Stretching-Dependent Thermoelectric Properties of a BDT Single-Molecule Junction

Renato B. Pontes, Alberto Torres, Antônio J. R. da Silva & Adalberto Fazzio

Introduction

Understanding the physical and chemical properties of molecular junctions is fundamental for developing organic-based devices. In particular, a lot of effort has been made to investigate both the low bias conductance and the thermoelectric properties of molecules coupled to gold leads.

Recently, Venkataraman et al.[1] performed the first concomitant determination of conductance (G) and Seebeck coefficient (S) of a single molecule junction, via the direct measurement of electrical and thermoelectric currents, by using a scanning tunnelling microscope-based breakjunction technique (STM-MCBJ). Thus, since the charge transport properties of molecular junctions depend on how the frontier orbitals are positioned in the vicinity of the Fermi level, a concurrent measurement of electrical and thermoelectric properties is now possible. Thus, it is interesting to consider what would happen with the thermoelectric properties of a single molecule junction as a function of the mechanical stretching. Here we show that the thermoelectric properties, thermopower (S), electronic heat conductance (kel) and efficiency, characterized by the figure of merit (ZT), can be tuned as a function of the electrode separation, in a single BDT molecule junction (Au/BDT/Au). We also propose a scheme to obtain the maximum ZT of molecular junctions in general[2].

Methods

Our results for the structural evolution of the junction Au/BDT/Au are based on first-principles spin-polarized total energy density functional theory (DFT) calculations[3,4]. We use a PBE-GGA functional and norm-conserving pseudo-potentials as implemented in the SIESTA code[5,6]. Numerical atomic orbitals are used as basis sets. We employed a split-valence double-zeta basis with a polarization function (DZP) for the whole system. The confining energy shift is 0.05 eV and an energy cut-off of 240 Ry is used to the grid integration. For the surface Brillouin zone (BZ) sampling we use a (4 x 4 x 1) Monkhorst–Pack set. Moreover, in our calculations the selfconsistency is achieved when the change in the total energy between cycles of the SCF procedure is below 10-4 eV and the density matrix change criterion of 10-4 is also satisfied. These criteria are enough to ensure convergence in the calculated total energy of 0.05 eV.

To obtain the geometries, the supercell is such that the molecule would be connected to the two sides of the Au slab. The Au slab is modelled by a (3 x 3) surface unit cell and five layers of gold. In all calculations the positions of the BDT atoms and the Au atoms on the first two layers at either side are allowed to relax until the forces are smaller than 0.02 eV/Å. All other atoms are held fixed at their bulk positions. The separation between the electrodes is increased in steps of 0.5 Å

and for each new supercell length the system is fully relaxed. The transport calculations are performed on TRANSAMPA code[7-11], which employs a non-equilibrium Green's function combined with density functional theory (NEGFDFT).

Result and Discussion

Fig. 1(a–i) shows nine panels depicting the representative geometries of the different stages of the evolution of the Au/BDT/Au junction during a STM-MCBJ experiment. For small electrode separations (panels a and b), the molecule is nearly parallel to the surface and as the electrodes are moved apart, the BDT molecule is pulled to an upright conformation (panel h). By further stretching the single-molecule junction rupture of the Au–S bond occurs (panel i). A detailed discussion about the structural evolution of the Au/BDT/Au junction is presented by Pontes et al.[11]

We show that the thermoelectric properties of a single molecule junction can be tuned by mechanic stretching. In Fig. 2. we show that the Seebeck coefficient is positive, indicating that it is dominated by the HOMO. Furthermore, it increases as the HOMO level, which is associated to the sulphur atom, tends towards energies close to the Fermi energy. To the end, by modelling the transmission coefficient of the system as a single Lorentzian peak(Fig. 3), we propose a scheme to obtain the maximum ZT of any molecular junction.

The scheme for maximizing the ZT involves two main points: (i) to obtain narrow resonances in the transmission coefficient spectrum and, (ii) the molecular orbital's energy shift, to tune the resonance. The narrow resonances can be obtained by mechanical stretching, as we previously showed. The molecular orbital's energy shift is possible by stretching, doping or even under an applied external electric field.

Conclusions

In conclusion, we investigate as a function of the stretching the behaviour of the thermoelectric properties – Seebeck coefficient(S), the electronic heat conductance (kel) and the figure of merit (ZT) – of a molecule-based
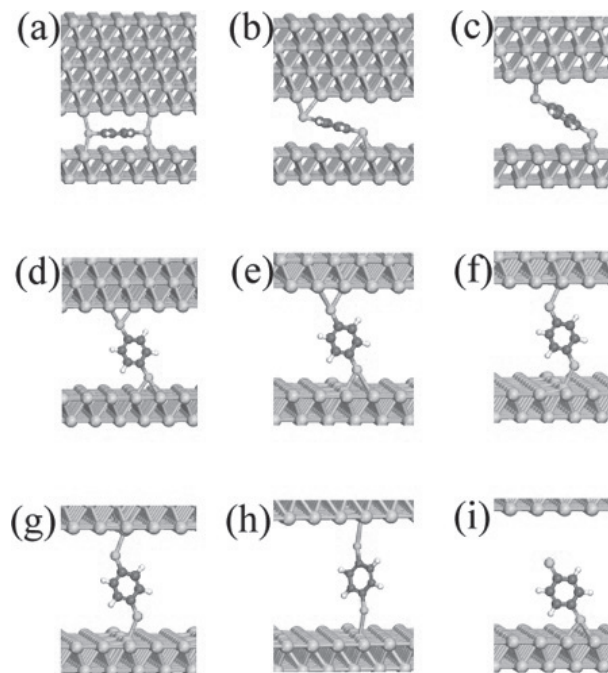

Figure 1. Ball-and-stick view of the optimized atomic structures, at different stages of the structural evolution of a single BDT molecule junction as a function of the stretching.
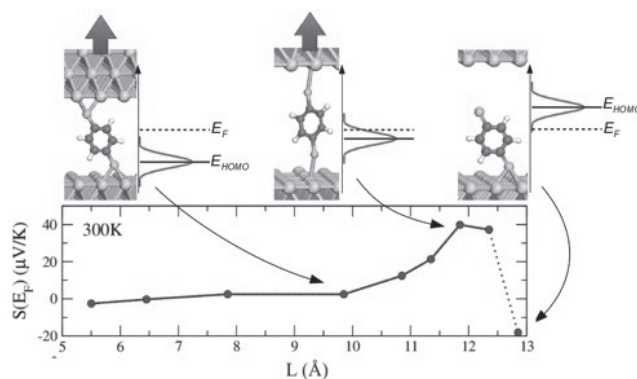

Figure 2. Seebeck coefficients, in the Fermi level [S(EF)], as a function of the lead-lead separation, for the temperature of 300 K. The associated Au/BDT/Au geometry is also shown.
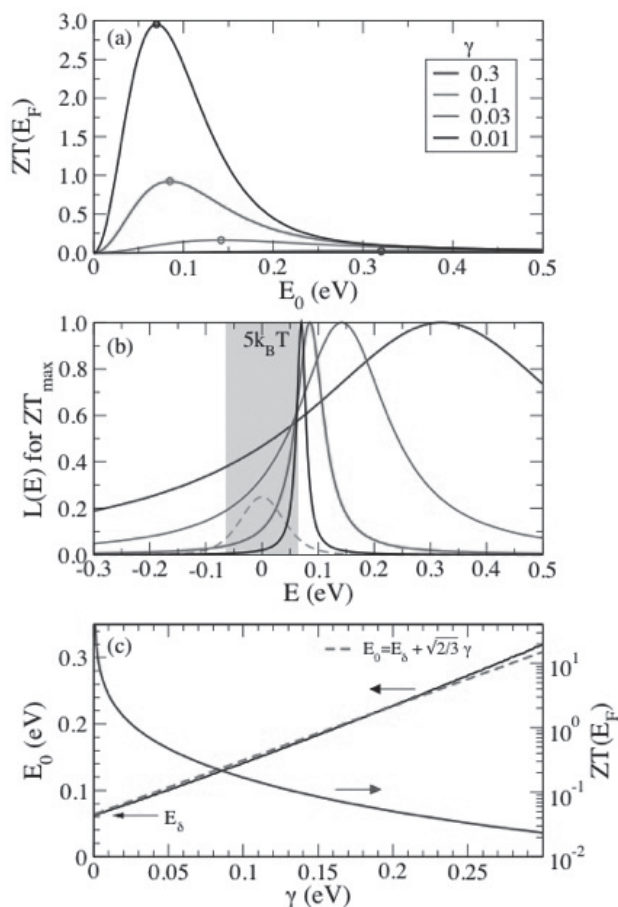
Figure 3. (a) Figure of merit, ZT, at the Fermi level, EF, for Lorentzian transmittances as a function peak position, E0, for several widths, γ. (b) Lorentzian transmittances for the E0 values which yield the maximum ZT in the upper panel, marked as dots in (a). (c) E0 that L(E) have to do in order to maximize ZT at the Fermi energy as function of the width, γ.

junction composed by a benzene-1,4-dithiol molecule (BDT) attached to Au(111) surfaces at room temperature. Based on our ab initio calculations, we show that the thermoelectric properties of a single molecule junction can be tuned by mechanic stretching. For the Au/BDT/Au junction, the Seebeck coefficient is positive, indicating that it is dominated by the HOMO. Furthermore, it increases as the HOMO level, which is associated to the sulphur atom, tends towards energies close to the Fermi energy. We also propose a simple and general scheme that can be used to obtain the maximum ZT of any molecular junction.

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