Length-dependent conductance and thermopower in metal-molecule-metal junctions

J. K. Viljas$^{1,2}$, F. Pauly$^{1,2}$, and J. C. Cuevas$^3$

$^1$Institut für Theoretische Festkörperphysik and DFG-Center for Functional Nanostructures, Universität Karlsruhe, D-76128 Karlsruhe, Germany
$^2$Forschungszentrum Karlsruhe, Institut für Nanotechnologie, D-76021 Karlsruhe, Germany
$^3$Departamento de Física Teórica de la Matemática Condensada C-V, Universidad Autónoma de Madrid, E-28049 Madrid, Spain

Introduction

Experiments and theory of single-molecule junctions have concentrated on studying the electrical conductance $G$ by applying voltages $\Delta V$ [1]. Recent experiments [1] also show the thermopower (Seebeck coefficient) $S$ of oligophenylenes based contacts was measured by applying a temperature difference $\Delta T$ over the contact. It was found that (i) the thermopower was positive, implying “hole-type” transport, and (ii) while $S$ decays exponentially with the number $N$ of phenyl rings, $\Delta G$ grows with $N$ roughly linearly. We have analyzed the experimental data [2,3] and find a good agreement. We also studied the effect of methyl side groups on $G$ and $S$. Such side-group effects were also recently studied experimentally [4,5].

Landauer-Büttiker theory

The transport equation for the current $I$ is given by

$$ I = \frac{e}{h} \int dE \sigma(E) \Delta \rho_{ab}(E) $$

where $\sigma(E)$ is the Landauer-Büttiker conductance matrix, $\Delta \rho_{ab}(E)$ is the change in the density of states at energy $E$, and $e/h$ is the conductance quantum. For the $N$-atom oligophenylene, the transmission coefficient is given by

$$ T(E) = \prod_{i=1}^{N} \left( 1 + \frac{1}{4} \frac{e^2}{\hbar^2} \frac{1}{\sqrt{v_i}} \right) $$

where $v_i$ is the velocity of the electron at the $i$-th atom and the product runs over all atoms.

DFT-based results

Based on DFT: TURBOMOLE (R. Ahlrichs et al., Karlsruhe)

- finite clusters (no periodic boundary conditions)
- BP86 exchange-correlation functional
- local SVP Gaussian basis set

Non-equilibrium Green-function method (NEGF)

- applied here for linear response

Transport method: DFT+NEGF [7]

- $G_{E,0}$ fitted to DFT results for both molecular junctions

Conclusions

Summary

- Simple arguments for scaling with length
- Conductance decays (exponentially)
- Seebeck coefficient increases (linearly)
- DFT simulations
- Agreement between theory and experiment
- Predictions on the effect of side groups
- Model calculations: effect is twofold
- Ring tilt alone reduces $G$ and $S$
- Side groups shift the energies

Future directions

- Effect of electron-vibration coupling [9] on O(10)
- Modification of the exponential and linear laws for large $N$
- Figure of merit $ZT=Q^2T/(h\nu_a^2)$

References