From Chemistry to Functionality: 
Trends for the Length Dependence of the Thermopower in Molecular Junctions.

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We present a systematic ab-initio study of the length dependence of the thermopower in molecular junctions. The systems under consideration are small saturated and conjugated molecular chains of varying length attached to gold electrodes via a number of different binding groups. Different scenarios are observed: linearly increasing and decreasing thermopower as function of the chain length as well as positive and negative values for the contact thermopower. Also deviation from the linear behaviour is found. The trends can be explained by details of the transmission, in particular the presence, position and shape of resonances from gateway states. We find that these gateway states do not only determine the contact thermopower, but can also have a large influence on the length-dependence itself. This demonstrates that simple models for electron transport do not apply in general and that chemical trends are hard to predict. Furthermore, we discuss the limits of our approach based on Density Functional Theory and compare to more sophisticated methods like self-energy corrections and the GW theory.

The perfect material for potential application in efficient thermo electrical devices should be small in size, stable and, most of all, highly tunable. In these respects, organic molecules seem very promising candidates, since chemistry offers a vast number of possibilities for designing their electrical and thermal properties. In particular, simple carbon-based molecular wires bridging two gold electrodes via selected binding groups can provide systematic insight into fundamental electronic and thermal transport mechanisms. Ideally, mapping out chemical trends would be a new and easy way for predicting a molecule’s function. However, only little is known about the interplay between chemical structure and thermo electric features like conductance or thermopower. The large number of degrees of freedom in molecular junctions, such as the junction geometry, conformation and the chemical structure, makes it particularly challenging to establish general trends.

Typical binding groups for gold electrodes are thiols and amines. More recently, the thermopower of single molecules linked via isocyanide groups as well as through direct covalent Au-C bonds has been measured. Amines exhibit a well-defined weak electronic coupling due to bonding of the N lone pair to an undercoordinated Au atom, allowing for stable measurements. Strong coupling is given by thiol binding groups, where a single sulfur atom can bond to up to three gold atoms. However, uncertainties in the contact geometry lead to large variations in the measured and calculated conductances. A well-defined contact geometry is achieved through the direct $\sigma$-type Au-C bond to an undercoordinated gold atom. This also allows for direct coupling of the electrodes into the carbon backbone of the molecule.

In the linear response regime, the thermopower (also called Seebeck coefficient), is defined as

$$S = -\frac{\Delta V}{\Delta T}_{I=0},$$

where $\Delta V$ is the thermally induced voltage at the steady state zero current due to an applied temperature difference, $\Delta T$, across the junction.

It has been widely stated that a positive thermopower corresponds to hole transport or tunnelling through the highest occupied molecular orbital (HOMO) and a negative thermopower to electron transport or tunnelling through the lowest unoccupied molecular orbital (LUMO). The question, however, is how these orbitals of the molecule in the junction compare to the situation of the molecule in the gas phase. In the presence of metallic electrodes, the molecular orbitals (MOs) become renormalized and broadened. Charge transfer can lead to partial occupation numbers. Due to hybridization of localized MOs with metallic states at the interface with the electrodes, so-called gateway states can appear within the HOMO-LUMO gap.

Experimentally, it has been found that the thermopower increases linearly with the length of a molecular chain, $N$. This is supported in theory for the off-resonant tunnelling regime, where the transmission is exponentially suppressed around the Fermi energy.

$$\tau(E) = \alpha(E)e^{-\beta(E)N},$$

with parameters $\beta(E)$ and $\alpha(E)$, which determine the decay factor and the contact resistance, respectively. Then, the thermopower becomes

$$S \propto \beta'(E)N - \frac{\alpha'(E)}{\alpha(E)}_{E=E_F}.$$
Here, \( \alpha \) denotes the derivative with respect to energy. Eq. (3) implies that the length dependence of the thermopower (the slope) is given by \( \beta_S = \beta'(E)|_{E=E_F} \), whereas the contact thermopower, \( S(N = 0) \), only depends on \( \alpha(E) \).

Recent tight-binding calculations support the common assumption that \( \beta(E) \) is related to the molecular backbone and position of the MO energies, since it is independent of the contact coupling\(^{26} \alpha(E) \), on the other hand, is directly associated with states on the binding groups and has a strong dependence on the coupling strength. Depending on the position of the Fermi level and the binding group energy, four different scenarios for the length dependence of the thermopower can in principal be found: positive or negative contact thermopower with increasing or decreasing values with length. A case, where the thermopower changes sign with increasing molecular length has been measured recently for the first time for oxidized oligothiophenes.\(^{28} \)

I. METHOD

The transmission, \( \tau(E, V) \), is calculated within the Landauer-Büttiker formalism for coherent transport\(^{29} \) using standard nonequilibrium Green’s Functions techniques based on Density Functional Theory (NEGF-DFT).\(^{30,33} \) Within this framework, the thermopower is given as

\[
S = -\frac{1}{eT} \int dE \tau(E, V = 0) \frac{f'(E, T)}{f(E, T)},
\]

where \( e \) is the elementary charge, \( T \) the absolute temperature and \( f(E, T) \) the Fermi distribution. In the limit of small temperature gradients, \( \Delta T \rightarrow 0 \), Eq. (4) reduces to\(^{34,37} \)

\[
S = -\frac{\pi^2 k_B^2 T}{3e} \left. \frac{\partial \ln(\tau(E, V = 0))}{\partial E} \right|_{E=E_F},
\]

where \( k_B \) is the Boltzmann constant. All thermopower values presented in this work have been calculated from Eq. (4) at room temperature \( (T = 300 \text{ K}) \). Eq. (4) illustrates that the thermopower is proportional to the negative logarithmic derivative of the transmission at the Fermi energy of the electrodes, \( E_F \).

All calculations have been carried out with the electronic structure code GPAW\(^{35} \) using the generalized gradient PBE exchange-correlation functional.\(^{36} A \) double-zeta polarized basis set of diffuse basis functions with a confinement-energy shift of 0.01 eV was employed.\(^{40} \) The junctions were modelled in supercells with 7-8 layers of gold containing 16 atoms each arranged in the fcc structure. A \( (4 \times 4) \) \( k \)-point sampling was applied in the directions of the electrode surface and the transmission was averaged over all \( k \) points.\(^{39,41} \) The coupling to the bulk electrodes is obtained using standard techniques.\(^{42,43} \)

The junction geometries are sketched in Fig. 1. Nitrogen and carbon atoms were chosen to bind to a single gold adatom at the tip of a small pyramid, whereas sulfur atoms were placed in a fcc-hollow site of a flat gold surface. For each binding group, alkanes (saturated carbon chains), alkynes (conjugated carbon chains with alternating single and double bonds) and alkenes (conjugated carbon chains with alternating single and triple bonds) with 2, 4, 6 and 8 carbon units were modelled. Geometry optimization was performed for all molecules (including the tip atoms in the pyramid configuration) on ideal gold surfaces.

II. RESULTS

A. Alkane chains

The thermopower for the alkane chains is shown in Fig. 2. It increases roughly linearly with length for all binding groups with a rather small prefactor of around \( 0.5 - 1.1 \mu V/K \) per methyl unit. The onset, however, is very different for the four binding groups considered here: NH\(_2\) gives a small and NC a large negative value, respectively, whereas the onset is close to 0 for sulfur and slightly positive for direct coupling. This results in different scenarios: Positive and increasing thermopower for thiol binding groups as well as direct coupling, and negative and increasing thermopower for isocyanide binding groups. For the amine linkers, the thermopower changes sign with increasing length, going from negative values for short chains to positive values for longer chains (\( \geq 4 \) methyl units).

The reasons for these different behaviours can be seen from the corresponding transmission curves presented in Fig. 3. For thiol end groups, a broad gateway state resonance originating from hybridization of states located on the sulfur atoms with Au d-states appears within the HOMO-LUMO gap about 1.2 eV below the Fermi level resulting in a negative slope of \( \tau(E) \) and thus a positive thermopower. With increasing chain length, the gap becomes deeper without changing the shape or position of the gateway state resonance. Since the center of the gap falls off faster than the resonance peak height, the slope of the transmission curve at \( E_F \) becomes steeper and the thermopower larger.

This situation is similar for the chains with direct coupling (see Supporting Information), where the gateway resonance is much broader. For the shortest chain, however, the hybridization is so strong that the transmission becomes very flat with values close to 1 around the Fermi energy. In this case, the transport mechanism is resonant tunnelling and Eqs. (2) and (3) do not apply.\(^{44} \) Therefore, the first data point in Fig. 2 is off the straight line.

For the isocyanides on the other hand, the transmission is dominated by a relatively sharp gateway state resonance slightly above the Fermi energy giving positive slopes and large negative Seebeck coefficients. As for the
FIG. 1. Left side: Chemical structure of (i) alkane, (ii) alkene and (iii) alkyne chains. X = S, NH₂, NC, - (direct coupling). N is the number of (CH₂)₂, (CH)₂ and (C)₂ units, respectively. Right side: Junction geometries for (a) thiol-, (b) isocyanide- and (c) amine-end groups and (d) direct coupling.

FIG. 2. Calculated thermopower for alkane chains with amine-, isocyanide- and sulfur-binding groups as well as direct coupling in the junction geometries of Fig. 1. Straight lines are linear fits to $S(N) = S(0) + \beta S \cdot N$, where $N$ is the number of (CH₂)₂ units. All fitted values are listed in Table I. The first data point is not considered in the fitting for direct coupling. The dotted horizontal line serves as guide for the eye at $S = 0$.

Previous molecules, the peak height does not drop off as fast as the center of the gap for longer chains. Additionally, the center of this peak moves slightly up in energy. This results in an increase of the slope of the transmission curve and thus the thermopower.

In the case of amine-end groups, the Fermi level is located around the middle of the HOMO-LUMO gap, where the transmission curve is very flat. This is why the obtained values for S are small and even subtle variations in the position of a resonance imply a change of sign of the thermopower.

TABLE I. Fitted contact thermopower, $S(0)$, and length dependence, $\beta S$.

|                      | $S(0) [\mu V/K]$ | $\beta S [\mu V/K]$ |
|----------------------|------------------|---------------------|
| alkane-NH₂           | -3.3             | 0.86                |
| alkane-NC            | -28.3            | 0.46                |
| alkane-S             | 1.8              | 1.14                |
| alkane-direct        | 4.6              | 1.09                |
| alkene-NH₂           | -72.8            | -8.60               |
| alkene-NC            | -44.9            | -6.91               |
| alkene-S             | 7.6              | 1.51                |
| alkene-direct        | -5.5             | 5.85                |

B. Alkene chains

The results for alkene chains are plotted in Fig. 4. Again, the calculated values for the thermopower for the amine-end groups are very small, but we cannot see a linear dependence with length. In the corresponding transmission curves (see SI), a sharp very resonance appears at around 0.5 eV above the Fermi energy, which arises from the LUMO of the molecule in the gas phase. This orbital is localized on the carbon backbone of the molecule and on the hydrogen atoms of the amine groups that stick out in the direction of the $\pi$-system of the chain, thereby forming a hyperconjugated state. There is no contribution on the nitrogen atoms. Therefore, this state does not couple to the gold electrodes when the
molecule is put into the junction in the given contact geometry. This situation makes it impossible to distinguish between backbone and end group effects on the transmission properties. A possible workaround would be to rotate the hydrogen atoms out of the $\pi$-system of the backbone. However, we could not find an energetically stable conformation or junction geometry for that.

A new situation occurs for the isocyanide end-groups: the thermopower has a large negative onset and decreases even more with length. As shown in Fig. 5, there is a sharp resonance from the LUMO slightly above $E_F$ reaching a transmission value of 1. It does neither decrease nor shift in energy for longer chains. Therefore, as the transmission gap deepens, the slope of the transmission becomes steeper and the thermopower decreases.

For the thiol-end groups, the thermopower is again positive and increasing as for the alkane chains, but with larger values for the onset and slope of $S(N)$. A small negative contact thermopower is found for the directly coupled chains, although the thermopower itself is positive for all molecules and increases with length. As opposed to the alkanes, we find a large spread of values for $\beta_S$ with both negative and positive values.

C. Alkyne chains

The results for alkyne chains are presented in Fig. 6 and are similar to the alkenes. There are four different scenarios for the length dependence of the thermopower: positive and increasing ($S$), negative and decreasing ($S^{-}$), positive and decreasing ($S^{+}$), and negative and increasing ($S^{-}$).
(NC), negative and increasing (direct) and changing sign from positive to negative (NH$_2$).

All further transmission curves are given in the Supporting Information. The fitted values for the contact thermopower and the slope are listed in Table III.

III. DISCUSSION

A. Contact thermopower

By comparing all of our results, we do see a trend for the contact thermopower, $S(0)$, for the different binding groups: For thiols, it is positive for all systems studied here. This is in agreement with experimental findings for alkane chains. For short lengths, respect to the Fermi energy, as mentioned in the previous section for alkane chains. For short lengths, resonant rather than off-resonant tunneling occurs.

The contact thermopower is expected to be around 0 for amine-terminated chains, which would agree with measurements on phenyldiamines and but no linear length dependence could be found for alkenes and alkynes. The calculated values for the thermopower itself, however, are all very close to 0.

B. Length dependence

The slope, $\beta_S$ does not follow a simple rule of thumb, since neither its value nor even its sign can be directly predicted from the properties of the backbone alone. In particular, we find a large variation for the conjugated molecules. However, this lies within the predictions of the tunneling model as described in Ref. 26. $\beta(E)$ exhibits a strong energy dependence and its derivative, $\beta'(E)$, changes sign around the Fermi level. Since end groups can strongly influence the position of MO energies with respect to $E_F$ (alteration of the band lineup or level alignment), they also effect $\beta_S = \beta'(E)|_{E=E_F}$. The length dependence of the thermopower is thus not only a property of the backbone, as previously assumed, but rather of the backbone + binding groups. In the presence of gateway states, it even depends on the whole junction.

Early measurements reported positive and decreasing thermopower with length for alkanedithiols, whereas positive and increasing values were measured more recently, the latter being consistent with our calculations. We note that we have also calculated the thermopower for S-terminated chains in the top-geometry (as for the other binding groups). While the transmission curves look very different (see SI), we still find a positive and increasing thermopower. However, our findings suggest that the length dependence can be very sensitive to details in the coupling, which might explain the differences in the two experiments.

In the experiments of Ref. 48, a positive and increasing thermopower was found for directly Au-C coupled alkane chains. The dependence was nonlinear and a saturation of $S$ with molecular length was observed for a length of 10 methyl units. However, this data set contained only three points. Thus, we don’t see a contradiction to our results.

C. Methodology

It is well known that DFT tends to overestimate conductances by up to several orders of magnitude and that higher levels of theory, such as the GW method, are required to bring calculated values in good agreement with experimental results. Even though the thermopower is most likely a more robust quantity, since it is found to be less sensitive to errors in method. DFT cannot be expected to give quantitatively accurate results. As discussed here, the thermopower depends mainly on the presence, position and shape of resonances from gateway states. DFT usually places molecular resonances too close to the Fermi level, leading to large errors in transport calculations. This is a consequence of the self-interaction error inherent in most functionals, which results in an inaccurate molecule-lead charge transfer. Another problem is the underestimation of the HOMOLUMO gap with DFT, resulting in far too low values.
for the conductance. Nevertheless, it is possible to predict qualitative trends. In particular, correct signs of the thermopower and the linear prefactor, $\beta_S$, have been found.\textsuperscript{20,52,54}

Good results for the conduction and thermopower could also be obtained within the DFT + $\Sigma$ approach, which corrects for static correlation and image charge effects.\textsuperscript{21,48,54,55} This method shifts all occupied (unoccupied) molecular orbitals down (up) in energy by a constant value. Thus, it moves the molecular resonances further away from the Fermi level, which results in a deepening of the transmission gap. It is, however, not clear how gateway states are affected. In any case, DFT + $\Sigma$ fails for systems where charge transfer from the electrodes leads to partial occupation of otherwise unoccupied molecular orbitals.\textsuperscript{22} This turned out to be the case for many of the systems in our study. A detailed comparison is given in the Supporting Information.

Much better results are expected for the GW method. This, however, is computationally extremely challenging and we were not able to converge results properly with respect to the basis set and the size of the interacting region for many of the structures.

IV. CONCLUSIONS

We have calculated the thermopower of small molecular chains attached to gold electrodes in well-defined and consistent binding geometries using Density Functional Theory. By varying the degree of conjugation and binding group, we have investigated the question to what extent their chemical properties determine the length dependence of the thermopower and if predictions can be made. A simple assumption that the thermopower depends linearly on the length and that this dependence is given by the nature of the molecular backbone does not hold. Instead, we find that in many cases resonances from gateway states dominate the electron transmission close to the Fermi level of the electrodes and thus the transport properties of the molecule. It is therefore the binding group, that not only dictates the contact thermopower, but also influences the length dependence to a large degree. A situation, where the gateway states are completely decoupled from the backbone in order to separate their effects would be desirable, but could not be realized with reasonable junction geometries for many of the short molecules. The importance of gateway resonances is diminished for longer chains. However, we expect their influence to be negligible only for much greater lengths than studied here. Overall, we can identify different scenarios for the length dependence. Amongst others, some where the thermopower changes sign with length.

Although DFT is not expected to yield quantitatively accurate results, we believe that it gives correct trends. Including static self-energy corrections in the so-called DFT + $\Sigma$ approach did not prove to be feasible in this broad study, since its validity is restricted to cases where interactions between molecule and electrode surface are sufficiently low. Unfortunately, the self-consistent GW method did not turn out to be generally applicable either, as many of the calculations were practically impossible to converge.

In summary, we have demonstrated that, although it is very difficult to separate end group from backbone effects, the thermopower can be tuned chemically, even for the simplest systems. Other chemical modifications may lead to further variations in the values for the thermopower. However, the influence from the binding groups cannot be neglected for short molecules.

V. ACKNOWLEDGEMENTS

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VI. SUPPLEMENTARY INFORMATION

Transmission curves obtained with DFT and DFT + $\Sigma$ for all 60 molecules (including an alternative binding geometry for thiols).

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