a Single-Molecule Junction by Mechanical Stretching[†]

Alberto Torres,^{a*} Renato B. Pontes,^b Antônio J. R. da Silva,^{a‡} and A. Fazzio^a

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Supplementary Information

Electronic Transport Calculations

The transport calculations were performed on TRANSAMPA code which employs non-equilibrium Green's function combined with density functional theory (NEGF-DFT). To perform these calculations the system is divided in three parts: left lead(L), scattering region(CC) and right lead(R) (see Fig. 1). We also assume that the leads only couple with the scattering region, but do not with each other.

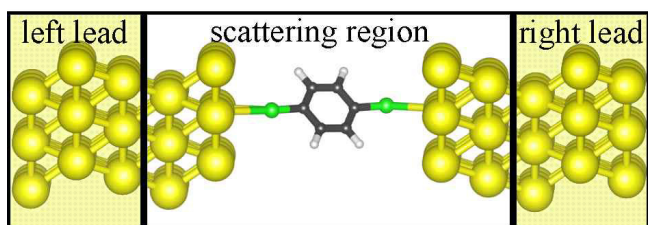


Fig. 1 Ball-and-stick representation of the set up used in the transport calculations.

The Hamiltonian matrix H for the system is an infinite Hermitian matrix. Firstly, we have to define principal layer(PL). A principal layer is the smallest cell that repeats periodically in the direction of the transport. For example, in this paper, it is composed by the atoms in the three outermost Au layers on each side of the system, as can be seen in Fig. 1.

^a Instituto de Física, Universidade de São Paulo, CP 66318, 05315-970, São Paulo, SP, Brazil. E-mail: fazzio@if.usp.br, E-mail: ajrsilva@if.usp.br

^b Instituto de Física, Universidade Federal de Goiás, CP 131, 74001-970, Goiânia, GO, Brazil; E-mail: pontes@ufg.br

* Present Address: Departamento de Física, Universidade Federal de Santa Catarina, 88040-900, Florianópolis, SC, Brazil; E-mail: alberto.trj@gmail.com

‡ Laboratório Nacional de Luz Síncrotron LNLS, 13083-970 Campinas-SP, Brazil

The Hamiltonian matrix for the system is

$$H = \begin{pmatrix} H_{LL} & H_{LC} & 0 \\ H_{CL} & H_{CC} & H_{CR} \\ 0 & H_{RC} & H_{RR} \end{pmatrix} \quad (1)$$

where, $H_{LL}(H_{RR})$ are infinite block-diagonal matrices with the following form:

$$H_{LL} = \begin{pmatrix} \ddots & \ddots & \ddots & \ddots & \vdots \\ 0 & H_{-1} & H_0 & H_1 & 0 \\ \dots & 0 & H_{-1} & H_0 & H_1 \\ \dots & \dots & 0 & H_{-1} & H_0 \end{pmatrix} \quad (2)$$

where H_0 is a matrix describing all interactions within a PL, and $H_{1(-1)}$ is a $N \times N$ matrix that describes the interaction between two PLs. N is the total number of basis function in the PL. It is assumed that there is no coupling between the left and the right leads ($H_{LR} = H_{RL} = 0$). The atoms in these regions were held fixed at their ideal bulk positions. $H_{LL}(H_{RR})$ are obtained in a bulk electronic structure calculation. H_{CC} stands for a $M \times M$ matrix that describes the interaction in the scattering region and, H_{RC} e H_{LC} stand for the matrices

$$H_{LC} = \begin{pmatrix} \vdots \\ 0 \\ H_1 \end{pmatrix} \quad (3)$$

which contains the interaction between the PL and the scattering region. For a system with time-reversal symmetry $H_{RC} = H_{CR}^\dagger$ and $H_{LC} = H_{CL}^\dagger$.

In the Landauer-Büttiker formalism, the current is given by

$$I = \frac{2e}{h} \int \mathcal{T}(E) [f_L(E) - f_R(E)] dE, \quad (4)$$

where $\mathcal{T}(E)$ stands for the transmission coefficient, $f(E)$ is the Fermi-Dirac distribution function. The conductance of the system, G , can be written as

$$G = \frac{2e^2}{h} \int \mathcal{T}(E) \left(-\frac{\partial f}{\partial E} \right) dE. \quad (5)$$

The transmission coefficient [$\mathcal{T}(E)$], which plays a central role in this formalism, can be obtained by using the standard Green's functions formalism.

The Schrödinger equation for the whole system (eq. 1) is

$$\begin{bmatrix} H_{LL} & H_{LC} & 0 \\ H_{CL} & H_{CC} & H_{MR} \\ 0 & H_{RC} & H_{RR} \end{bmatrix} \begin{bmatrix} \Psi_{LL} \\ \Psi_{CC} \\ \Psi_{RR} \end{bmatrix} = E \begin{bmatrix} \Psi_{LL} \\ \Psi_{CC} \\ \Psi_{RR} \end{bmatrix}. \quad (7)$$

However, as we see above, the Hamiltonian matrices which describe the leads, $H_{LL(RR)}$, and their coupling with the scattering region are semi-infinite, which makes the problem hard to solve.

Thus, we will turn our attention to the Green's functions. Within the single particle picture, the Green's function can be calculated from its definition

$$(H - E)G^r = \mathbf{1}. \quad (8)$$

where G^r stands for the the retarded Green's function for the whole system.

In a matrix form, we can write

$$\begin{bmatrix} H_{LL} - E & H_{LC} & 0 \\ H_{CL} & H_{CC} - E & H_{CR} \\ 0 & H_{RC} & H_{RR} - E \end{bmatrix} \begin{bmatrix} G_{LL}^r & G_{LC}^r & G_{LR}^r \\ G_{CL}^r & G_{CC}^r & G_{CR}^r \\ G_{RL}^r & G_{RC}^r & G_{RR}^r \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \quad (9)$$

After some algebra, we get

$$(H_{LL} - E)G_{LC}^r + H_{LC}G_{CC}^r = 0 \quad (10)$$

$$H_{CL}G_{LC}^r + (H_{CC} - E)G_{CC}^r + H_{CR}G_{RC}^r = 1 \quad (11)$$

$$H_{RC}G_{CC}^r + (H_{RR} - E)G_{RC}^r = 0, \quad (12)$$

where we can write,

$$(10) \Rightarrow G_{LC}^r = -g_{LL}^r H_{LC} G_{CC}^r \quad (13)$$

$$(12) \Rightarrow G_{RC}^r = -g_{RR}^r H_{RC} G_{CC}^r, \quad (14)$$

where $g_{LL(RR)}^r$ is the Green's function of the left(right) lead, defined as $(H_{L(R)} - E)g_{LL(RR)}^r = 1$. Putting G_{LC}^r (eq. 13) and G_{RC}^r (eq. 14) on equation 11, we get

$$H_{CL}(-g_{LL}^r H_{LC} G_{CC}^r) + (H_{CC} - E)G_{CC}^r + H_{CR}(-g_{RR}^r H_{RC} G_{CC}^r) = 1. \quad (15)$$

Rearranging the terms, we obtain

$$[H_{CC} - E - (H_{CL}g_{LL}^r H_{LC}) - (H_{CR}g_{RR}^r H_{RC})]G_{CC}^r = 1 \quad (16)$$

Thus, as final result, we get

$$G_{CC}^r(E) = [(H_{CC} + \Sigma_{LL}^r(E) + \Sigma_{RR}^r(E)) - E]^{-1}, \quad (17)$$

where we define the self-energies

$$\Sigma_{LL}^r(E) = -H_{CL}g_{LL}^r(E)H_{LC} \quad (18)$$

$$\Sigma_{RR}^r(E) = -H_{CR}g_{RR}^r(E)H_{RC}. \quad (19)$$

Therefore, the effect of the leads over the scattering region is to add the self-energies Σ_{LL}^r e Σ_{RR}^r to the Hamiltonian H_{CC} . It is interesting to note that inspite the matrices $H_{CL(R)}$, $g_{LL(RR)}^r$ and $H_{L(R)C}$ be semi-infinite, the product between them results in a finite matrix.

As we have the Green's function of the scattering region, we can calculate the transmission coefficient. Within the non-equilibrium Green's function formalism, $\mathcal{T}(E)$ can be written as,

$$\mathcal{T}(E) = Tr \{ \Gamma_{LL} G_{CC}^r \Gamma_{RR} G_{CC}^a \}, \quad (20)$$

where $G_{CC}^{r(a)}$ is the retarded(advanced) Green's function, and the matrices $\Gamma_{LL(RR)}$ which describe the coupling of the scattering region with the leads, are given by

$$\Gamma_{LL(RR)}(E) = i \{ \Sigma_{LL(RR)}^r(E) - [\Sigma_{LL(RR)}^r(E)]^\dagger \} \quad (21)$$

$$= -2Im \{ \Sigma_{LL(RR)}^r(E) \}. \quad (22)$$

Thus, we complete the presentation of the formalism used for the calculations of the electronic transport properties.

Thermal Transport Calculations

Seebeck effect

The Seebeck effect, deals with the conversion of thermal energy into electrical energy, or more specifically, the appearance of an electric field due to a temperature difference between the ends of a material.

The physical mechanism behind this effect is conceptually simple: the electronic distribution function (the Fermi-Dirac distribution function) has a higher electron population in the levels with energy above Fermi energy at the hotter end than in the colder end. Thus, there will be more electrons flowing from the hot side to the cold side than vice-versa, which generates a potential difference across the ends, as shown in Fig. 2. If the circuit is open, the system reaches equilibrium due to accumulation of charge in the ends. However, if it is closed, electrons can keep flowing in a denominated thermocurrent. This is the principle behind the thermoelectric generators.

The Seebeck coefficient (S) is a measure of the magnitude of the induced thermoelectric voltage (ΔV), when the material is under an applied temperature difference (ΔT). If ΔT between the two ends of a material is small, we can write:

$$\Delta V = S \Delta T. \quad (23)$$

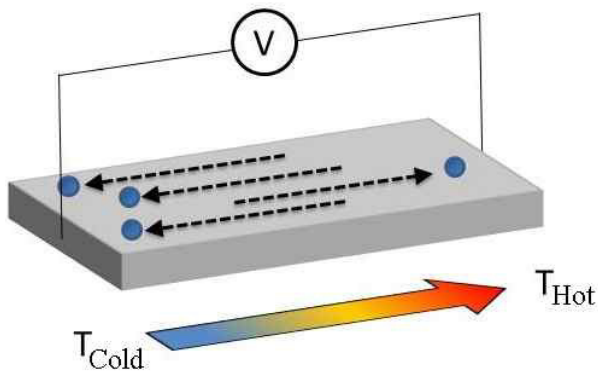


Fig. 2 Schematic illustration of the Seebeck effect. The electrons from the hot side (T_{Hot}), which are more energetic, move to the cold side (T_{Cold}) with a tax greater than the electrons from the cold side, generating an electrical potential difference.

Experimentally, the Seebeck coefficient can be defined as the external electrical potential difference needed to make the thermo-voltage null. Thus, for a null electric current:

$$S = \left. \frac{V_{ext}}{\Delta T} \right|_{I=0} = - \left. \frac{\Delta V}{\Delta T} \right|_{I=0}. \quad (24)$$

In the Landauer formalism, the current of a two terminal device coupled to a reservoir with left and right chemical potentials (μ_L and μ_R) and left and right temperatures (T_L and T_R) is given by:

$$I(\mu_L, T_L; \mu_R, T_R) = \frac{e}{\pi\hbar} \int \mathcal{F}(E) [f(E, \mu_L, T_L) - f(E, \mu_R, T_R)] dE \quad (25)$$

Applying the Sommerfeld expansion to both the electrochemical potential and the temperature, we get the current for small electrical potential difference, $\Delta\mu = e\Delta V$, and temperature, ΔT ,

$$I = \frac{e}{\pi\hbar} \mathcal{F}(E_F) \Delta V - \frac{e}{\pi\hbar} \frac{\pi^2 k_B^2 \bar{T}}{3} \frac{\partial T}{\partial E} \Big|_{E_F} \Delta T \quad (26)$$

where \bar{T} stands for the average temperature between the leads.

For $I = 0$, in Eq. 26, we obtain an expression to the thermo-voltage:

$$\Delta V = \frac{\pi^2 k_B^2 \bar{T}}{3e} \frac{1}{T} \frac{\partial T}{\partial E} \Big|_{E_F} \Delta T \quad (27)$$

$$= \frac{\pi^2 k_B^2 \bar{T}}{3e} \frac{\partial \ln(T)}{\partial E} \Big|_{E_F} \Delta T. \quad (28)$$

Then, the resultant Seebeck coefficient is:

$$S = - \frac{\Delta V}{\Delta T} = - \frac{\pi^2 k_B^2 \bar{T}}{3e} \frac{\partial \ln(T)}{\partial E} \Big|_{E_F}. \quad (29)$$

The derivative, in Eq. 29, can be computed by two distinct forms. The first form is to calculate the $\ln(T(E))$ and to take the derivative

$$\frac{\partial}{\partial E} [\ln(\mathcal{F}(E))]. \quad (30)$$

The second possible way is by using the chain rule, which results in

$$\frac{1}{\mathcal{F}(E)} \frac{\partial \mathcal{F}(E)}{\partial E}. \quad (31)$$

We choose the second form, since the logarithmic function varies very fast if $\mathcal{F}(E) < 1$. More than that, using Eq. 31 we add one more point in the numerical derivative calculation.

Considering, now, a variation in the current produced by small variation in both electrochemical potential and temperature, $\Delta\mu = e\Delta V/2$ and $\Delta T' = \Delta T/2$, that is

$$\Delta I = I(\mu_L + \Delta\mu, T_L + \Delta T'; \mu_R - \Delta\mu, T_R - \Delta T') - I(\mu_L, T_L; \mu_R, T_R). \quad (32)$$

Instead of performing the Sommerfeld expansion in Eq. 32, it is possible to perform the expansion in a Taylor series, on the Fermi-Dirac distribution. Thus, considering only the first-order terms, we get

$$\begin{aligned} f(E, \mu + \Delta\mu, T_i + \Delta T') &= f(E, \mu, T) + \frac{\partial f}{\partial \mu} \Delta\mu + \frac{\partial f}{\partial T} \Delta T' \\ &= f(E, \mu, T) - \frac{\partial f}{\partial E} \Delta\mu - \frac{\partial f}{\partial E} (E - \mu) \frac{\Delta T'}{T_i + \Delta T'} \end{aligned} \quad (33)$$

where $i = L, R$. In this way, the expression to the current variation under an applied ΔV and ΔT is

$$\begin{aligned} \Delta I &= \frac{e^2 \Delta V}{2\pi\hbar} \int \mathcal{F}(E) \left(-\frac{\partial f_L}{\partial E} - \frac{\partial f_R}{\partial E} \right) dE \\ &+ \frac{e \Delta T}{2\pi\hbar \bar{T}} \int \mathcal{F}(E) \left[-\frac{\partial f_L}{\partial E} (E - \mu_R) - \frac{\partial f_L}{\partial E} (E - \mu_R) \right] dE \end{aligned} \quad (34)$$

where $f_{L/R} \equiv f(E, \mu_{L(R)}, T_{L(R)})$ and $(T_L + T_R)/2$ is the average temperature of the electrodes.

Defining the terms,

$$K_n = \int \mathcal{F}(E) \left(-\frac{\partial f}{\partial E} \right) (E - \mu)^n dE \quad (35)$$

and substituting it in the Eq.35 we get

$$\Delta I = \frac{e^2 \Delta V}{2\pi\hbar} (K_0^L + K_0^R) + \frac{e \Delta T}{2\pi\hbar \bar{T}} (K_1^L + K_1^R) \quad (36)$$

where the superscript $L(R)$ in $K_n^{L(R)}$ indicates that we are considering $\mu = \mu_{L(R)}$. If we consider $\Delta I = 0$, we obtain a new equation to the thermopower or Seebeck coefficient (S)

$$S = -\frac{1}{eT} \frac{(K_1^L + K_1^R)}{(K_0^L + K_0^R)}. \quad (37)$$

In the linear regime, low temperatures and low voltages, $\mu_L \approx \mu_R \approx \mu$ and $T_L \approx T_R \approx \bar{T}$, we can write:

$$S = -\frac{1}{e\bar{T}} \frac{K_1}{K_0}. \quad (38)$$

Figure of Merit (ZT)

The thermoelectric devices are, in their inwardness, thermal machines and they must obey the thermodynamics laws. Then, we can calculate the theoretical maximum efficiency from these devices. For electrical generators, the maximum efficiency is provided by the expression:

$$\eta_{max} = \frac{T_H - T_C}{T_H} \left(1 - \frac{1 + T_C/T_H}{\sqrt{1 + ZT} + T_C/T_H} \right), \quad (39)$$

where $T_{H(C)}$ is the temperature of the hot(cold) source and ZT is the named figure of merit, with Z defined as:

$$Z = \frac{GS^2}{\kappa} = \frac{GS^2}{\kappa_{ph} + \kappa_{el}}, \quad (40)$$

being G the electronic conductance, S the Seebeck coefficient and κ the thermal conductance. From the equation to η_{max} , eq. 39, it is possible to see that greater is ZT (unlimited, in principle) closer to the Carnot efficient limit, ($\frac{T_H - T_C}{T_H}$), η_{max} is (if $ZT = \infty$, $\eta_{max} = \eta_{Carnot}$).

Based on this analysis, it is possible to see that the figure of merit ZT is a simple parameter that determines the thermoelectric efficacy of a material or device. To optimize Z , i.e. to reach the highest value possible, we have to simultaneously optimize G and S , which must be as greater as possible, and κ_{el} and κ_{ph} must be as lower as possible. This is not a easy task, since these quantities are not completely independent.

Now, we are going to discuss an approximation that makes the calculation of the figure of merit easier. In the case of materials with high electronic mobility, and therefore, high electronic conductance G , the thermal electronic conductivity κ_{el} is also high. Whether κ_{el} is greater than κ_{ph} , in a first approximation, it is quite reasonable to neglect the κ_{ph} in eq.40. Then, we have to keep in mind that we are calculating the upper limit of Z .

Considering the above approximation, we obtain

$$Z = \frac{GS^2}{\kappa_{el}}. \quad (41)$$

By using the K_n terms presented in eq. 35, we can write G , S and κ_{el} like:

$$G = \frac{e^2}{h} K_0 \quad (42)$$

$$S = -\frac{1}{eT} \frac{K_1}{K_0} \quad (43)$$

$$\kappa_{el} = \frac{1}{h} \left(K_1 eS + \frac{K_2}{T} \right) \quad (44)$$

and, consequently, we obtain

$$ZT = \left(\frac{K_2 K_0}{K_1^2} - 1 \right)^{-1}. \quad (45)$$

Additional Figures

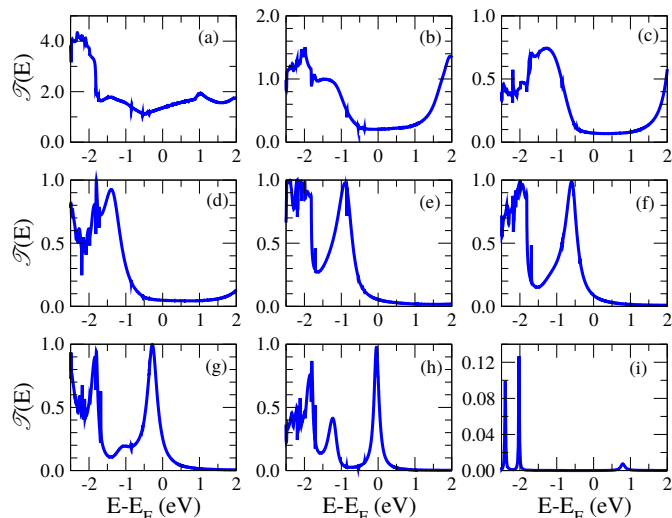


Fig. 3 Upper panels: Self-Interaction corrected transmission coefficient plots for the representative geometries of a BDT molecule attached to Au electrodes. Lower panel: Self-Interaction corrected transmission coefficient, at the Fermi level, as a function of the electrodes separation.

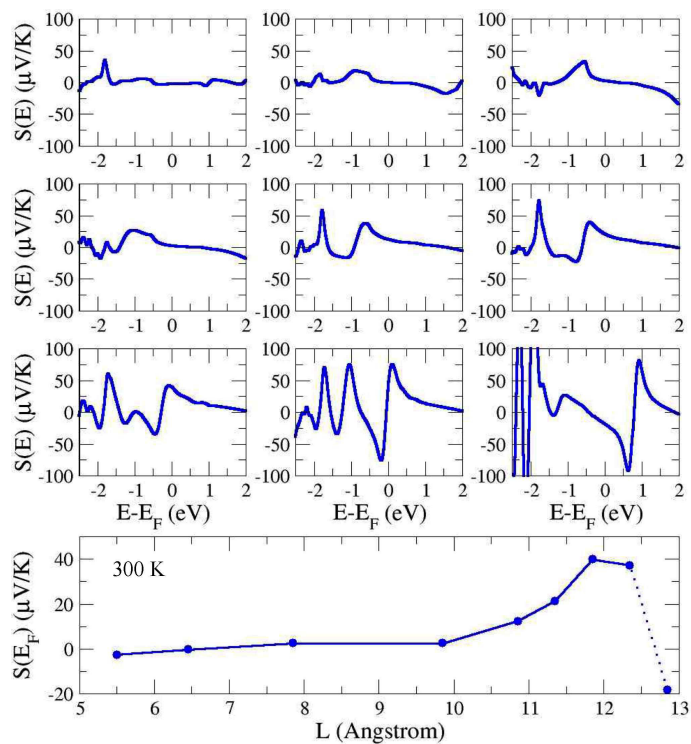


Fig. 4 Upper panels: Seebeck coefficient plots for the representative geometries of a BDT molecule attached to Au electrodes. Lower panel: Seebeck coefficients calculated at the Fermi level as a function of the electrodes separation for all the geometries investigated

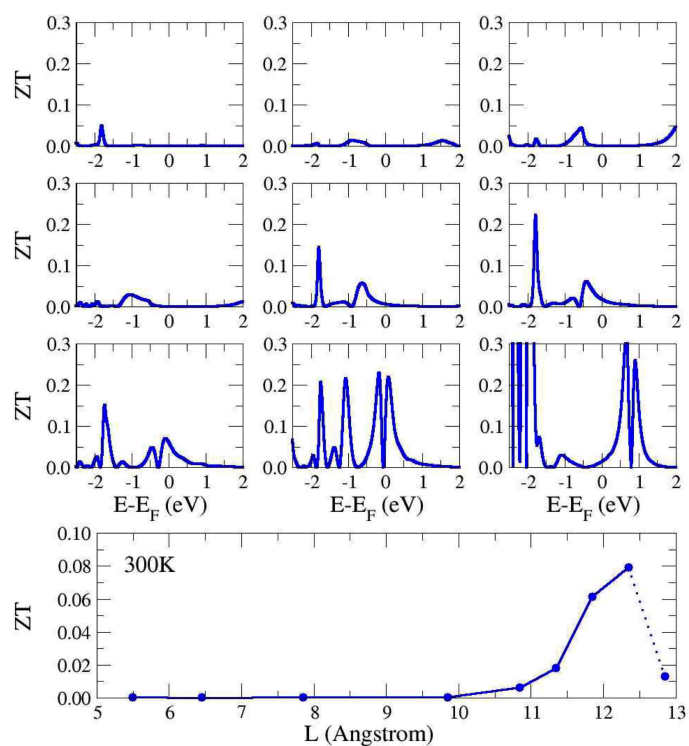


Fig. 5 Upper panels: Figure of merit (ZT) plots for the representative geometries of the structural evolution of the Au/BDT/Au junction. Lower panel: Figure of merit calculated at the Fermi level as a function of the electrodes separation for all the geometries investigated