CECAM Workshop Scientific Report

Workshop: Molecular electronics: Quo vadis

Organizers: Thomas Frauenheim, University of Bremen (Germany)
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Location: University of Bremen, Germany,
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I. Summary

The workshop "Molecular electronics: Quo vadis" was held at the University of Bremen, Germany from March 4th to 8th 2013. In total, 99 participants from China, Denmark, France, Germany, Italy, Israel, The Netherlands, Spain, Sweden, South Korea, USA, UK and Switzerland attended the workshop.

The programme consisted of 41 invited lectures, one poster session presenting 49 posters and many events (reception / conference dinner) to allow for informal exchange and discussion. The lectures were scheduled to last 40 and 30 min, including 5 min discussion time. In addition to this extended time for discussion, the chairpersons were instructed to introduce the subject of the session and to actively participate in the discussion. This "Gordon-conference-style" was essential to guarantee a vivid discussion. The organizers ensured that well-established scientists acted as invited speakers and chairpersons. The workshop included 24 invited talks of the Principal Investigators of the DFG-SPP 1243 (Priority Program), 30 minutes each) giving reports of their research progress over the last years. Since the SPP 1243 is closing the funding in June 2013, this CECAM Workshop simultaneously was the Final Report Meeting of the Priority Program. In addition 18 leading international scientists presented their most recent results and view on the molecular electronic subject in key-note talks. As special guest Dr. Stefan Hildebrandt, the Editor in Chief of physica status solidi b attended the workshop. He invited all speakers to contribute to a high-level topical special issue of pss(b) that will cover the Priority Program 1243 `Quantum transport on the molecular scale´ as well as results presented at the CECAM workshop on molecular electronics in Bremen. The special issue will comprise the final report of results achieved within projects during the 6-year priority program lifetime, which is drawing to an end in mid-2013.

Concerning the poster session, we accepted 49 posters to allow for an intense exchange of ideas at each single poster. Here, we encouraged in particular the young scientists to ask questions. The participation of Postdocs and PhD students was supported by partly covering local accommodation costs.

Due to the compact organization and accommodation in one hotel only all participants had to stay together for the whole time of the conference, which additionally enforced the scientific discussion which was mandatory since scientists from various separated fields, i.e. advanced quantum chemistry, quantum Monte-Carlo, many-body physics, DFT and beyond, Scanning Probe and Break Junction Techniques, etc. were attending the meeting to merge ideas and formulate a common goal for future directions and collaborations of theory groups with experimental groups.

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II. Scientific content, main outcome of key presentations, selected discussions

Various sessions have been related to the topics (a) Single molecule transport, sample growth and even applications, (b) Charge transport and environment coupling, (c) Quantitative accurate transport theory, (d) Phonon transport and thermoelectric coupling, (e) devices, (f) Spin transport and (g) Time-dependent processes. These topics are commonly related to each other. So, extensive attentions and discussions have been stimulated between researchers from different fields.

Molecular electronics – the use of single molecules as functional entities in electronic devices – about 10 years ago heralded as a replacement for the conventional CMOS approach which faces physical limits in further miniaturization. Even though if consumer products based on this technology will not emerge in the near future, single molecule devices have shown to offer a unique test bed to explore fundamental aspects of both physics and chemistry today.

As one of the possible routes for the further development of the field, light-matter interaction has certainly an important role to play. In the session on time dependent processes, Abraham Nitzan provided an excellent overview over the multiple facets of this topic. As he pointed out, light might be used to characterize the geometry of contacted molecules and their vibrational excitation. The strong field enhancement close to metallic tips allows one to record Raman signals that provide direct information on the temperature. Besides this *junction spectroscopy*, light might also act as a handle to enhance or suppress the conduction, providing additional control over the transport properties of a molecular device. Other speakers highlighted the importance of dynamical simulations in studies of transport through biological systems in solution. Here the static Landauer picture breaks down and one has to resort to more advanced techniques. Such beyond-Landauer approaches were discussed in a couple of talks, with emphasis on different aspects, be it the improved description of electron-electron interactions or the practical implementation for real world devices. The theoretical consideration were nicely augmented by Jose Ignacio Pascual, who presented measurements on light emission from STM junctions and discussed the interplay of vibrational and plasmonic excitations.

Electron-electron interactions play a crucial role not only in strongly correlated systems, but are mandatory to describe correctly dynamical screening and image charge effects in metal-organic junctions. As discussed by Kristian Thygesen and Ferdinand Evers, including such effects is mandatory to obtain quantitative agreement between theory and experiment even to predict the zero bias conductance of simple molecular junctions. A many body GW approximation can provide the correct description and, remarkably, the technique is very robust respect to the initial basis set, so that the quasi-particle solution can be calculated on the top of a common DFT-GGA. On the other hand, Kieron Burke pointed out that the need for many body corrections comes from a poor approximation of commonly used DFT functionals. He showed that in line of principle it is possible to derive the exact Kohn Sham potential for some test system, therefore reproducing complex many-body phenomena such as Kondo effects by means of exact DFT. Many body interactions are commonly described in a model Hamiltonian picture, therefore the route to

achieve parameter-free methods go through a coarse-grained representation where typically a few relevant molecular orbitals are retained. Similarly, time-dependent treatment must also rely on coarse-grained schemes to overcome the high computational cost. For example, Marcus Elstner showed applications of similar schemes in non-adiabatic time dependent propagation; Dmitry Ryndyk showed techniques to derive the many body models on localized molecular orbitals obtained from ab-initio DFT. Some time dependent schemes capable to scale up hundreds of basis function have been shown by Guanhua Chen, demonstrating that a full-basis treatment is in line of principle accessible in the near future.

Several experimental contributions focused on molecule transport studies in solution at room as well as at variable temperatures employing either scanning tunneling microscopy (STM)/spectroscopy (STS) or a mechanically controlled break junction approach. Case studies with aliphatic and aromatic (oligo(phenylene ethynylenes) (OPE), oligoynes) molecular wires revealed clear evidence for **single** molecular measurements and highly reliable correlations between molecular structure and transport properties, often based on a statistical analysis of a large number of individual measurements and in combination with DFT-based transport calculations. Examples are the dependence of molecular conductance on the torsion angle for a family of biphenyl derivatives, the transition from tunneling to hoping as demonstrated for OPE-derivatives with 1 nm up 9 nm lengths, as well as the electronic and structure coupling of various anchoring groups to external leads. The latter was also evaluated in simultaneous measurements of conductance and force employing current-probe atomic force microscopy (CP-AFM). The simultaneous access of electrical and mechanical properties provides new structure insight into the formation and breaking of (single) molecular junctions and environmental modulated effects, such as dipolar binding and pi-stacking between molecules.

The concept of electrolyte gating was demonstrated as a powerful approach to manipulated charge transport characteristics at the nanoscale. Examples discussed involved orientation-, conformation and redox-gating with single molecules and clusters, which lead to functional and electrically addressable building blocks. The latter was, for instance, demonstrated in an anthraquinone-based redox-switch, which could be tuned in and out of a quantum interference state leading to the modulation of the **single junction conductance** by up to **three orders of magnitude**.

Most interesting discussions

A reoccurring topic in the discussions was the question to which extent density functional theory is capable of describing the transport through strongly correlated systems, i.e. whether Coulomb blockade and Kondo physics would be accessible if the exact exchange-correlation functional was available. Several speakers pointed out that in the limit of zero temperature and zero bias this is indeed possible. Beyond this, additional information from time dependent DFT needs to be incorporated in the theory.

Similarly, the importance of time-dependent description has been underlined in several contests. The Landauer picture, useful for the description of systems in which charge transport occurs via adiabatic tunneling, can break down in small linear chains. Several speakers showed experimental setups, or even devices, beyond the single molecule concept, where oligomers and alkane chains or DNA strands up to several nanometers are connected to leads and exhibit transport regime beyond

coherent transport. This possibly suggests an increasing interest in intermediate transport regimes.

All contributions on transport experiments in solution showed the interdisciplinary character of this research, the need of close collaborations between experimentalists (physists, chemists, engineers) und theoreticians at both the conceptual level as well as at the experimental level, to explore new phenomena and to design tailored approaches. Transport experiments in solution might pave the way towards information processing in the chemical and biological world. However, they still require a higher level of structure and stability control. These approaches might involve the development of covalent contact concepts, such as carbon-metal and/or carbon-carbon bond formation, the exploitation of new developments in “controlled” self-assembly, and to combine transport investigations with spectroscopic measurements with a particular focus on new developments in nanoplasmonics. High demand exists also towards theory to provide reliable representations of the solvent (and ionic) environment as well as of the electric field distribution in confined. These joined efforts between experiment and theory may pave the way towards controlled reactivity studies in nanoscale junctions exploiting unique transport phenomena.

III. Assessment of the results and impact on future direction of the field

The foremost objective of the proposed workshop was to bring together leading and active researchers who work on Molecular electronics in both experiment and theory and to discuss about possible solutions to improve the quality and tailor the materials based upon computational approaches from physics and chemistry. Aiming for a focused meeting with about 100 participants we have brought together world leading experts to discuss recent advances in experimental techniques and current theoretical methodologies, to disseminate and discuss the latest developments in the field of emerging electronics, and to identify the challenges and opportunities in the field as well as future directions for research and development of state-of-the-art simulation tools for next generation electronics. Moreover, we have emphasized to strengthen the links between experimental and computational groups in this fast-developing and cross-disciplinary moving field and to interconnect current model-type and first-principles descriptions.

The composition of the scientific program with 13 experimental and 28 theoretical invited talks reflects this ambition. Several key lectures on contemporary measurements have presented most recent results in order to uncover remaining and new challenges for the theory of molecular conduction.

The workshop became a forum to discuss about possible solutions of tailoring molecular junctions and correlating experiment and theory on a highly predictive level. We have been able to achieve the following key objective:

1. The workshop stimulated the interconnection of phenomenological model-type and computational first-principles approaches. Phenomenological theorists and computational materials scientists will foster mutual interactions not only to supply practical parameter inputs for theoretical models, but also to realize interesting proposals using explicit materials.

Into the Future The advent of molecular electronics followed directly from the development of new techniques–the non-equilibrium Green’s function (NEGF) technique for computation, and the scanning probe technique for measurement. New techniques will help, but will not be necessary for molecular electronics to progress

away from a fascination with the very simple question (that has dominated the last four decades) of how current travels through molecular junctions. Instead, the future will hold more complex and more interesting issues, issues that utilize the particular behavior of molecules when subjected both to electromagnetic forces and to mechanical forces (as in the mechanical break junction). Prognostication is difficult, but six particular issues we believe will certainly be a part of the future of molecular electronics, two of which are outlined here:

Broken symmetry This is a continuation of the work described above - when the symmetry of space is broken (for example by polarization of photons, or by chirality of molecular shapes, or by odd spins in the general area of spintronics), the transport rules that normally follow from NEGF do not necessarily work any longer. This could have major implications for fundamental understanding (with ferromagnetic electrodes and a non-zero spin molecule, exactly how do the majority and minority carriers proceed, and how does that change with field strength, geometry temperature)? Moreover, broken symmetry could result in substantial changes in transport, that are not deducible from simple arguments concerning barriers. The Pauli exclusion principle is in play here, and therefore one could imagine using broken symmetry to completely block the transport of the minority or majority carriers. Dealing with these problems of spin behavior, especially if they are coupled with polarization and/or chirality, will require extensive expansion of the simple methodologies now used for calculation of transport. Some preliminary work in this area has already been published, but both experiment and modeling will almost certainly extend their investigation of broken symmetry situations.

New variables The independent variables in simple transport are the structure of the molecule and its environment, and the nature of the external potential or potentials applied to the molecule. The beginnings of thermoelectric behavior in molecular junctions have already appeared Similarly, spintronics measures the transport of spins at the same time as the transport of charge, while memristors correspond to two-terminal non-volatile memory devices based on resistance switching - there has been extensive work trying to develop this since it was first proposed by Chua; the HP laboratories have developed what may be a semiconductor-based memristor, and Chen’s group in Singapore has actually demonstrated memristor behavior in a molecular junction using the biomolecule ferritin as the functional component. Other new variables would certainly include mixed photonic excitation (which could provide time-dependent pulses to drive transport in different directions), magnetic fields across the device, ultrasonic excitation and non-equilibrium chemical reactions resulting in oscillatory behavior. While not all of these will be examined, these new variables will once again require further understanding, appropriate experiments, and appropriate extension of current theoretical models.

March 10th 2013

The Organizers

Program of the International CECAM-Workshop

"Molecular electronics: Quo vadis?"

Bremen Center for Computational Materials Science – BCCMS

University of Bremen, March 4th – 8th 2013

Conference site: House of Science, Bremen Downtown

Tuesday, March 5th 2013 (House of Science Bremen Downtown)

07:30	**–**	**08:30**	**Registration**
08:30	**–**	**08:40**	**Opening and welcome, Thomas Frauenheim**
Session:			**Single molecule transport**
			Chair: Thomas Frauenheim
08:40	**–**	**09:20**	Mark Ratner, Northwestern University, Evanston (US) *Phases, coherence, and charge transfer/transport in molecular systems*
09:20	**–**	**10:00**	Sense Jan van der Molen, Leiden University (The Netherlands) *Manipulating transport through molecular junctions*
10:00	**–**	**10:30**	Dmitry Ryndyk, University of Regensburg (Germany) *Many-body localized molecular orbital approach to molecular transport*
10:30	**–**	**11:00**	**Coffee Break**
11:00	**–**	**11:30**	Silvia Karthaeuser, Research Center Juelich (Germany) *Electronic mapping of molecular orbitals at the metal-molecule interface*
11:30	**–**	**12:10**	Michel Calame, University of Basel (Switzerland) *Characterizing the electronic and mechanical structure of molecular junctions*
12:10	**–**	**12:40**	Thomas Wandlowski, University of Bern (Switzerland) *Charge transport with single molecules and cluster: An electrochemical approach and beyond*
12:40	**–**	**14:20**	**Lunch Break and Coffee**
Session:			**Charge transport and environment coupling**
			Chair: César A. Rodríguez-Rosario
14:20	**–**	**14:50**	Goeran Wendin, Chalmers University, Gothenburg (Sweden) *Toward bioinspired information processing with molecular electronics*
14:50	**–**	**15:20**	Marcus Elstner, Karlsruhe Institute of Technology (Germany) *A coarse grained QM/MM approach for the description of charge transfer in complex systems*
15:20	**–**	**15:50**	Artur Erbe, Helmholtz Center, Rossendorf-Dresden (Germany) *Conductance measurements of short DNA fragments in mechanically controllable break junctions*
15:50	**–**	**16:20**	Vincent Meunier, Rensselaer Polytechnic Institute, Troy (US) *Surface-assisted nanostructure assemblies: Intrinsic transport properties and applications*
19:00	**–**	**21:30**	**Welcome Reception (Bremen Town Hall)**

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Wednesday, March 6th 2013 (House of Science Bremen Downtown)

Session:			**Accurate transport theory (I)**
			Chair: Alessandro Pecchia
08:30	–	**09:10**	Kristian Thygesen, Technical University of Denmark, Lingby (DK) *Quantitatively accurate GW transport calculations for molecular junctions*
09:10	**–**	**09:50**	Kieron Burke, University of California, Irvine (US) *Density functional theory, strong correlation and molecular electronics*
09:50	**–**	**10:20**	Ferdinand Evers, Karlsruhe Institute of Technology (Germany) *Fundamental aspects of density functional transport theories and the GW-approach*
10:20	**–**	**10:50**	**Coffee Break**
Session:			**Accurate transport theory (II)**
			Chair: Gemma Solomon
10:50	**–**	**11:30**	Jeffrey Neaton, Lawrence Berkeley National Laboratory (US) *Quantitative first-principles approaches to charge transport in molecular junctions*
11:30	**–**	**12:00**	Silvia Kusminskiy, Free University Berlin (Germany) *Scattering theory of current-induced forces*
12:00	**–**	**12:30**	Michael Rohlfing, University of Osnabrueck (Germany) *Molecular electronic spectrum on a metal substrate: Quasiparticle energies and Kondo resonance*
12:30	**–**	**13:10**	Avik Ghosh, University of Virginia, Charlottesville (US) *Electronics with molecules - lessons learned*
13:10	**–**	**15:00**	**Lunch Break and Coffee**
Session:			**Devices**
			Chair: Gabriele Penazzi
15:00	**–**	**15:40**	Richard Berndt, University of Kiel (Germany) *Plasmons, forces and currents in atomic and molecular contacts*
15:40	**–**	**16:20**	Takhee Lee, Gwangju Institute of Science and Technology (Korea) *Orbital-gated molecular transistors and organic memory devices*
16:20	**–**	**17:00**	Herre van der Zant, Delft University of Technology (The Netherlands) *Three-terminal molecular transport*
17:00	**–**	**17:30**	Klaus Kern, Max Planck Institute Stuttgart (Germany) *Quantum point contact microscopy and spectroscopy*
19:00	**–**	**22:30**	**Conference Dinner (Juergenshof)**

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Thursday, March 7th 2013 (House of Science Bremen Downtown)

Session:			**Phonon transport and thermoelectric coupling**
			Chair: Anders Niklasson
08:30	**–**	**09:00**	Wolfgang Haeusler, University of Augsburg (Germany) *Quantum transport in graphene with time dependent barriers*
09:00	**–**	**09:30**	Rafael Gutierrez, Dresden University of Technology (Germany) *Molecular electronics : Beyond charge transport*
09:30	**–**	**10:00**	Michael Thoss, University of Erlangen (Germany) *Quantum interference, vibrationally induced decoherence and time-dependent phenomena in molecular junctions*
10:00	**–**	**10:30**	Elke Scheer, University of Konstanz (Germany) *Transport properties of optically driven molecular switches*
10:30	**–**	**11:00**	**Coffee Break**
11:00	**–**	**11:40**	Mads Brandbyge, Technical University of Denmark, Lyngby *Electron-phonon coupling and molecular dynamics in the presence of current*
11:40	**–**	**12:10**	Heiko Weber, University of Erlangen (Germany) *Vibrational, magnetic degrees of freedom in single-molecule junctions*
12:10	**–**	**12:40**	Andrea Donarini, University of Erlangen (Germany) *Theory of STM junctions for pi-conjugated molecules on thin insulating films*
12:40	**–**	**13:10**	Fabian Pauly, Karlsruhe Institute of Technology (Germany) *From ab-initio inelastic transport theory to thermoelectric properties and heating in molecular junctions*
13:10	**–**	**14:40**	**Lunch Break and Coffee**
Session:			**Spin transport**
			Chair: Milena Grifoni
14:40	**–**	**15:10**	Wulf Wulfhekel, Karlsruhe Institute of Technology (Germany) *Spin transport through single molecules*
15:10	**–**	**15:40**	Carmen Herrmann, University of Hamburg (Germany) *Molecular spintronics from a theoretical point of view*
15:40	**–**	**16:10**	Marten Wegewijs, RWTH Aachen University (Germany) *Spin-multipoletronics*
16:10	**–**	**16:40**	Michael Thorwart, University of Hamburg (Germany) *Iterative real-time path integral simulations of nonequilibrium quantum transport*
16:40	**–**	**17:10**	Stefan Tautz, Research Center Juelich (Germany) *Metal-molecule contacts: From adsorption to charge transport*
18:00	**–**	**21:00**	**Poster Session and Catering Buffet**

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Friday, March 8th 2013 (House of Science Bremen Downtown)

Session:			**Time dependent processes**
			Chair: Thomas Niehaus
08:30	**–**	**09:10**	Abraham Nitzan, Tel Aviv University (Israel) *Light in molecular conduction junctions*
09:10	**–**	**10:50**	Eberhard K. U. Gross, Max Planck Institute Halle (Germany) *What's the correct classical force on the nuclei*
09:50	**–**	**10:20**	Ulrich Kleinekathoefer, Jacobs University Bremen (Germany) *Treatment of time-dependent effects in currents through molecular junctions*
10:20	**–**	**10:50**	Jose Ignacio Pascual, NanoGUNE Center, San Sebastian (Spain) *Sensing elementary processes in a molecular junction through force and light spectroscopy*
10:50	**–**	**11:20**	**Coffee Break**
11:20	**–**	**12:00**	Guanhua Chen, University of Hongkong (Hongkong) *Time-dependent quantum transport through metallic wires*
12:00	**–**	**12:40**	Gianluca Stefanucci, University Tor Vergata Rome (Italy) *Correlation effects in time-dependent quantum transport*
12:40	**–**	**13:20**	Stefan Kurth, Nano-Bio Spectroscopy Group, Ikerbasque, San Sebastian (Spain) *The derivative discontinuity in transport*
13:20	**–**	**13:30**	**Closing words**
13:30			**Departure**