

Subproject C3.06

Theory of Transport through Single Molecules

Principal Investigators:

Gerd Schön, Fabian Pauly (KIT Young Investigator Group Leader 2007-2011)

CFN financed scientists:

Michael Häfner (39 months 0,5), Janne Viljas (16 months 0,5), Marius Bürkle (4 months 0,75), Falco Hüser (6 months 0,75)

Further contributing scientists:

**Juan Carlos Cuevas (Helmholtz Young Investigator Group Leader until 12.07),
Matthias Hettler (INT), Wolfgang Wenzel (INT)**

**Institut für Theoretische Festkörperphysik
Karlsruhe Institute of Technology**

**Institut für Nanotechnologie
Karlsruhe Institute of Technology**

Theory of transport through single molecules

Introduction and summary

Advances in the experimental techniques to manipulate atomic-sized objects have made it possible to contact single molecules to metallic electrodes and determine their electronic transport properties. With further progress the vision of molecular electronics, i.e., functional electronic circuits realized by molecular building blocks may turn into reality. At present, however, many basic problems still need to be solved, including, e.g., a higher stability of the contacts and a more complete theoretical understanding of the charge transport.

While the early experiments mostly determined the current-voltage (I-V) characteristics or dc conductance of single-molecule contacts [1], further techniques have been developed recently to obtain a more detailed picture of their physical properties. Thus, signatures in the electric current due to the excitation of molecular vibrations [2] or the local heating by Raman scattering [3] have been measured, as well as the shot noise [C3.6:13] and the thermopower [4, 5].

To develop a theoretical understanding of the experiments we proceeded in a twofold way. On one hand, a tight-binding parameterization of the electronic Hamiltonian was used to obtain on a phenomenological level insight into basic principles. On the other hand, we have developed an *ab-initio* approach to quantum transport based on density functional theory (DFT) as implemented in the quantum chemistry software package TURBOMOLE. The use of DFT allows us to treat, e.g., the charge transfer effects involved in the bonding of different chemical elements. Clearly, they are essential for the accurate description of the electronic structure of metal-molecule-metal contacts. Furthermore, with the help of DFT we can determine, without system-dependent parameters, the equilibrium geometries based on total energies. A recent extension, for which we hope to obtain results soon, includes the extraction of electron-vibration couplings, which will allow us to study how the current-carrying electrons couple to molecular vibrations. In most of the studies Green's function techniques were applied to calculate physical observables such as the electric current.

During the previous funding period we have applied our methods to a number of problems, including:

- Influence of conjugation on transport for biphenyl molecules,
- length-dependent conductance and thermopower of oligophenylene contacts,
- effect of the anchoring groups on transport and junction stability (benzene molecules bonded directly to platinum electrodes, tolane molecules with different anchors, biphenyls with cyano termini)
- photoconductance of single-atom and single-molecule junctions,
- transport through DNA.

These topics are reviewed on the following pages.

1 DFT-based studies of transport through atomic and molecular contacts

1.1 Cluster-based method

In order to study phase-coherent charge transport in nanostructures on an ab-initio level we have developed a DFT-based approach [C3.6:12], which is flexible and can be applied to a large class of different materials. Both single-atom and single-molecule contacts with arbitrary organic and inorganic molecules and various electrode metals can be treated. The material dependent parameters are extracted from finite clusters, as described in the captions of Figs. 1 and 2.

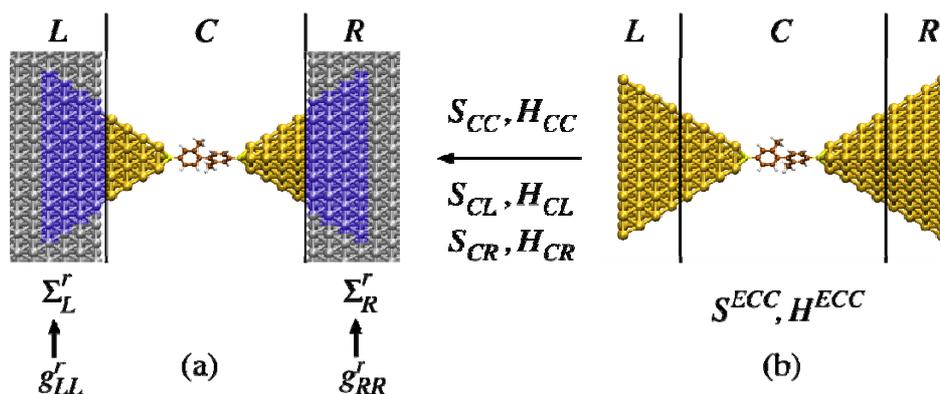


Fig. 1: Elements of the ab-initio description of an atomic-sized contact between bulk electrodes. The system is divided into a C region and two semi-infinite L and R electrodes. Using a similar division as for the contact, properties of the electronic structure of the C region (S_{CC}, H_{CC}) as well as the CL and CR couplings (S_{CL}, H_{CL} and S_{CR}, H_{CR}) are extracted from the extended central cluster (ECC) shown in (b). In order to obtain the self-energies Σ_L^r and Σ_R^r (a), the remaining task is to determine the electrode surface Green's functions g_{LL}^r and g_{RR}^r (see Ref. [C3.6:12]).

A similar procedure, restricted to nearest-neighbor interactions in the electrodes, has been presented earlier [6]. In our recent work we could systematically improve the description of the electrodes by extracting bulk parameters from sufficiently large metal clusters. In this way we avoid problems arising from the use of nonorthogonal basis functions. Our studies crucially rely on the accurate and efficient quantum-chemical treatment of systems consisting of several hundred atoms. This is achieved with the help of the quantum chemistry package TURBOMOLE, which had been developed by R. Ahlrichs. As compared to supercell approaches where periodic boundary conditions are applied in all three dimensions, our method has the advantage to genuinely describe single-atom or single-molecule contacts. Furthermore the inclusion of surface dipoles for the isolated clusters sets the vacuum level as a common reference and allows us to compare the resulting energies to experimental work functions.

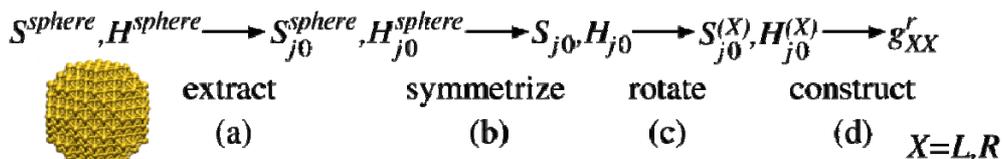


Fig. 2: The electrode Green's functions g_{XX}^r for lead $X = L, R$ are obtained from bulk parameters of large metal clusters. In a first step (a) we extract overlap and hopping elements, $S_{j_0}^{sphere}, H_{j_0}^{sphere}$, from the cluster's central atom to all its neighbors. They are (b) symmetrized by imposing the space-group of the electrode lattice. After (c) a rotation to adapt them to the orientation of the respective electrode, (d) g_{XX}^r is constructed by a decimation procedure (see Ref. [C3.6:12]).

We have applied our DFT-based method to describe electron transport through molecules [C3.6:10-17, C3.6:25-27]. Below, we will present several selected applications with organic molecules. The technique can also serve as the basis of an ab-initio description of metallic atomic contacts [7,8]. Related results are described in the report of subproject B1.7.

1.2 Selected applications

1.2.1 Conformation-dependent conductance of biphenyl-dithiol contacts

In several articles [C3.6:15, C3.6:26] we have analyzed various aspects of charge transport through dithiolated biphenyls contacted to Au electrodes.

In a first, purely theoretical study, we analyzed for a set of three biphenyl molecules temperature-dependent effects for the conductance and its fluctuations [C3.6:15]. Different torsion angles φ between the phenyl rings were realized by using methyl side groups. The temperature dependence was studied by considering both the thermal smearing in the leads and a (classical) thermal average over different molecular conformations. Our results suggest that the variations of the conductance due the latter effect can be reduced by an appropriate design of the molecule.

More recently, we studied together with CFN colleagues the transport for a larger series of biphenyls (see Fig. 3) [C3.6:26]. In order to gradually adjust the torsion angle between the phenyl rings and to avoid the strongly electron-donating or electron-withdrawing substituents used in Ref. [9], alkyl-chains and methyl groups were used.

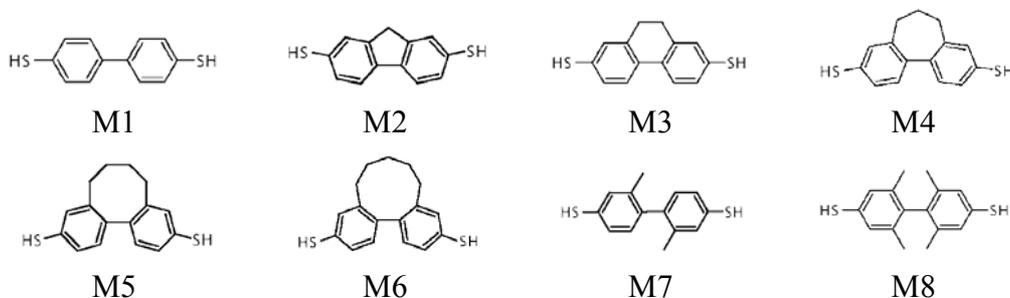


Fig. 3: Structure of the molecules studied in Ref. [C3.6:26]. When they are connected to the gold electrodes, the terminal hydrogen atoms are removed.

We determined in the frame of DFT the conductance of the different molecules with torsion angle φ and compared also to a two-level model (TLM). With the exception of one molecule (M2), the results fitted well to a $\cos^2\varphi$ law (see Fig. 4), in good agreement with the experiments. The TLM describes the pair of hybridizing highest occupied molecular orbital (HOMO) states on the phenyl rings and illustrates that the π - π coupling dominates the transport under “off-resonance” conditions where the HOMO levels are well separated from the Fermi energy.

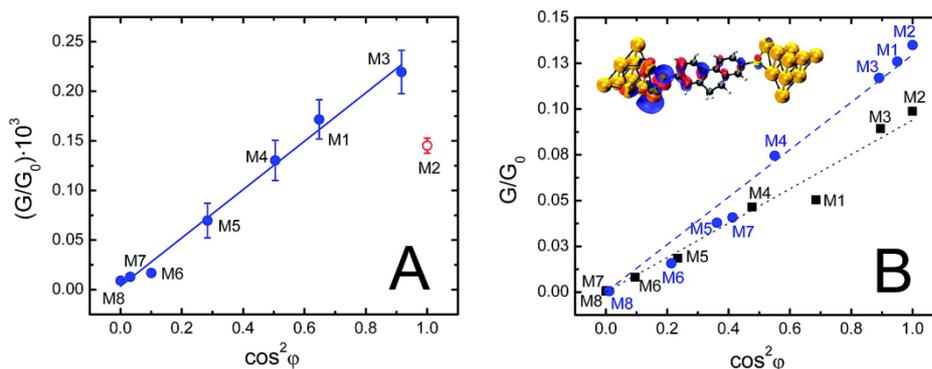


Fig. 4: (A) Experimentally determined conductance of thiol-terminated biphenyl molecules vs. $\cos^2\varphi$, where φ is the torsion angle of the molecules as obtained from X-ray data. The solid line is the linear fit to all molecules studied, M2 excluded. (B) Conductance obtained from DFT-based transport calculations as a function of $\cos^2\varphi$: (squares) atop-atop and (circles) bridge-bridge bonding. Dotted and dashed lines represent linear fits $G = a_{\text{DFT}} \cdot \cos^2\varphi$ with slopes $a_{\text{DFT}} = 0.094G_0$ (atop-atop) and $a_{\text{DFT}} = 0.130G_0$ (bridge-bridge). Variations of φ for the molecules (e.g., M1, M7) arise from different geometric constraints imposed when constructing the contacts. Inset upper left: Dominant transport channel for M3, demonstrating the importance of the π states for conduction. From Ref. [C3.6:26].

1.2.2 Length-dependent conductance and thermopower in single-molecule junctions of dithiolated oligophenylene derivatives

Motivated by recent experiments, we studied theoretically the length dependence of both conductance G and thermopower Q in metal-molecule-metal junctions made up of dithiolated oligophenylenes contacted to gold electrodes [C3.6:16]. The isolated molecules are shown in Fig. 5.

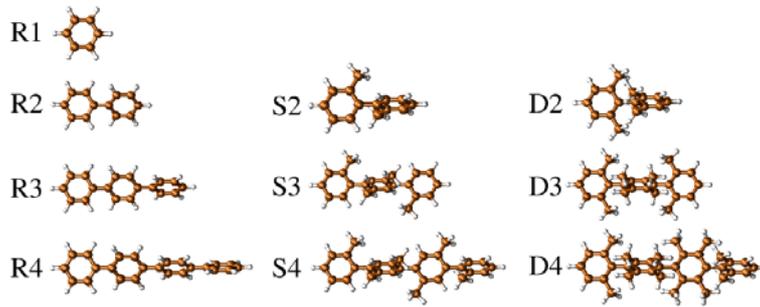


Fig. 5: The oligophenylene molecules studied in Ref. [C3.6:16]. When they are contacted to the gold electrodes, sulfur atoms replace the terminal hydrogen atoms.

The thermopower (or Seebeck coefficient) can provide useful information, not accessible via the conductance. It measures the voltage ΔV induced over a conducting material at vanishing steady-state electric current I , when a small temperature difference ΔT is applied: $Q = -\Delta V/\Delta T|_{I=0}$. In bulk materials the sign of the thermopower is related to the sign of the main charge carriers. If $Q < 0$ ($Q > 0$), charge is carried by electron-like (hole-like) quasiparticles, as in an n -doped (p -doped) semiconductor [10]. Analogously, the thermopower of the molecular junction gives information about the alignment of the energies of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) with respect to the metal's Fermi energy E_F [11]. In the experiment [4], Q was measured for gold electrodes bridged by dithiolated oligophenylene molecules. It was found to be positive, which indicates that E_F lies closer to the HOMO than to the LUMO. Also, it was observed that Q grows roughly linearly with the number N of the phenyl rings in the molecule.

In our analysis we found that while the conductance decays exponentially with increasing molecular length, the thermopower increases linearly. This is consistent with the experiments of Ref. [4] (see Fig. 6), and more recent measurements confirm the linear trend of Q [12]. In addition, we analyzed how the transport properties can be tuned with methyl side groups. We could explain qualitative features of our *ab-initio* results by considering the level shifts due to the side groups' electron-donating character as well as the torsion-angle dependence of both the conductance and thermopower.

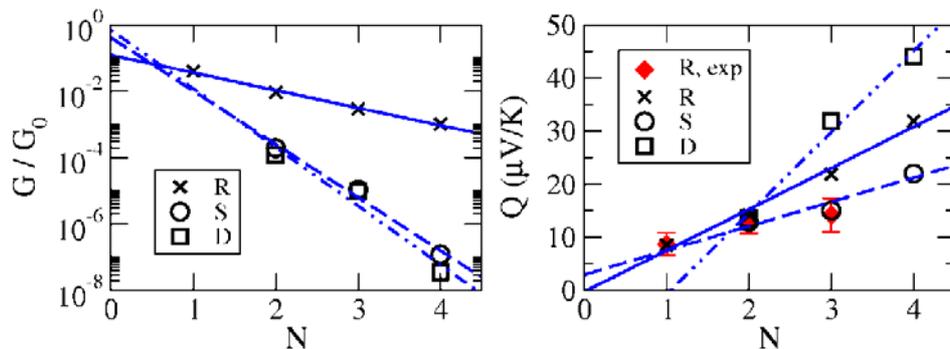


Fig. 6: Conductance G (left panel) and thermopower Q (right panel) as a function of molecular length [C3.6:16]. The straight lines are best fits to the numerical results for R (solid line), S (dashed line), and D (dashed-dotted line) molecules of Fig. 5. The experimental data in the right panel are from Ref. [4].

1.2.3 Highly conducting molecular junctions based on direct binding of benzene to platinum

Connecting a molecule as a bridge between two conducting electrodes is one of the fundamental challenges involved in the study of electron transport through molecular junctions. Difficulties stem from a variety of requirements which are sometimes contradictory: a good molecule-electrode contact should be easy to achieve but chemically insensitive to environmental influences, mechanically stable but flexible enough to allow molecular rearrangement, provide a good electronic coupling between the molecule and the conducting electrodes but still preserve to some degree the individual electronic properties of the molecule. A frequently used approach in fabrication of such molecular junctions utilizes functional side groups attached to the main molecule structure as anchoring “arms” that chemically bind to metallic leads (e.g., thiol, amine, or carboxylic groups). In general, however, the anchoring groups act as resistive spacers between the electrodes and the molecule. This leads to low conductivity and sensitivity to different environmental effects such as neighboring adsorbed species.

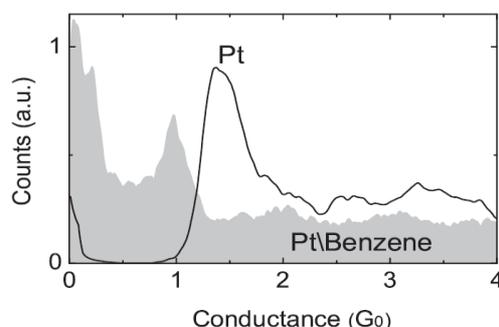


Fig. 7: Conductance histograms (normalized to the area under the curves) for a Pt junction (black), and for Pt after introducing benzene (filled). Each conductance histogram is constructed from more than 3000 conductance traces recorded with a bias of 0.1 V during repeated breaking of the contact. From Ref. [C3.6:13].

In an experiment-theory collaboration between the group of J. M. van Ruitenbeek and us [C3.6:13], we observed that highly conductive molecular junctions were formed by direct binding of benzene molecules between two platinum (Pt) electrodes (see Fig. 7). Measurements of the conductance, isotopic shift in inelastic spectroscopy, and shot noise, when compared with our theory, provided indications for a stable molecular junction, where the benzene molecule is preserved intact and bonded to the Pt leads via carbon atoms. The junction has a conductance comparable to that for metallic atomic junctions (around $0.1-1G_0$), where the conductance and the number of transmission channels are controlled by the molecule’s orientation at different interelectrode distances.

Our work on this problem attracted much attention and was chosen as “Editor’s selection”. It was published with an accompanying “Viewpoint commentary” [13].

1.2.4 Role of anchoring groups for single-molecule conduction

Together with the groups of A. Erbe (FZ Dresden-Rossendorf), E. Scheer (Uni Konstanz), and J. C. Cuevas (UA Madrid), we performed a combined experimental and theoretical study of

the influence of the metal-molecule coupling on the electronic transport through single-molecule junctions [C3.6:25]. Transport experiments through tolane molecules attached to gold electrodes via thiol, nitro, and cyano anchoring groups were carried out with the technique of mechanically controllable break junctions. By fitting the experimental I-V characteristics (see Fig. 8) to a single-level model, we extracted both the position of the molecular orbital closest to the Fermi energy and the strength of the metal-molecule coupling. The values were compared to those extracted from the DFT-based transport calculations. We showed that the anchoring groups determine the junction conductance by controlling not only the strength of the coupling to the metal, but also the position of the relevant molecular energy levels.

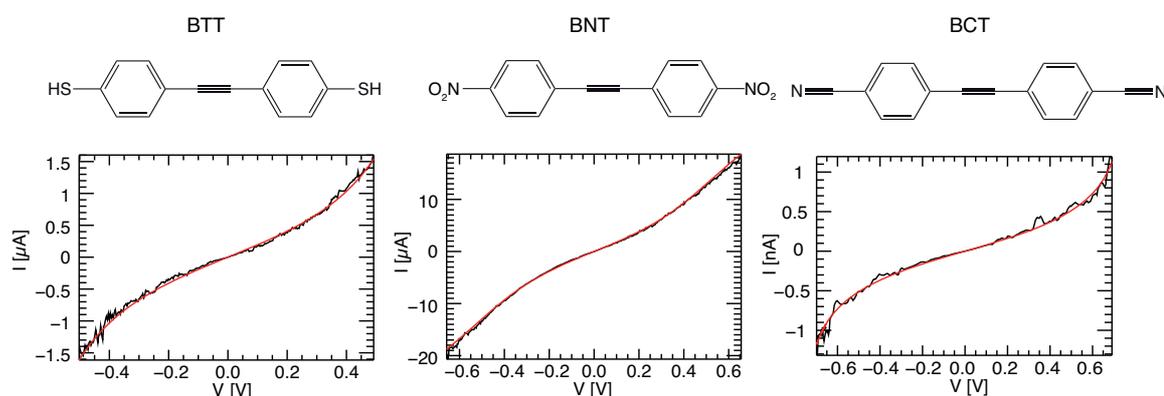


Fig. 8: Top: Molecules investigated: 4,4'-bisthiotolane (BTT), 4,4'-bisnitrotolane (BNT), and 4,4'-biscyanotolane (BCT). Bottom: Typical I-V characteristics measured for junctions with the three molecules under study. The curves were recorded by sweeping the voltage from 0 V to 0.5 V to -0.5 V back to 0 V. For clarity only the sweep from 0.5 V to -0.5 V is shown (black curve). The red curve shows the fit to the single-level model. The parameters used in the fits are: $\Gamma = 43$ meV, $E_0 = 0.45$ eV for BTT, $\Gamma = 70$ meV, $E_0 = 0.27$ eV for BNT and $\Gamma = 0.85$ meV, $E_0 = 0.54$ eV for BCT. From Ref. [C3.6:25].

1.2.5 Single molecule junctions based on nitrile-terminated biphenyls: A new promising anchoring group

In another study together with the experimental groups of T. Wandlowski (Uni Basel) and a CFN chemist, Marcel Mayor, we studied the electric transport through single molecule junctions based on nitrile-terminated biphenyl derivatives [C3.6:27]. Using a scanning-tunneling-microscope-based break-junction technique we showed that the nitrile-terminated compounds give rise to well-defined peaks in the conductance histograms. This is in contrast to our previous studies using thiol anchors, where a selection of conductance-distance curves was found necessary for observing “typical single-molecule conductances” as maxima in conductance histograms [C3.6:26]. Our *ab-initio* calculations reveal that the nitrogen atom of nitrile binds selectively to single Au surface atoms (see Fig. 9), explaining the experimental observation of well-defined contacts. Also, they indicate that the transport takes place through the tail of the LUMO. Furthermore, we find both theoretically and experimentally that the conductance of the molecular junctions is roughly proportional to $\cos^2\varphi$ where φ is the torsion

angle between the two benzene rings of the biphenyl core (see Fig. 9). This behavior should indeed be independent of HOMO- or LUMO-transport, but it is generally expected for off-resonant transport.

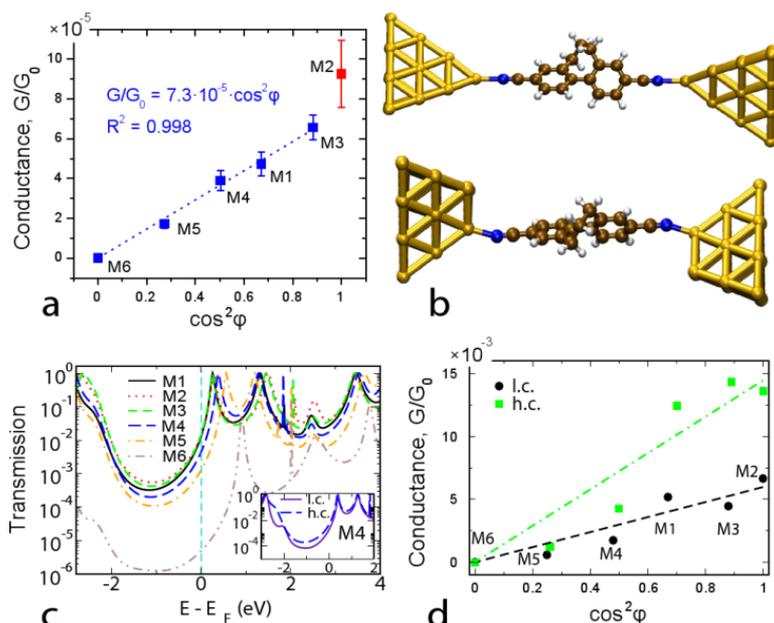


Fig. 9: (a) Measured conductances G ($G_0=2e^2/h$) of six biphenyl dinitriles as a function of $\cos^2 \varphi$. (b) Optimized geometries of molecule M4 contacted at both ends to Au $\langle 111 \rangle$ electrodes in a low-coordinated (l.c., upper panel) and high-coordinated (h.c., lower panel) geometry. (c) Transmission as a function of energy (with respect to the Fermi energy E_F) for all molecules in the h.c. geometry. The inset shows the comparison of the transmission curves of M4 bound in the h.c. and l.c. geometry, respectively. (d) Computed conductances of M1 to M6 as a function of $\cos^2 \varphi$ for both contact geometries. From Ref. [C3.6:27].

2 Description of transport through atomic and molecular contacts: Tight-binding parameterization

2.1 Photoconductance of metallic atomic contacts and single-molecule junctions

The major part of research in the field of molecular electronics has so far concentrated on stationary transport properties, while systems being driven by time-dependent external fields such as laser light have received less attention. Recent experiments on laser-irradiated gold contacts support the idea that photo-assisted processes may play an important role in their transport properties [14,15]. As first steps toward a microscopic description of experiments of this type we addressed the role of electronic structure in photo-assisted transport through atomic-sized and molecular junctions. For this purpose we treated the electromagnetic radiation classically, assuming its effect to be the generation of an ac voltage over the contact [C3.6:9]. We derived an expression for the dc current and computed the linear conductance in one-atom contacts as a function of the ac frequency.

First we applied our formalism to metallic atomic contacts of Al, Pt, and Au [C3.6:9]. Depending on the frequency and the metal, the radiation can either enhance or reduce the conductance. An approximate expression was derived to understand this behavior in terms of the energy dependence of the transmission of the contacts in the absence of radiation.

Next, we analyzed the photo-conductance of organic single-molecule contacts (see Fig. 11) [C3.6:10,C3.6:18]. In agreement with previous predictions, we find that the radiation can lead to a large enhancement of the conductance of such contacts by bringing off-resonant levels into resonance through photo-assisted processes. We showed that the exponential decay of the conductance with the length of the molecule can be replaced by a length-independent value in the presence of radiation.

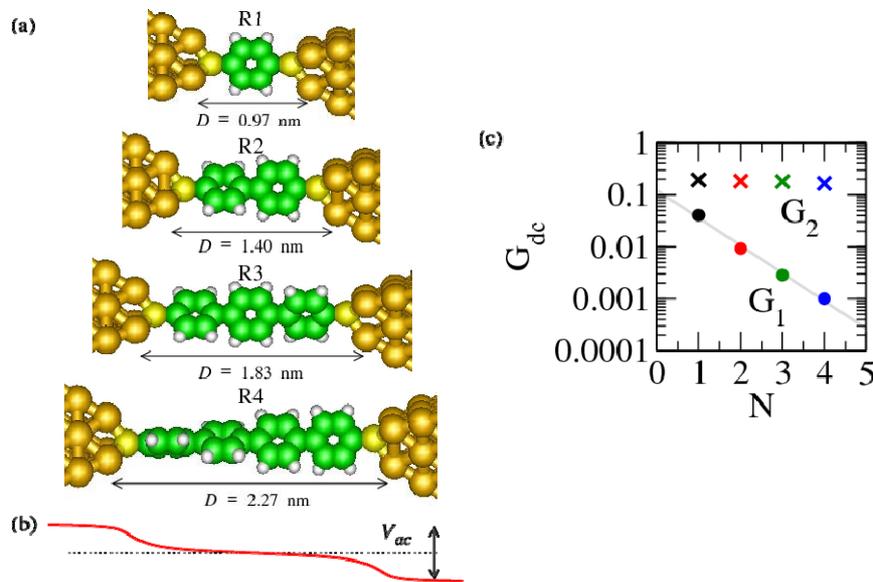


Fig. 11: (a) Four molecular contacts containing oligophenylenes with one to four phenyl rings and coupled to Au $\langle 111 \rangle$ pyramids through sulfur atoms. (b) We assume the induced ac voltage V_{ac} to drop in a double-step manner, as illustrated for contact R4. (c) The dc conductances without (G_1 , dots) and with (G_2 , crosses) radiation with $\hbar\omega=1.5$ eV and $\alpha=eV_{ac}/\hbar\omega=1.8$ for a growing number N of phenyl rings. The results for G_1 fit to an exponential law. From Ref. [C3.6:10].

2.2 Transport through DNA

There has been much interest in the electrical properties of DNA. Indeed, recent studies showed that it is possible to record the current–voltage characteristics of both single-stranded and double-stranded DNA immobilized between metal electrodes in an ambient or aqueous environment. As in the case of organic molecular bridges, there is also great interest in predicting the conductance of DNA over a range of temperatures.

In the course of the project we have developed a novel method to compute the ballistic conductance through DNA with atomic resolution [C3.6:3]. Starting from a given conformation of a molecule and its coupling to the electrodes, we resolve the electronic structure of the molecule in a tight-binding parameterization. The electric conductance as a function of the applied bias voltage is then calculated using a recursive Green’s function technique. In this way we can treat much larger systems than with conventional electronic

structure methods. In a cooperation with experimentalists (R.J. Nichols, Uni Liverpool) we performed a study of temperature effects on the single molecule conductance of double stranded oligodeoxynucleotides with homogeneous canonical base pair sequences (adenine-thymine (AT) and guanine-cytosine (GC)) [C3.6:1]. To explain the experimental results we carried out a series of DNA conductance calculations using a completely atomistic approach. We studied the influence of the deformations arising from acoustic modes on the valence band transmission spectrum of $(dA)_{15}-(dT)_{15}$ and $(dG)_{15}-(dC)_{15}$ and could demonstrate that the DNA acoustic modes gave rise to the observed temperature dependence of the conductivity at ambient temperatures (see Fig. 12). We found that different acoustic modes for the same sequence give very different valence band transmission spectra, which might result in a temperature-dependent conductance. This experimental result is consistent with the simulations for the valence band transmission spectra.

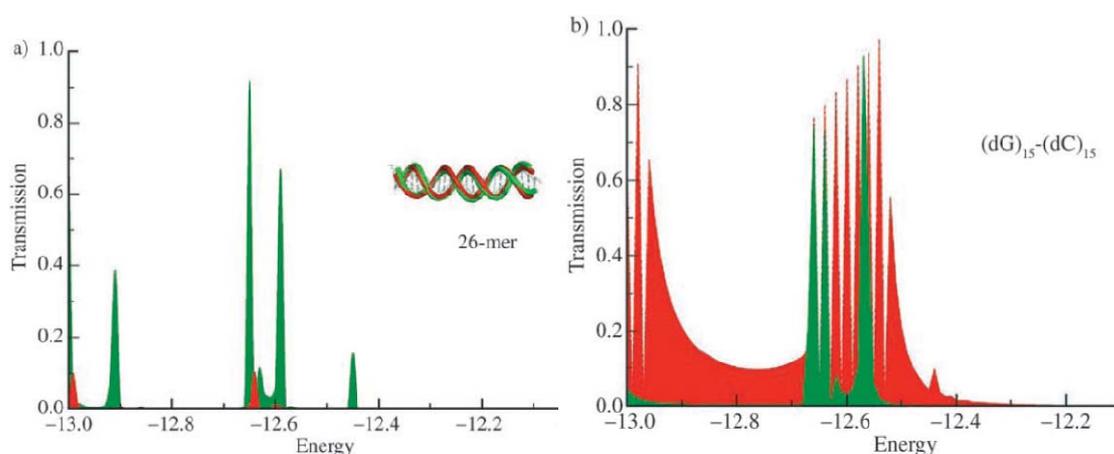


Fig. 12. Comparison of calculated transmission spectra at the upper edge of the valence band for a 26-mer duplex (inset shows the mode of DNA duplex deformation). Red graphs correspond to the transmission spectra of the duplexes in their ideal B-DNA conformation, the green ones depict those in the presence of deformations along DNA acoustic modes. From Ref. [C3.6:1].

We also studied the non-equilibrium transport through short DNA chains with various sequences between voltage-biased leads [C3.6:7,C3.6:8,C3.6:21,C3.6:24]. The strong coupling of the charge carriers to local vibrational modes of the base pairs leads to the formation of polarons, i.e., a combination of a charge carrier with a local deformation, which lowers the system energy (polaron shift or reorganization energy). At room temperature the transport is then dominated by sequential (incoherent) hopping of polarons along the DNA chain. We calculated the rates for these processes, extending what is known as $P(E)$ -theory of single-electron tunneling to the situation with site-specific local oscillators. The applied bias voltage induces a non-equilibrium charge rearrangement along the DNA, which in turn leads to sequence-dependent current thresholds of the 'semi-conducting' current-voltage characteristics. Except for fully symmetric sequences of DNA, this also results in rectifying behaviour. The current is thermally activated with an activation energy that approaches the bulk value (polaron shift) for long homogeneous chains and voltages above the threshold. Our results are consistent with experiments [16].

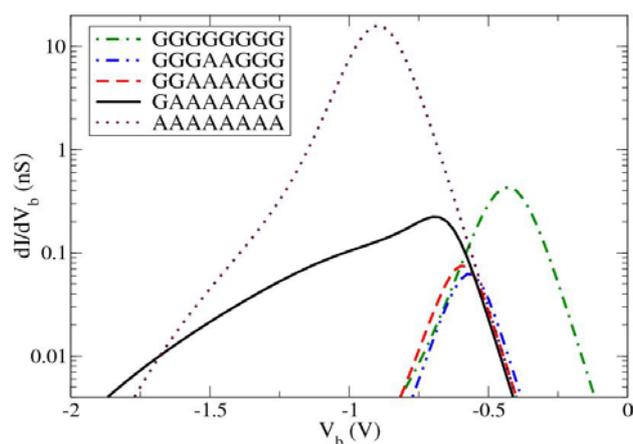


Fig. 13: Differential conductance vs. bias voltage for various DNA sequences. The threshold voltage (peak position) depends on the sequence, a result of the non-equilibrium charge rearrangement [C3.6:21].

2.5 Nanoelectromechanical Switch Operating by Tunneling of an Entire C_{60} Molecule

In collaboration with experimentalists (T. Bjørnholm, Uni Copenhagen) we studied a single-molecule switch made of a C_{60} molecule placed in a nanogap between two silver electrodes [C3.6:19]. The system is found to have two stable configurations with higher and lower values of the conductance. The switching between the two states is a random process triggered by changing of bias voltage or temperature. The statistics of around 100.000 switching events has been collected and analysed. The data are well described by a simple model of tunnelling between two minima of a double well potential. The height of the barrier between the minima is found to vary from 100 to 200 meV depending on the bias voltage, while the oscillation frequency in the potential wells corresponds to the energy of about 3 meV. These parameter values suggest that the switching of the system is associated with the small rotation of the C_{60} molecule as a whole.

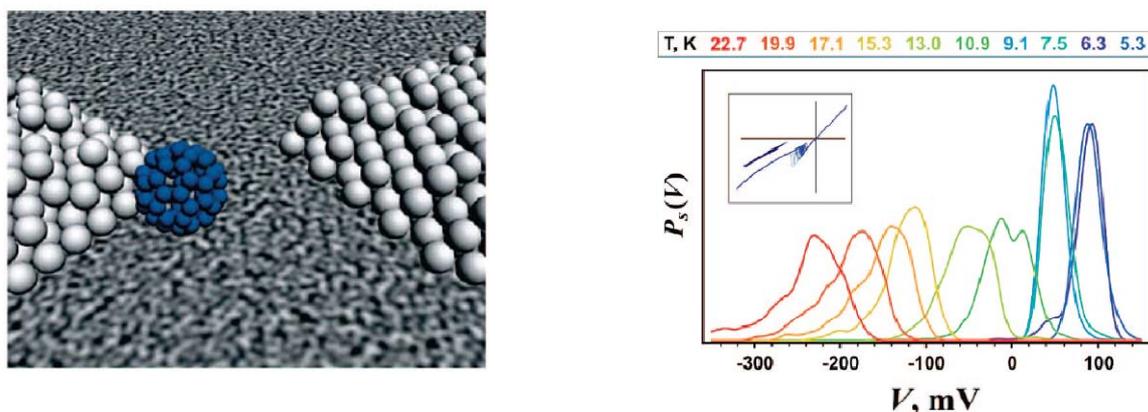


Fig. 14: Electric transport through a fullerene. Left panel: C_{60} molecule between two silver electrodes. Right panel: Switching probability $P_s(V)$ between the two configurations, measured at constant sweeping rate, plotted as a function of the bias voltage, and taken at different temperatures. Inset: A set of the I-V curves, where the arrow indicates the sweeping direction. From Ref. [C3.6:19].

For references labeled as [C3.6:...] see the list of publications of the subproject.

Additional References:

- [1] M. A. Reed *et al.*, *Science* **278**, 252 (1997).
- [2] R. H. M. Smit *et al.*, *Nature* **419**, 906 (2002).
- [3] Z. Ioffe *et al.*, *Nature Nanotechnology* **3**, 727 (2008).
- [4] P. Reddy *et al.*, *Science* **315**, 1568 (2007).
- [5] J. A. Malen *et al.*, *Chem. Phys. Lett.* **491**, 109 (2010).
- [6] P. Damle, A. W. Ghosh, and S. Datta, *Chem. Phys.* **281**, 171 (2002).
- [7] F.-Q. Xie, F. Hüser, F. Pauly, Ch. Obermair, G. Schön, and Th. Schimmel, *Conductance of atomic-scale Pb contacts in an electrochemical environment*, *Phys. Rev. B* **82**, 075417 (2010);
- [8] D. R. Ward, F. Hüser, F. Pauly, J. C. Cuevas, and D. Natelson, *Optical Rectification and Field Enhancement in a Plasmonic Nanogap*, *Nature Nanotech.* **5**, 732 (2010)
- [9] L. Venkataraman *et al.*, *Nature* **442**, 904 (2006).
- [10] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders, New York, 1976).
- [11] M. Paulsson and S. Datta, *Phys. Rev. B* **67**, 241403 (2003).
- [12] J. A. Malen *et al.*, *Nano Lett.* **9**, 1164 (2009).
- [13] L. Venkataraman, *Physics* **1** (2008).
- [14] D. C. Guhr *et al.*, *Phys. Rev. Lett.* **99**, 086801 (2007).
- [15] N. Ittah *et al.*, *Nano Lett.* **9**, 1615 (2009).
- [16] K. H. Yoo *et al.*, *Phys. Rev. Lett.* **87**, 198102 (2001).