

Thermoelectric properties of molecular junctions

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Here we study the thermoelectric transport properties of single molecule devices. Using density functional theory (DFT) combined with nonequilibrium greens function (NEGF) technique we study the thermoelectric transport properties of molecular junction, namely paracyclophane based single molecule devices. We included the electronic as well as the phononic degree of freedom consistently in the frame work of our DFT+NEGF approach [1,2]. Eventually this enables us to calculate all thermoelectric transport coefficients that is the conductance G , the thermopower S and the thermal conductance $\kappa = \kappa_{el} + \kappa_{ph}$, with electronic κ_{el} and phononic κ_{ph} contribution, from first principles. Density functional theory derived phonon and in general total energy properties are often in very good agreement with experimental results, on the other hand although that DFT is able to capture important trends and chemical properties DFT usually leads to a large overestimation of the electric conductance of semi-conduction systems. This is related to the self-interaction error and missing long-range correlation in approximate DFT schemes. Therefore we include an approximate self-energy correction based on the DFT+ Σ approach to correct both shortcomings [3]. Despite being computationally very cheap the DFT+ Σ approach usually yields accurate molecular conductance especially for weakly coupled systems.

In this work we apply our methodology to paracyclophane based single molecule junctions. Paracyclophane molecules are stacked benzol units hold together by alkene side chains. We investigate the length dependence of the transport and find an exponential decrease of the conductance and a linear increase of the thermopower with increasing molecular length. Whereas the calculated decay constant is in very good agreement with the experimentally determined one. To tailor the electronic contribution to the thermoelectric transport coefficients we functionalize the molecule by replacing two hydrogen atoms in pseudo-para position by either electron donating (NH_2 and OH) or electron withdrawing (NO_2 and COCF_3) side groups. We find that the sign of the thermopower is related to the Hammett constant,

namely NH_2 and OH give rise to positive thermopower and NO_2 and COCF_3 to negative thermopower respectively. Additionally also the absolute value of the thermopower is largely increase as compared to the unsubstituted paracyclophane. This leads to a considerable enhancement of the power factor and respectively also to an increase of the electronic contribution to the figure of merit $Z_e T$. However including the phononic contribution to the heat current which is found to be at least one order of magnitude larger than the electronic contribution the overall ZT is suppressed strongly. Nevertheless we could demonstrate for a set of commercially readily available molecules that it is possible to chemically tune the transport characteristics.

Additionally to the ballistic transport properties we extend our transport approach also into nonlinear regime. Here especially anharmonic phonon-phonon scattering is expected to have a large influence onto the phonon thermal conductance. Therefore we include the effect of cubic and quartic anharmonicities at the level of first order self-consistent born approximation into our NEGF scheme. Both the cubic and quartic anharmonic force constants are obtained within DFT. As a first test study we apply this to 1D systems which show a large suppression of the thermal current at room temperature.

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