DIPC-PAMS theory workshop

Towards reality in modelling of molecular electronics

Donostia-San Sebastián, Spain

June 13-17, 2016



Institutional support and funding



Organizing committee

Daniel Sanchez-Portal, UPV/EHU (chair) Adam Foster, Aalto Univ. Pedro Brandimarte, UPV/EHU Mads Engelund, UPV/EHU Thomas Frederiksen, DIPC Aran Garcia Lekue, DIPC Karmela Alonso Arreche, DIPC (secretary)

Preface

As standard silicon technologies approach their fundamental limits, the exploration of molecular electronics, and other related bottom-up technologies, as viable alternatives is attracting an increasing amount of attention worldwide. Molecular electronics opens a wealth of opportunities related to the use of building blocks with built-in functionalities defined with atomic-scale precision by chemical means. However, it is also creates many difficult challenges related, for example, to the optimization of the device architectures and the control of interfaces between the device and electrodes and gates.

Theory also faces important challenges to understand and simulate the properties of these new devices. Some of these challenges are fundamental, and related to the complex interplay between electron-electron corr elations, electron-phonon interactions and interference in open quantum systems, pointing to the limitations of the current theoretical frameworks to correctly describe those phenomena. The complex and largely un known (and difficult to control) structure of molecular junctions, and the links of the molecular blocks to the electrodes, also poses a fundamental problem for reliably predicting their properties. New theories and methodologies are being developed to overcome some of these limitations with the ultimate goal of optimizing the design and predicting the properties of molecular electronic devices.

In this workshop we will bring together researchers actively working in different aspects of transport properties of atomic and molecular scale devices to advance towards this common goal. The focus will be on the ory with connections to current experimental activity.

The workshop aims to cover the following topics:

- Large-scale calculations of quantum transport
- Architectures: towards molecular-scale devices
- Inelastic transport: vibrations and magnetic excitations
- Multi-scale modeling of molecular electronics
- Coupling of transport to light
- Time dependences in molecular-scale transport
- Effect of electron-electron interactions and correlations
- Prediction of complex structures and growth

General program structure

Approx. times	Monday June 13	Tuesday June 14	Wednesday June 15	Thursday June 16	Friday June 17
08:00-09:00	Registration				
09:00-11:00	Session	Session	Session	Session	Session
11:00-13:00	Session	Session	Session	Session	Session
13:00-15:30	Lunch Break	Lunch Break	Lunch Break	Lunch Break	Closing
15:00-17:00	Session	Session		Session	
17:00-19:00	Session	Posters		Session	
21:00-23:30				Dinner	

Monday June 13

08:00-09:00	Registration	
	Chair: Massimiliano Di Ventra	
09:00-09:35	Ferrer	
09:35-10:00	Fediai	
10:00-10:25	Palacios	
10:25-11:00	Coffee break	
	Chair: Uri Peskin	
11:00-11:35	Stokbro	
11:35-12:10	Pecchia	
12:10-12:35	Novotny	
12:35-13:00	Dridi	
13:00-15:30	Lunch break	
	Chair: Vincent Meunier	
15:30-16:05	Papior	
16:05-16:30	Brandimarte	
16:30-17:00	Coffee break	
	Chair: Dvira Segal	
17:00-17:35	Di Ventra	
17:35-18:10	Lambert	
18:10-18:35	Nozaki	

Tuesday June 14

	Chair: Fernando Delgado
09:00-09:35	Pauly
09:35-10:00	Baugh
10:00-10:25	Garcia-Lekue
10:25-11:00	Coffee break
	Chair: Antti-Pekka Jauho
11:00-11:35	Peskin
11:35-12:10	Wang
12:10-12:35	Alberga
12:35-13:00	Costuas
13:00-15:30	Lunch break
	Chair: Stefan Roche
15:30-16:05	Thoss
16:05-16:30	Cucinotta
16:30-18:30	Poster session (soft drinks and coffee)

Wednesday June 15

	Chair: Colin J. Lambert	
09:00-09:35	Roche	
09:35-10:00	Trioni	
10:00-10:25	Del-Castillo	
10:25-11:00	Coffee break	
	Chair: Alessandro Pecchia	
11:00-11:35	Segal	
11:35-12:10	Nikolic	
12:10-12:35	Avriller	
12:35-13:00	Popescu	
13:00-	Free afternoon	

Thursday June 16

	Chair: Rafael Gutierrez
09:00-09:35	Kurth
09:35-10:00	Kelly
10:00-10:25	Krasovskii
10:25-11:00	Coffee break
	Chair: Andrea Donarini
11:00-11:35	Jauho
11:35-12:10	Meunier
12:10-12:35	Garcia-Mota
12:35-13:00	Foti
13:00-15:30	Lunch break
	Chair: Alexandre Reily Rocha
15:30-16:05	Gutierrez
16:05-16:30	Faizy
16:30-17:00	Coffee break
	Chair: Stefan Kurth
17:00-17:35	Rocha
17:35-18:10	Kim
18:10-18:35	Soler
21:00-23:30	Conference dinner

Friday June 17

	Chair: Fabian Pauly
09:30-10:05	Bezanilla
10:05-10:30	Achilli
10:30-11:00	Coffee break
	Chair: Jian-Sheng Wang
11:00-11:35	Delgado
11:35-12:10	Donarini
12:10-12:35	Minamitani
12:35-13:00	Droghetti
13:00-13:10	Closing remarks

Monday June 13

INVITED TALK GOLLUM: an efficient tool for ab-initio molecular electronics with non-trivial examples

Jaime Ferrer^{1,2}

¹Faculta de Ciencias, Univerdad de Oviedo, 33007 Oviedo, Spain ²Research Centre on Nanomaterials and Nanotechnology - CINN

I will present in the first part of this talk the transport code GOLLUM, describing some of its non-trivial functionalities with specific examples. The second part of the talk will be used to describe simulations of the self-assembly of iso-cyano functionalized molecules in the presence of gold electrodes.

CONTRIBUTED TALK New combination of DFT and Green function formalism pushes the limits of extended contacts simulations

<u>A. Fediai^{1,2}, D. Ryndyk^{1,2}, and G. Cuniberti^{1,2,3}</u>

¹Institute for Materials Science and Max Bergmann Center of Biomaterials, TU Dresden, Germany ²Center for Advancing Electronics Dresden, TU Dresden, Germany ³Dresden Center for Computational Materials Science, TU Dresden, 01062 Dresden, Germany

The so-called extended contacts between metallic electrodes and materials with the reduced dimensionality are practically and theoretically important systems. Common examples are side-contacts between the carbon nanotube and metallic electrodes in carbon nanotube field-effect transistors (CNTFETs), and planar contacts between the graphene and metallic electrodes in graphene field-effect transistors (GFETs). A very active field of research are novel 2D materials that can be used as a channel of field-effect transistors (metal dichalcogenides, black phosphorus, etc.), and they need a proper theoretical treatment. What is common for all mentioned contacts is that the electric current can enter the corresponding 2D material or the tube gradually at a distance of up to 100 nm, which has been proven experimentally for CNTFETs and GFETs [1, 2].

Such a distributed current injection in extended contacts differs strongly from that occurring in the common set-ups considering in molecular electronics, which imply that the central part of the device has a local contact to the leads. If we would treat the device with extended contacts within the conventional combination of the DFT and NEGF formalism, we would need to simulate explicitly a 100 nm long system, which is numerically prohibitively expensive.

However, we have shown how to overcome this seemingly unresolvable issue in [3], and have applied this approach in order to predict the scaling of the contact resistance in the CNTFETS [4]. Here we show an application of the approach [3] to graphene-metal contact in GFETs. Figure 1 (a, b) shows geometry of the simulated system, which is a graphene sheet of top of two TiN electrodes. Figure 1(c) shows the scaling of the contact resistivity for three different metals (Pd, Ni, Ti) and one alloy (TiN) calculated from the first principles.



Figure 1: Top (a) and front (b) view of the GFET based on extended graphene – TiN contact. Simulated dependence of the contact resistivity of the GFET as a function of contact length for three metal and one alloy (c).

[1] A. Franklin et al., ACS Nano 8 (7), 7333 (2014).

[2] A. Franklin et al., IEEE Electron Dev. Lett. 32 (8) (2011).

[3] A. Fediai et al., Phys. Rev. B. 91, 165404 (2015).

[4] A. Fediai et al., (accepted manuscript) Nanoscale (2016).

CONTRIBUTED TALK A fully first-principles molecular orbital approach to the Kondo effect in organic molecules

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We present a generic parameter-free approach to the Kondo problem, which is particularly suitable for carbonbased molecules or organic radicals in contact to metal electrodes. In these molecules the screened spin may originate in an unpaired delocalized n electron. Our proposed method is structured in three distinct stages. In the first stage we perform a density functional theory (DFT) calculation for an open system consisting of the molecule attached to infinite electrodes. Second, we make use of the DFT results to obtain the three fundamental ingredients of an Anderson impurity model (AIM), i.e., the energy of the impurity levels (molecular orbitals here), the hybridization function, and the electron--electron interactions. In the final stage we solve the AIM through an impurity solver to include the dynamical correlations. This parameter-free theory is successfully tested on the case of a C_{60} molecule in a transistor configuration (see Fig.1), correctly reproducing the zero-bias features arising in the charge sector 1 (spin-1/2 Kondo), and in the charge sector 2 where a singlet-triplet quantum phase transition has been reported experimentally (see Fig. 2 and Ref. 1).



Figure 1. C₆₀ molecule in a transistor configuration

[1] N. Roch, S. Florens, V. Bouchiat, W. Wernsdorfer, and F. Balestro, Nature 453, 633 (2008).

INVITED TALK Simulation of single electron molecular transistors

Kurt Stokbro¹ and James Avery²

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In this presentation we present simulations with the Atomistix ToolKit of a molecule weakly coupled with metallic electrodes [2]. The device is operating in the incoherent regime, i.e. a single electron molecular transistor. The theoretical methodology of the simulation is illustrated for a benzene and C_{60} molecular transistor [2]. The main objective is the simulation of a single OPV5-tBu molecule between gold electrodes. This system was previously experimentally investigated by Kubatkin et al. [1]. In order to directly simulate the experimental geometry we have developed a finite-element DFT method that allows efficient treatment of complex molecules interacting with arbitrarily large electrostatic environments [3]. The details of the implementation will be discussed. The simulations are compared with experimental data of Kubatkin et al. [1]. We find quite different properties than in the experiment and point to a number of possible reasons for the discrepancy.



Figure 1: (top) OPV5 transistor setup. (bottom) The simulation setup with the finite element mesh. The mesh is fine around the molecule and coarse away from the molecule.

[1] S. Kubatkin et al., Nature **425**, 698 (2003).

[2] K. Stokbro, Journal of Physical Chemistry C **114**, 20461–20465 (2010).

[3] J. Avery, PhD Thesis, Copenhagen University (2011).

INVITED TALK Transport in molecular junctions beyond the coherent picture

<u>A. Pecchia¹, J. Lykkebo², G. Penazzi³, G. Romano⁴, A. Gagliardi⁵, and G. C. Solomon²</u>

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³BCCMS, Bremen Centre of Computational Materials Sciance, Univ. Bremen, Germany

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⁵Technische Universität München, Electrical Engineering and Information Technology, Arcisstr. 21, 80333 München, Germany

Molecular electronics has opened many field of research and it is still a rather lively subject of investigations across Europe. In this talk coherent and incoherent transport in molecular junctions based on the nonequilibrium Green's function formalism and the density-functional tight-binding method will be discussed [1]. Transport in controlled STM junctions can lead to unexpected transport behaviors due to conformational changes of the molecule induced by the tip. The interplay between interference and electron-vibron scattering in cross-conjugated molecules will be presented [2-4].

[1] A. Pecchia, G. Penazzi, L. Salvucci, and A. Di Carlo, New Journal of Physics 10, 065022 (2008).

J. Lykkebo, A. Gagliardi, A. Pecchia, and G. C. Solomon, ACS Nano 7, 9183-9194 (2013).
J. Lykkebo, A. Gagliardi, A. Pecchia, and G. C. Solomon, J. Chem. Phys. 141, 124119 (2014).
J. Lykkebo, G. Romano, A. Gagliardi, A. Pecchia, and G. C. Solomon, J. Chem. Phys. 144 (2015).

CONTRIBUTED TALK Quantum interference effects on IETS signals

<u>T. Novotný</u>¹, T. Hellmuth², and F. Pauly²

¹Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University in Prague, Czech Republic

²Department of Physics, University of Konstanz, Germany

We study characteristics of the IETS signal in molecules exhibiting destructive quantum interference in the elastic transmission such as meta-benzene or cross-conjugated molecules. We formulate a simple propensity rule based on the Hückel model for the molecule, which states that antisymmetric vibrational modes do not contribute to the IETS spectra. This analytical rule is verified by full ab-initio calculations based on DFT [1,2]. Our results are at variance with previous calculations by Lykkebo *et al.* [3,4] claiming strong suppression of all fundamental vibrational modes. In fact, we observe that for closely related pairs of molecules with/without the destructive interference features (e.g., meta- vs. para-benzene or linearly vs. cross-conjugated) the IETS spectra are very similar (apart from an overall decrease of magnitude by a factor ~10 for molecules with interference features), see Fig. 1, or even those for molecules with interferences in the numerical evaluation of the electron-vibration coupling elements by various IETS codes [2,5]. These findings raise the issue of the reliability and reality of calculations of electron-vibration interaction.



Figure 1: IETS signals and corresponding vibrational modes for a linearly conjugated molecule (a,b) with no destructive interference and for a cross-conjugated molecule (c,d) exhibiting the destructive interference in the elastic transmission. Apart from an overall scaling down of the magnitude the two sets show no dramatic changes in the character.

- [1] J. K. Viljas *et al.*, Phys. Rev. B **72**, 245415 (2005).
- [2] M. Bürkle et al., Phys. Status Solidi B 250, 2468 (2013).
- [3] J. Lykkebo *et al.*, ACS Nano **7**, 9183 (2013).
- [4] J. Lykkebo et al., J. Chem. Phys. 141, 124119 (2014).
- [5] A. Gagliardi *et al.*, Phys. Rev. B **75**, 174306 (2007).

CONTRIBUTED TALK

A novel design of quantum half adder using Quantum Hamiltonian Computing (QHC) approach: comparative study with the Qubit half adder

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Nowadays, the realization of reversible arithmetic and logical operation using quantum mechanical phenomenon is one of the most challenging problems in modern technology. However, it is commonly believed that a large number of quantum states is needed to realize even small quantum logic gates. This large number of quantum states provides a major obstacle for building more complex logic functions and serious barrier for a full-scale implementation because the larger the quantum system is, the greater the interaction with the external environment will be important causing the loss of information. Thus a superior approach is needed to minimize the total number of states required to realize these quantum logic gates. The Quantum Hamiltonian Computing (QHC) approach appeared to be a good candidate to construct complex quantum circuits with a minimum number of states [1]. The capability of QHC approach to minimize the total number of quantum states comes from the fact that we do not need that the quantum system be divided in qubits. Therefore, we can take the advantage of the total quantum system to perform a logic function but with a minimum spatial extension of the quantum system.

In this presentation, we compare the QHC approach with the Qubit approch through the study of the standard quantum half adder. We will show first of all how the QHC approch is able to greatly minimize the number of states required to construct this complex logic function. We will show in particular that only a 4 states are needed to construct a QHC half adder. We also show that the measurement of the frequency [2] instead of the population provides another advantage agains Qubit in terms of robustness of the logic gates. we will discuss for each approch the energy efficiency of the gate as the minimum energy needed to perform the calculation and the speed of calculation.

[1] G. Dridi, R. Julien, M. Hliwa, and C. Joachim, *The mathematic of a Quantum Hamiltonian Compulsion half adder Boolean logic gates*, Nanotechnologie **34**, 344003 (2015).

[2] N. Renaud and C. Joachim, *Classical Boolean logic gates with quantum systems*, J. Phys. A: Math and Theor. **44**, 15 (2011).

NVITED TALK N21 NEGF calculations & molecular projected transport

N. Papior^{1,2}

¹Catalan Institute of Nanoscience Nanotechnology, Campus UAB, Bellaterra, Spain ²Center for Nanostructured Graphene (CNG), DTU Nanotech, DTU, Denmark

I will present the recent development of $N \ge 1$ electrode NEGF simulations which enables simulations of multiprobe physics. The specific implementation will be presented [1,2] and the efficiency and scalability of the code (TranSIESTA) will be emphasized. The code implements hybrid parallelization which easily enables efficient calculations of systems with more than 10,000 orbitals under non-equilibrium, see Fig. 1 which shows the maximum memory usage with respect to system size (*x*-axis) and electrode size (*y*-axis), left. The right shows the computation time of a single SCF with NEGF. Using the *N* electrode capability I will present initial 3 terminal results based on a 2D-graphene interconnects [3].

After having introduced the NEGF method I expand on the transmission calculations where I will focus on projected molecular transport, see Fig. 2. Projections enable spectroscopy of molecular eigenstates and the identification of the electron carrying pathways. They will provide an intuitive understanding of the physics governing the transport properties of the junction. I will analyze the transport projection of the C_{60} molecule in a close packed Cu surface [4]. Importantly the projection is not limited to molecules and it will be shown that a generic projection onto *k*-resolved eigenstates is also possible.



Fig. 1: Memory/Time use of 2-terminal NEGF calculations.

Fig. 2: Transmission projection of molecule eigenstates.

[3] Jacobsen *et al.*, Carbon **101**, 101-106 (2016).

[1] Papior, PhD thesis (2016).[2] Papior *et al.* (to be submitted).

[4] Schneider et al., Journal of Physics Condensed Matter 27, 015001 (2014).

CONTRIBUTED TALK Aspects of graphene nanoribbon device simulations

<u>Pedro Brandimarte</u>^{1,2}, Nick R. Papior^{3,4}, Mads Engelund^{1,2}, Aran Garcia-Lekue^{2,5}, Thomas Frederiksen^{2,5}, Eduard Carbonell-Sanromà⁶, Martina Corso^{1,5,6}, Richard Balog⁶, Shigeki Kawaii^{7,8}, Shohei Saito^{8,9}, Shinichiro Osumi⁹, Shigehiro Yamaguchi^{9,10,11}, Jose I. Pascual^{1,5,6}, and Daniel Sánchez-Portal^{1,2}

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³Catalan Institute of Nanoscience Nanotechnology - Campus UAB, Spain
⁴Center for Nanostructured Graphene (CNG) - DTU Nanotech, Denmark
⁵IKERBASQUE, Basque Foundation for Science, Spain
⁶CIC nanoGUNE, Spain
⁷Department of Physics - University of Basel, Switzerland
⁸PRESTO - Japan Science and Technology Agency, Japan
⁹Department of Chemistry from Graduate School of Science - Nagoya University, Japan
¹⁰Institute of Transformative Bio-molecules - Nagoya University, Japan

Graphene nanoribbons (GNRs) have been considered as strong candidates for electronics, since they incorporate some of the remarkable properties from graphene while presenting a band gap [1]. These structures can be fabricated nowadays with a high control on the edge structure with the so-called bottom-up approaches [2]. Together with these experimental breakthrough a major effort has been devoted to the theoretical and computational methods developments. In this talk I will show some challenging features found when simulating GNRs based devices, such as: 1. The effects on the transport properties of 4-terminal crossed GNRs devices when varying the structural parameters determining the crossing; 2. The effect of substitutional chemical defects on the transmission channels and the importance of a proper description of the electrostatics in quasi 1-dimension systems.



Figure 1: Direct (left) and inter-ribbon (right) transmissions at V=0 in a crossbar system with 60° rotation angle.



Figure 2: Project density of states from a substitutional boron-doped armchair graphene nanoribbon.

L. Yang *et al.*, Phys. Rev. Lett. **99**, 186801 (2007).
J. Cai *et al.*, Nature **466**, 470-473 (2010).

INVITED TALK Functional theories of thermoelectric phenomena

Massimiliano Di Ventra

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I will discuss non-equilibrium density functional theories of local temperatures and associated heat currents that are particularly suited for the study of thermoelectric phenomena. In one case, I will introduce a functional theory of open quantum systems [1] that allows for the study of local temperatures by the introduction of local thermal probes. In another [2], we couple the local temperature field to an energy density operator. I will also provide predictions on the local temperature oscillations in atomic wires [3], carbon nanoribbons and graphene junctions [4], and discuss similarities and differences between the different local temperature definitions in the strongly-correlated regime [5].

[1] M. Di Ventra and R. D'Agosta, Phys. Rev. Lett. **98**, 226403 (2007).

- [2] F. Eich, G. Vignale and M. Di Ventra, Phys. Rev. Lett. **112**, 196401 (2014).
- [3] Y. Dubi and M. Di Ventra, Nano Lett. 9, 97 (2008).
- [4] J. P. Bergfield, M. A. Ratner, C. A. Stafford, and M. Di Ventra, Phys. Rev. B 91, 125407 (2015).
- [5] L. Z. Ye, D. Hou, X. Zheng, Y.J. Yan, and M. Di Ventra, Phys. Rev. B **91**, 205106 (2015).

INVITED TALK

Quantum-interference-enhanced thermoelectricity in single molecule junctions

Colin Lambert

Department of Physics, Lancaster University, UK

Although the dream of manipulating quantum interference in single molecules has been discussed for many years, experimental evidence of the effect of quantum interference on the room-temperature electrical conductance of single-molecules was reported only recently [1].

In this talk, I will present a brief outline of recent advances in our understanding of quantum interference in single-molecules [2] and then discuss how quantum interference can be exploited to increase the thermoelectric performance of single molecules [3] and assemblies of molecules connected to nano-gap electrodes.

[1] J. Am. Chem. Soc. **133**, 11426, (2011); Nature Nano. **7**, 305 (2012); Nat. Nano. **7**, 663 (2012); Phys. Rev. Lett. **109**, 056801 (2012); Nano. Lett. **6**, 1643-1647 (2012); J. Am. Chem. Soc. **134**, 5262 (2012); Beilstein J. Nanotech. **2**, 699 (2011) and refs. therein.

[2] C. J. Lambert, Chem. Soc. Rev. **44**, 875-888 (2015); Y. Geng et al., J. Am. Chem. Soc. **137**, 4469 (2015); Sangtarash et al., J. Am. Chem. Soc. **137**, 11425 (2015); D. Manrique, et al., Nature Comm. **6**, 6389 (2015); Berritta et al, Nanoscale **7**, 1096 (2015).

[3] Evangeli et al., Nano Lett. **13**, 2141-2145 (2013); Garcia-Suarez et al., Nanotechnology **25**, 205402 (2014); Rincón-García et al., Nature Mat. **15**, 289 (2016); Sadeghi et al., Nano Lett. October (2015) DOI: 10.1021/acs.nanolett.5b03033; Ismael et al., Nanoscale **7** 17338 (2015).

CONTRIBUTED TALK Quantum interference in open quantum systems: design of transmission spectra and analysis on thermoelectric properties

<u>Daijiro Nozaki^{1,2}, Haldun Sevinçli², Stanislaw. M. Avdoshenko², Rafael Gutierrez², and Gianaurelio Cuniberti²</u>

¹Department of Theoretical Physics, University of Paderborn, Germany ²Institute for Materials Science, TU Dresden, Germany

Quantum interference (QI) in molecular devices has drawn an increasing attention in the last decades because of unique features observed in conductance spectra applicable to thermoelectric devices and molecular switches [1-3]. In order to tailor the molecular devices exploiting QI effects, it is of great theoretical and practical interest to clarify the relationship between the line shape of conductance spectra including QI features and controlling parameters such as electronic structures (on-site energies and transfer integrals) and topologies of molecules.

In this talk, we present a simple graphical method (parabolic diagram) that we developed to visualize the relation between the electronic parameters and line shape of conductance spectrum influenced by QI effect in the molecular junction with a side group (T-shaped molecule, Fig. 1) [4,5]. We will also present systematic analysis of thermoelectric properties in a series of molecular junctions having different topologies and QI features in toy model basis [6]. In this work, we consider a homogeneous toy model where all on-site energies are identical and model four types of molecular junctions due to their topological connectivities. We systematically analyze their transmission spectra, density of states, and thermoelectric properties. Even without the degree of freedom of on-site energies an asymmetric Fano peak could be realized in the homogeneous systems with the cyclic configuration. We also calculate the thermoelectric properties of the model systems with and without fluctuation of on-site energies. Even under the fluctuation of the on-site energies, the finite thermoelectrics are preserved for the Fano resonance, thus cyclic configuration is promising for thermoelectric applications.



Figure 1: (a) Electronic parameters in a T-shaped molecule. (b) A parabolic diagram. Drawing a parabola with set of parameters (ϵ_0 , ϵ_1 and V) allows one to visualize the relationship between (anti-) resonances and the electronic parameters as shown in panel (c).

[1] S. V. Aradhya and L. Venkataraman, Nat. Nanotechnol. 8, 399 (2013).

[2] W. Hong et al., Beilstein J. Nanotechnol. 2, 699 (2011).

[3] C. M. Guédon et al. Nat. Nanotechnol. 7, 305 (2012).

[4] DN, H. Sevinçli, S. M. Avdoshenko, R. Gutierrez, G. Cuniberti, J. Phys. Conf. Ser. 427, 012013 (2013).

- [5] DN, H. Sevinçli, S. M. Avdoshenko, R. Gutierrez, G. Cuniberti, PCCP 15, 13951 (2013).
- [6] DN, S. M. Avdoshenko, H. Sevinçli, G. Cuniberti J. Appl. Phys. 117, 074308 (2014).

Tuesday June 14

INVITED TALK Charge and energy transport in atomic and molecular junctions

Fabian Pauly

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Single-atom and single-molecule junctions represent the ultimate limit to the miniaturization of electrical circuits. They are also ideal platforms for testing quantum transport theories that are required to describe charge and energy transfer in novel functional nanometer-scale devices.

In this seminar, I will review the recent theoretical progress of my group towards the description of elastic and inelastic charge transport in atomic and molecular junctions as well as thermoelectric phenomena and heat dissipation. After a brief introduction, I will discuss results on the conductance [1,2], inelastic electron tunneling spectra [3,4] and the thermopower [5-8]. Next, I will show an ab-initio characterization of the thermoelectric figure of merit of molecular junctions including both electronic and phononic contributions to the thermal conductance [9]. Finally, I will present combined experimental and theoretical efforts to understand the heat dissipation in atomic-scale junctions [10,11].

[1] *Influence of conformation on conductance of biphenyl-dithiol single-molecule contacts*, A. Mishchenko, D. Vonlanthen, V. Meded, M. Bürkle, C. Li, I. V. Pobelov, A. Bagrets, J. K. Viljas, F. Pauly, F. Evers, M. Mayor, and T. Wandlowski, Nano Lett. **10**, 156 (2010).

[2] Conduction mechanisms in biphenyl-dithiol single-molecule junctions, M. Bürkle, J. K. Viljas, A. Mishchenko, D.

Vonlanthen, G. Schön, M. Mayor, T. Wandlowski, and F. Pauly, Phys. Rev. B 85, 075417 (2012).

[3] Influence of vibrations on electron transport through nanoscale contacts, M. Bürkle, J. K. Viljas, T. J. Hellmuth, E. Scheer, F. Weigend, G. Schön, F. Pauly, Phys. Status Solidi B **250**, 2468 (2013).

[4] *Identification of the current path for a conductive molecular wire on a tripodal platform*, M. A. Karimi, S. G. Bahoosh, M. Valášek, M. Bürkle, M. Mayor, F. Pauly, and E. Scheer (submitted).

[5] Ab initio study of the thermopower of biphenyl-based single-molecule junctions, M. Bürkle, L. A. Zotti, J. K. Viljas, D. Vonlanthen, A. Mishchenko, T. Wandlowski, M. Mayor, G. Schön, F. Pauly, Phys. Rev. B **86**, 115304 (2012).

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CONTRIBUTED TALK Vibrationally-mediated single molecule switching studied by low-temperature STM

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Recent experimental results for the intra-molecular hydrogen-transfer reaction, tautormization, of a single Porphycene molecule on the Cu(110) surface will be reported. The reversible cis-cis switching is directly observed and controlled by scanning tunneling microscopy (STM) and the reaction yield, probability per electron, is investigated as function of the tunneling current and bias voltage. The yield shows a steep increase at the energy of vibrational excitation of porphycene, and also exhibits a clear isotope effect when substituting the transferred H-atoms with deuterium, revealing a vibrationally mediated process. These results indicate that the reaction coordinate involves a skeletal motion of porphycene, particularly the "door-wayâ € vibrational modes, that couples with the N-H(D) stretching mode and which shows a pronounced anharmonicity because of the intramolecular H-bonds. Therefore, the molecular swtitching process is an inherently multidimensional problem and a true understanding of the H-transfer resulting in the Cis-Cis transformation might require a multidimensional molecular dynamics calculation. Moreover, since the nuclear quantum effects like tunneling and zero-point energy would contribute to the process due to the small mass of H-atom, quantum mechanical treatments may also be required for the complete description of switching process. Specifically, a microscopic understanding electron-phonon coupling to induce vibrational excitation within a single molecule and how the dynamics of the subsequent IVR results in the excitation of the switching/reaction coordinate.

CONTRIBUTED TALK Ab initio quantum transport calculations using plane waves

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Since the advent of the scanning tunneling microscope (STM), a major effort has been devoted to the development of computational methods appropriate for the theoretical investigation of electron transport at the nanoscale. In particular, given the high sensitivity of conductance to atomic-structure details, density functional theory (DFT) has become an essential tool in transport calculations. The most commonly employed method combines the nonequilibrium Green's function (NEGF) with a DFT electronic structure, which are usually based on localized basis set. An alternative route is to explicitly solve the scattering states, although this approach is in most cases extremely expensive.

In this talk, I will describe a method to efficiently calculate the scattering states in quantum-transport problems using a plane-wave basis set [1]. Our approach is valid for any applied bias voltage since the current is calculated self-consistently, and can include exact evanescent states, which are also calculated using plane waves. The scattering states are solved exactly in a fast and numerically stable procedure with a computational time similar to a conventional ground state calculation. Based on these scattering states one can straightforwardly calculate the transmission coefficients and the corresponding electronic current.

Here, I will present several examples using this method, which range from electron tunneling to molecular electronics [2]. Our results demonstrate that our method is a good practical and accurate approach to study elastic quantum transport for a variety of problems. Particularly, it is useful to study tunneling through vacuum where the localized atomic orbital based method might face a difficulty to describe the electronic wave functions [3].



Figure: Total transmission at the Fermi level for a broken Au chain as a function of the vacuum-gap width obtained using plane waves (solid line), atomic orbitals (dashed line) and atomic orbitals with ghost atoms (dashed dotted line). [*] M. Brandbyge et al., Phys. Rev. B **65**, 165401 (2002).

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INVITED TALK

Time-dependent phenomena in single molecule junctions: Coherent electron pumps, transient currents and the directional photo-electric effect

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The study of charge and energy transport in single molecule junctions out of equilibrium introduces unique theoretical and experimental challenges. In the talk, theoretical studies of field-driven molecular junctions are presented which suggest new manifestations of unique single molecule properties in macroscopic observables. Having a molecule as the 'bottle neck' for charge and energy transport, the characteristic length and time scales suggest that coherent dynamics dominates the transport properties, and therefore the transport can be coherently controlled. In particular we shall focus on 'electron pumps' which convert radiation field into directed electronic currents. The principle of operation and the experimental manifestations will be analyzed theoretically under conditions ranging from a sudden pulse to cw excitation, and from direct excitation of the molecule to excitation through the leads plasmons. The latter suggest the existence of a single molecule-based directional photo-electric effect.

INVITED TALK Nonequilibrium Green's function method and near-field radiation

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The nonequilibrium Green's function (NEGF) method is a powerful technique for studying quantum transport. We begin with a brief introduction of NEGF, emphasizing the role of contour order in defining the Green's functions. After a briefly mentioning of few applications, we discuss the problem of near-field radiation between metal plates. In dealing with the quantum field of the electromagnetism, an operator normal order is essential in using the Poynting vector to compute the radiation energy flux. We then present results of our model calculations.

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CONTRIBUTED TALK Hole transporter materials for organic photovoltaics: a theoretical approach

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Organic solar cells (OSC) based on π-conjugated polymers and organic molecules have seen increasing interest in recent years as an alternative to inorganic photovoltaics due to their possible low cost application in large area and flexible devices. The hole-transporter material (HTM) is one of the key components of an OSC having the function to transport the holes generated from the exciton dissociation to the electrical contact. In this context computational techniques can provide valuable insights in the characterization of electronic, optical and charge transport properties of a HTM. First we explore the relation between the morphological and the hole transport properties of P3HT and PBTTT polymers in crystalline phase [1]. Using molecular dynamics (MD) to simulate bulk supercells and the Marcus theory to calculate the hole mobility we show that PBTTT displays a larger charge mobility than P3HT due to the interdigitation of the side chains enhancing the stability of the conjugated rings on the backbones. Then we present combined MD-DFT calculations to investigate six triphenylamine-based hole-transporter materials [2] used in solid-state dye-sensitized solar cells (ssDSSC), including the state-of-the-art material in this field, spiro-OMeTAD. We find that all of the studied materials present typical features of a HTM: (1) delocalized highest occupied molecular orbital (HOMO); (2) hole reorganization energies higher than the electronic ones; and (3) transparency in the visible region of the electromagnetic spectrum. Among the investigated compounds, 4-(4-phenyl-4-a-naphthylbutadienyl)-N,N-di(4tolyl)-phenylamine (HTM1) shows the most promising features in terms of optimal charge delocalization, high electronic couplings, and low energetic disorder that cause a high hole mobility in the amorphous phase. The obtained results are in qualitative and quantitative agreement with the experimental data and suggest that the current computational approach could be further employed to obtain valuable insights for the design of new HTMs aiming at improving the performances of presently available OSCs.



Figure 1: Schematic representation of a ssDSSC and hole mobility calculated for the six HTMs studied.

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CONTRIBUTED TALK Multifunctional organometallic molecular junctions

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Molecular materials based on the assemblage of metallic fragments and conjugated organic or inorganic ligands present additional features compare to pure organic systems. This is due to their relatively good stability combined with active excited-states and redox properties which confer them interesting physical properties in several domains (magnetism, optics, electrochemistry...). These multifunctional systems are promising candidates to be incorporated in nanoscale devices for molecular electronics, opto-electronics and/or spintronics.

The control and manipulation of the physical properties of such systems is the key element for the developments of this research, but it presents considerable conceptual challenges. These challenges can be met by combining experimental and theoretical studies. Using results obtained by quantum chemical calculations, mainly of density-functional theory (DFT)-type, associated with experimental measurements, some physical properties of representative compounds can be explained and predicted. Particular emphasis will be put on the electronic reasons of the changes of physical properties upon oxidation or reduction, or upon structure modifications induced by irradiation or temperatue. This will be illustrated by detailing recent studies performed in our groups briefly explained in Figure 1 [1,2].



Figure 1: Representation of the photo- and electro-chromic system (left) which was immobilized in gold-gold junction (top right). Conductivity was studied experimentally and theoretically (NEGF formalism, bottom right: molecular projected spectrum Hamiltonian at the Fermi level represented at zero-bias).

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INVITED TALK

Simulation of electron transport in molecular junctions using multiconfiguration wavefunction and reduced density matrix methods

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Nonequilibrium electron transport in molecular junctions often involves correlation effects due to electronelectron or electron-vibrational interaction. In this talk, methods are discussed, which allow an accurate description of correlated electron transport, including the hierarchical master equation approach and the multilayer multiconfiguration time-dependent Hartree (ML-MCTDH) method [1]. Moreover, the combination of the ML-MCTDH method with reduced density matrix theory is outlined [2]. The performance of the methods is discussed based on models for vibrationally coupled electron transport in molecular junctions, including both time-dependent and steady-state transport.

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CONTRIBUTED TALK Current induced phonons renormalization in molecular junctions

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Current-induced forces are at the origin of a rich variety of effects, including vibrations, rotations as well as mass and energy flow at interfaces [1]. We explain how the electrical current flow in a molecular junction can modify the vibrational spectrum of the molecule by renormalizing its normal modes of oscillations.

This is demonstrated with first-principles self-consistent transport theory, where the current-induced forces are evaluated from the expectation value of the ionic momentum operator.

The redistribution of the electron density caused by the presence of a stationary current – causing atomic rearrangements and modifying the instantaneous Hamiltonian – is calculated using the non-equilibrium Green's function formalism combined with Density Functional Theory.

We explore here the case of H_2 sandwiched between two Au electrodes and show that the current produces stiffening of the transverse translational and rotational modes and softening of the stretching one along the current direction. Such behavior is understood in terms of charge redistribution, potential drop and elasticity changes as a function of the current.

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Wednesday June 15

INVITED TALK

Real space computational approaches for exploring charge/spin/thermal transport in materials with billions of atoms

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I will overview two decades of development of real space developments of quantum transport methodologies which have allowed simulations of bulk charge/thermal and spin transport in model systems of remarkable complexity, including all sort of disorder (static and vibrational), varying dimensionality and system sizes reaching the experimental and technology relevant scales (for technical details read [1]). After some introduction of the scope of those methods, I will focus on most recent developments on quantum Hall (spin) conductivities which have allowed the exploration of unprecedented transport features in disordered Dirac Matter, including our recent exploration of spin dynamics in graphene and topological insulators which demonstrate the brute force capability of such methods as unrivaled tools for new fundamental discoveries [2,3].



Figure 1: The unrivalled scaling behavior of real space quantum transport methodologies.

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CONTRIBUTED TALK Spin-filtering in graphene junctions with Ti and Co adsorbates

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Organic materials have recently demonstrated their potentiality for applications in molecular spintronics due to their electronic and magnetic properties that, for some aspects, differentiate from those of the conventional inorganic metals and semiconductors. Carbon-based structures have been investigated as possible spintronics components [1,2], exploiting the possibility of inducing and controlling magnetism in graphene. The adsorption of transition metals (TM) is one of the most appealing techniques [3,4] because it can turn graphene into a half-metal [5].

We will analyze the spin-dependent current and spin-filtering efficiency of a graphene sheet adsorbed with TM atoms (Ti and Co), from first principles. Our calculation, exploiting the Non-Equilibrium Green's Function (NEGF) formalism implemented in TranSIESTA [6], shows that the adsorption of transition metal atoms on graphene induces the opening of a gap in the transmission function in one spin channel only. Charge carriers flowing through the nanojunction in Ti@graphene and Co@graphene belong almost entirely to the minority and majority spin component, respectively. This gives rise to a spin polarization of the current of about 100%.

Also the analysis of the non equilibrium electron density distribution indicates that a spin separation between the left and the right portions of the device occurs. This strong spin asymmetry suggests that transition metal adatoms have the potential of turning graphene into an efficient spin-filtering device.



Figure 1: Electronic current and its spin polarization in Ti@graphene (left) and Co@graphene (right).

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CONTRIBUTED TALK Electron transport in a Fe-Porphyrin/Graphene junction

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A relatively new field of investigation is molecular spintronics, in which magnetic molecular junctions are used as spin transport channels [1]. Both experiments and theoretical works suggest that organic materials can offer similar and perhaps superior performances in making spin-devices than the more conventional inorganic metals and semiconductors [2]. Among organic materials, porphyrins are considered promising candidates because they offer a variety of desirable features such as highly conjugated structure, rigid planar geometry and good chemical stability [3].

In this work we study by first principles the transport properties of a magnetic molecular junction consisting of Fe-porphyrin molecule connected with two semi-infinite graphene electrodes. The calculations were performed using the TranSIESTA code [4], which combines the non-equilibrium Green's function (NEGF) technique with DFT. We find that the localized Fe states do not produce relevant effects on the current which in fact displays only a slight polarization.

We further investigate the electron transport through the same molecular junction contacted with boron and nitrogen doped graphene electrodes. The presence of the dopants leads to a non negligible density of states around the Fermi level allowing the hybridization between iron and carbon states. In the case of B-doped electrodes a current polarization is observed, while in the N-doped case a Negative Differential Resistance effect can be pointed out. With differently doped electrodes, one with boron and the other with nitrogen, the junction displays a partial rectification behavior.

Since the electronic properties of the metal atom can be modulated by the adsorption of a gas molecule, we study the effect of a gas molecule adsorption on the charge transport and we observe a quenching of the current polarization in the B-doped system.



Figure 1: Local density of states of a molecular hybridized state of the nanojunction.

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INVITED TALK Buttiker's probes in molecular electronics: Applications to charge and heat transport

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The role of incoherent (elastic, inelastic) scattering effects on charge and heat conduction in molecules is explored using the phenomenological Buttiker's probe method. In the past 30 years this easy-to-implement approach has been extensively employed to research inelastic effects in the transport behavior of mesoscopic devices, yet limited to the linear response regime. Our recent work has been focused on extending this method to far-from-equilibrium applications. In a series of recent papers we showed that the probe technique can reliably mimic incoherent charge transfer phenomena under finite voltage biases [1-3], as well as vibrational heat conduction under large temperature differences [4-5].

Concerning incoherent electronic conduction, I will begin by defining two types of constructions, the dephasing and voltage probes. I will then show that these probes can properly reproduce the tunneling-tohopping crossover in conductance at low applied bias [1]. At high bias, we will identify signatures of elastic and inelastic scattering processes in the electrical current [3], use Buttiker's probes to examine the robustness of tunneling diodes [2], and propose mechanisms for environmentally-induced diodes [3]. If time allows, I will discuss applications of Buttiker's probes in studies of vibrational heat transfer through molecules, placed under high temperature differences. I will particularly demonstrate the utility of the method in materializing nonlinear function, e.g., thermal diodes operating in the quantum regime [4-5].

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INVITED TALK

Diagrammatic and resummation algorithms for electron-phonon and electron-magnon interacting systems in nanojunctions far from equilibrium

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The nanoelectronic and spintronic devices based on single-molecule or magnetic tunnel junctions are typically operated by finite bias voltage which can lead to highly nonequilibrium states of electrons and bosons (such as phonons or magnons). While nonequilibrium Green function (NEGF) formalism offers a rigorous theoretical and computational framework to describe the effect of their mutual interaction on charge and spin currents underlying the device functionality, the computational complexity of standard self-consistent diagrammatic many-body perturbation scheme for NEGFs has restricted simulations to very small junctions (containing few tens of atomic orbitals). Furthermore, magnons have small bandwidth meaning that weak interactions felt by electrons turns out to be strongly coupled regime for magnons, thereby requiring higher order diagrams in the expansion of magnonic NEGF. On the other hand, as the interactions strength increases, self-consistent diagrammatic series often converges to the unphysical branch. This talk will overview our recent NEGF-based approach [1] to nonequilibrium electron-magnon systems in magnetic tunnel junctions, where magnons become guasiparticles dressed by the cloud of virtual electron-hole pairs while electrons scattering of low frequency magnons experience anomaly in their current-voltage characteristics at small bias voltage. I will then use an example of a single molecule nanojunction to show how self-consistent diagrammatic series for NEGFs describing electron-phonon (or electron-magnon) inelastic scattering can be evaded by evaluating only fourth-order bare diagrams [2] and subsequently performing very recently proposed [3] hypergeometric resummation that preserves conservation laws and can make possible simulations of electron-boson coupled systems in devices containing very large number of atoms.



Figure 1: Example of self-consistent diagrammatic series for (a) electronic NEGF or (b) magnonic NEGF in nonequilibrium electron-magnon system, as well as fourth-order bare diagrammatic series for NEGF of electrons interacting with phonons which is used as an input for hypergeometric resummation.

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CONTRIBUTED TALK

Some aspects of electron-phonon interactions in molecular junctions: Toward a description of time-dependent quantum transport

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Molecular electronics represents the ultimate limit of the "up-bottom" miniaturization process initiated by the semiconductor industry. Along this path, the laws of quantum mechanics have been found to impose fundamental limitations, especially in the ultimate case of molecular and atomic sized electronic junctions.

Despite several decades of investigations, a global understanding of current-voltage characteristics I(V), mechanical stability and heat losses of such molecular junctions is still lacking. A key mechanism for understanding all this phenomena lies in the coupling between electronic degrees of freedom (giving rise to an electronic current) and local vibrational modes of the junction (phonons giving rise to dissipation).

This presentation aims at reviewing recent advances in this field of research. In particular, we will show that, due to inelastic scattering with phonons, some information about electronic and vibrational properties of the junction, electronic correlations and effective lattice temperature is encoded into the electrical current noise curves ("shot-noise"), that is not present in standard *I(V)* characteristics. This opens up new technological perspectives and complementary spectroscopic tools at the nanoscale. We will present the first experimental evidence of this phenomenon [1] as well as its theoretical analysis, based on recent first-principle calculations [2]. Finally, we will provide a general picture and explore new directions and open questions arising from recent theoretical advances [3] dealing with the investigation of time-dependent quantum transport using NEGF techniques in the (ultra-fast) transient regime.

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CONTRIBUTED TALK Improved auxiliary-mode approach to time-dependent electron transport

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The theoretical description of time-resolved phenomena in nanoscale devices remains a very challenging task. Several formalisms are available, but efficient approaches for general-purpose computations are still under investigation [1]. In Ref. [2] it was proposed to use an auxiliary-mode expansion of the self-energies arising in the time-dependent non-equilibrium Green's functions (TD-NEGF) formalism. To this end the Fermi function and the level-width function are expanded in terms of simple poles in the complex plane. By means of this parametrization, the equations of the NEGF theory, in particular the integro-differential equation for the reduced density-matrix, are converted into a set of coupled differential equations for auxiliary matrices.

This method is suited to describe time-dependent effects which stem from coupling the electronic system to other degrees of freedom, e.g., in the case of molecular systems where the influence of vibrational modes on electron transport plays a prominent role. Moreover, this approach has been used to study, e.g., electron transport through long molecular chains in the presence of thermal fluctuations from surrounding solvent molecules [3], or to characterize dynamical interference effects through meta- and para-aligned benzene molecules [4].

In the present contribution we discuss an improved new version of the auxiliary-mode approach, where the auxiliary matrices are replaced by vectors or scalars. This drastically reduces the overall computational effort and memory requirement. We demonstrate the method using a molecular wire as well as a closed ring structure, where we discuss propagation and interference of Leviton wave-packets.

See for example: A.-P. Jauho, N. S. Wingreen and Y. Meir, Phys. Rev. B **50**, 5528 (1994). S. Kurth *et al.*, Phys. Rev. B **72**, 035308 (2005). For a recent overview of the field see: B. Gaury *et al.*, Phys. Rep. **534**, 1 (2014) and references therein.
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Thursday June 16

INVITED TALK Steady-state density functional theory for finite bias conductances

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In the framework of density functional theory a formalism to describe electronic transport in the steady state is proposed which uses the density on the junction and the steady current as basic variables. In a finite window around zero bias, a one-to-one map is established between the basic variables and both local potential on as well as bias across the junction. The resulting Kohn-Sham system features two exchange-correlation (xc) potentials, a local xc potential and an xc contribution to the bias. For weakly coupled junctions the xc potentials exhibit steps in the density-current plane which are shown to be crucial to describe the Coulomb blockade diamonds. At small currents these steps emerge as the equilibrium xc discontinuity bifurcates. The formalism is applied to a model benzene junction, finding perfect agreement with the orthodox theory of Coulomb blockade.

CONTRIBUTED TALK Giant room temperature interface spin Hall and inverse spin Hall effects

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The spin Hall angle (SHA) is a measure of the efficiency with which a transverse spin current is generated from a charge current by the spin-orbit coupling and disorder in the spin Hall effect (SHE). In a study of the SHE for a Pt|Py (Py=Ni₈₀Fe₂₀) bilayer using a first-principles scattering approach, we find a SHA that increases monotonically with temperature and is proportional to the resistivity for bulk Pt. By decomposing the room temperature SHE and inverse SHE currents into bulk and interface terms, we discover a giant interface SHA that dominates the total inverse SHE current with potentially major consequences for applications [1].

To study bulk Pt, we set up a scattering geometry consisting of two crystalline semi-infinite Pt leads sandwiching a scattering region of length L_{Pt} of disordered Pt with atoms displaced from their equilibrium positions by populating phonon modes, as sketched in Fig. 1a. For the resistivity and spin-flip diffusion length, this approach has been shown to yield essentially perfect agreement with experiment [2]. We study the SHE by calculating local longitudinal and transverse charge and spin current densities in the scattering region so that both intrinsic and extrinsic contributions are naturally included. To study interface effects, we model a Py/Pt bilayer by matching 9×9 interface unit cells of Py to $3\sqrt{7}\times3\sqrt{7}$ unit cells of Pt [3] including both lattice and spin disorder in Py. Fig. 1b shows the results obtained for bulk Pt at room temperature. This presentation will review the computational procedures that make these calculations possible [4].



Figure 1: (a) Schematic illustration of the scattering geometry. Electrons flow i_c^z from the perfectly crystalline left lead to the right one through a disordered region of pure bulk Pt where atoms are displaced from their equilibrium positions by populating phonons. Transverse spin currents arising from the SHE flowing along x and -y directions are polarized in the $y \mathbf{j}_{sy}^{x}$ and \mathbf{j}_{sx}^{y} directions, respectively. (b) Calculated transverse spin-current densities in Pt normalized by \mathbf{j}_{c}^{z} at room temperature. The error bars are a measure of the spread of 10 random configurations of disorder. The dashed black line shows the extracted SHA. Inset: integrated spin current density in a length L_{Pt} of disordered Pt. The dashed black line illustrates a linear least squares fit from which a SHA for pure bulk Pt of Θ_{sH} =0.033 ± 0.001 is extracted.

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CONTRIBUTED TALK Propagation of a Bloch-wave packet excited by a femtosecond ultraviolet pulse

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Transport properties of electron wave packets underlie the functioning of electronic devices and are an important factor in time-resolved photoemission spectroscopies. Here we consider the photoelectron motion in an attosecond streaking experiment [1] and focus on the hitherto neglected aspect: the interaction with the exciting field in the course of propagation. The non-stationary Schrödinger equation is solved numerically exactly for a model that realistically describes the lattice scattering [2]. We go beyond the standard treatment of inelastic processes with an absorbing potential and develop a microscopic approach to it.

We theoretically establish that in a crystal an optically excited electron may propagate faster than with the group velocity and faster than the free electron. The essence is that the interaction of the wave packet with the crystal lattice slows down the temporal evolution of its energy spectrum (see figure), and while the spectrum keeps changing the packet propagates faster than a packet with a stationary spectrum. At the same time, for a weak lattice scattering, the phenomenological result that the photoelectron moves with the group velocity $dE/d\hbar k$ and traverses on average the distance equal to the mean free path is proved to hold even at very short travelling times. These findings offer a novel interpretation of the delay time in the streaking experiment and shed new light on tunneling in optoelectronic devices [3].



Figure: Temporal evolution of the photoelectron spectrum from a localized state at E=-41 eV excited by a light pulse of duration 1000 asec and $\hbar\omega=80 \text{ eV}$ (a) and 100 eV (b). The gaps in the spectrum (at 39 and at 48 eV) are caused by the interaction with the crystal lattice. Owing to gaps, at 80 eV the evolution is much slower: at t=200 asec the spectrum is still spread over a range of 40 eV.

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INVITED TALK Transport properties of nanostructured graphene

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Despite of its many wonderful properties, pristine graphene has one major drawback: being a semimetal it does not have a band gap, which complicates its applications in electronic devices. Many routes have been suggested to overcome this difficulty, such as cutting graphene into nanoribbons, using chemical methods, or making regular nanoperforations, also known antidot lattices. All these ideas work beautifully in theory, but realizing them in the lab is very difficult because all fabrication steps induce disorder and other nonidealities, with potentially disasterous consequences for the intended device operation. In this talk I introduce these ideas and review the state-of-the-art both from the theoretical and the experimental points of view. I also introduce some new ideas, such as sublattice asymmetric doping (which Nature allows!), triangular antidots, and nanobubbles formed in graphene. Our simulations, relying on advanced numerical techniques, show that it may be possible to generate very high quality spin- and valley polarized currents with these structures – something that has not yet been achieved in the lab. Importantly, our simulations involve millions of atoms which is necessary in order to address structures feasible in the lab.

INVITED TALK Modeling vertical and lateral electron transport across heterostructures

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This talk will concentrate on recent developments for the understanding of charge transport across heterostructures between nanostructured materials, including one-dimensional and two-dimensional systems.

In the first part of my talk, I will focus on electron transport taking place along heterosctructures characterized by covalent bonding [1]. I will show how controlled doping on one side of the junction can lead to device properties that are well suited for photovoltaics and photocatalysis properties.

In the second part of my talk, I will present our recent work on the role of collective motion in the ultrafast charge transfer in van der Waals heterostructures (Figure 1). [2] Using time-dependent density functional theory molecular dynamics, we find that the collective motion of excitons at the interface lead to plasma oscillations associated with optical excitation. Application to the MoS_2/WS_2 heterostructure yields good agreement with experiment, indicating near complete charge transfer within a timescale of 100 fs.

Finally, I will briefly present recent theoretical developments for the understanding of electronic band gap renormalization induced by substrate polarization effects, taking adsorbate size into account.



Figure 1: Atomic and electronic structures of MoS_2/WS_2 heterostructures. a) Illustration of the heterostructure, where a WS_2 monolayer lies on top of a MoS2 monolayer. Electron and hole carriers excited by incident light separate by hole transfer onto the WS_2 . b) Band structure of the heterostructure, showing an indirect bandgap from Γ to K. c) Band structure in the vicinity of K-point in the Brillouin zone.

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CONTRIBUTED TALK

Integration of graphene into nanoelectronic devices: insights from atomistic simulations

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The preparation of high quality graphene as host material is pivotal for further device applications. As such, a deep knowledge on the electronic and transport properties of graphene derivatives is critical to successful integration of graphene into future nanoelectronic devices. In this work, the influence of gas adsorption on the electrical characteristics of graphene, and the effect of intrinsic defects on graphene electronic properties are explored by performing Density Functional Theory (DFT) calculations using SIESTA code [1]. Contact resistance between graphene and metal electrodes is also critical for obtaining efficient graphene devices. [2] The contact resistance between graphene and various metals in different geometries is characterized by performing first-principles quantum transport calculations. The TranSiesta code [1], which implements the NEGF formalism in systems with periodic boundary conditions perpendicular to the current, is used to obtain the conductance of the suspended graphene for Pd and Al electrodes and various contact lengths.



Figure 1: Structurally relaxed Pd(111)/graphene top contact, with a finite overlap (side view). Numbers indicate the amount of C atom pairs overlapping the Pd(111) contact.

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CONTRIBUTED TALK Atomic scale design of electrode terminations: gating of molecular levels in carbene-based junctions

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N-heterocyclic carbenes [1] have recently attracted much attention for their interesting optical properties and high thermal stability [2]. These characteristics make carbenes particularly attractive for possible applications in the field of molecular electronics and optoelectronics. However, a detailed study of their charge transport properties is still missing. Here we explore by means of ab-initio calculations based on density functional theory (DFT) and nonequilibrium Green's functions formalism (NEGF) the electronic and charge transport properties of a series of carbene-based molecular junctions. We focus on the effect of the geometric structure of the electrodes [3] and consider a tetramer (T), an adatom (A), a pyramid (P) and a chain-like geometry (C). We found that the LUMO level (dominating charge transport at the Fermi level) shifts by almost 0.8 eV with tip shape. This results in a strong modulation of the conductance at the Fermi level. We studied the electrostatics controlling level position for each tip geometry and rationalized these shifts in terms of the tip-dependent work function and charge rearrangement at the metal-molecule interface. We found that longer electrode terminations with a lower coordination number of the conductance in carbene-based molecular circuits.

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INVITED TALK Charge transport through dangling bond nanostructures on Si(2×1):H surfaces

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Implementing atomic and molecular scale electronic functionalities represents one of the major challenges in current nano-electronic developments. Engineered dangling bond (DB) nanostructures on Silicon or Germanium surfaces possess the potential to provide novel routes towards the development of non-conventional electronic circuits. These structures are built by selectively removing hydrogen atoms from an otherwise fully passivated Si(100) or Ge(100) substrate. In this presentation we will address charge transport signatures of dangling bond nanostructures, covering (i) quantum interference effects in DB loops, (ii) the implementation of Boolean gates by exploiting quantum interference effects, and (iii) charge transport under the influence of a periodic time-dependent modulation, mimicking irradiation with monochromatic light. We use electronic structure methodologies to address the electronic properties of the DB nanostructures in contact with mesoscopic electrodes combined with Green's function based approaches to deal with charge transport through these nanoscale systems.

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CONTRIBUTED TALK Designing all simple logic gates and half-adder circuit on a Si(100)–H surface

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Belonging to the Quantum Hamiltonian Computing (QHC) branch of quantum control [1-2], atomic-scale Boolean logic gates (LGs) with two inputs – one output (OR, NOR, AND, NAND, XOR, NXOR) and – two outputs (half-adder circuit) were designed on a Si(100)-(2×1)–H surface following the experimental realization of a QHC NOR gate [3] and the formal design of an half adder with 6 guantum states in the calculating block [4]. The logical inputs are determined by two nearest neighbor crossing surface Si dangling bonds, which can be, for example, activated by adding or extracting two hydrogen atoms per input. QHC circuit design rules together with semi-empirical full valence K-ESQC transport calculations were used to determine the output current intensity of the designed LGs when interconnected to the metallic nano-pads by surface atomic-scale wires. Our calculations demonstrate that the proposed devices can reach a "0" to "1" logical output ratio up to 10 000 for a running current in the 0.2 µA range for 50 mV to 150 mV bias voltage around the nano-pads Fermi level.

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INVITED TALK Simulating DNA sequencing using a combination of nonequilibrium Green's functions and QM/MM methods

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The quest for rapid whole-genome sequencing using new inexpensive techniques is at the forefront of scientific research as we aim to reliably determine genetic predispositions to diseases and gain a deep understanding of our genetic code [1]. Unfortunately, currently available techniques are unlikely to reach the low cost per genome required for this procedure to become widely available in preventive healthcare [2].

Third-generation devices, in particular, sequencing with nanopores [3,4], is widely regarded as the most promising approach to enable inexpensive whole-genome sequencing and provide orders of magnitude longer base read-lengths. The fabrication of solid-state nanopores along with their envisioned application for rapid whole-genome sequencing is becoming increasingly sophisticated. However, many extremely challenging questions remain unanswered, especially how to achieve single-base resolution during polynucleotide translocation through the nanopore. One proposal is to use tunneling current across the membrane containing the nanopore and use the different electronic transport signals as a signature of the electronic structure of the different nucleotides [5].

From the theoretical point of view this is a challenging, yet exciting task. On the one hand one must simulate the dynamics of DNA as it passes through a nanopore. The molecule is surrounded by a physiological solution. At the same electrons must be explicitly tread as one wishes to calculate the current passing through the device. In this talk I will discuss recent progress in our group towards completely and realistically simulating a nanopore-based sequencing device [6]. In order to do this, I'll demonstrate how we combine quantum and classical methodologies in order to address the electronic conductance and the possibility of using graphene-based devices for single-shot DNA sequencing.

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INVITED TALK Towards reality in modeling of molecule-electrode contacts

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Molecule-electrode contacts are the critical factor that determines the characteristics of molecular electronic devices, but their atomic-scale understanding and controlling still remains elusive. In this talk, I will present several recent works within our group that are concerned with the molecule-electrode contacts. First, focusing on the ubiquitous S-Au contacts in molecular electronics, I will discuss how the single-molecule conductance is correlated with the S-Au linkage coordination number (CN). *Ab initio* molecular dynamics (MD) simulations show that CN three that is stable in vacuum becomes destabilized upon solvation and spontaneously converts into CN two, which will reduce the number of multiple conductance peaks robustly observed across different experimental platforms. It will be shown that our popular force fields (FFs) optimized for self-assembled monolayers [1] fail to give the correct CN-dependent conductance ordering for single-molecule junctions, and an improved FF parameterization will be presented.

In the second part, I will consider the DNA sequencing based on low-dimensional carbon nanoelectrodes. Controlling the dynamics of DNA translocation is again a central issue in the emerging solid-state DNA sequencing approach [2]. Performing large-scale FF molecular dynamics simulations, I will show that the N doping of carbon nanoelectrdoes not only increases the sensitivity and selectivity for tunneling-current nucleobase reading [3] but also benefits the control of DNA conformations by slowing down the translocation speed and reducing structural fluctuations of nucleobases.

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CONTRIBUTED TALK Modeling the conductivity of MMX molecular wires

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One-dimensional conductive polymers are attractive materials for flexible and transparent electronics. However, structural disorder represents a major hurdle to achieve high conductivities at both macro and nanoscales. MMX metal-organic polymers are made by a linear chain of metal and halogen atoms, bonded to lateral organic units. They have been shown to present an exceptionally high intrinsic conductivity, as well as the potential to be isolated as fibers of a few, or even a single molecular chain [1,2]. The dependence of fiber conductivity versus length depends critically on the concentration and distribution of defects, as well as on the conductance of these defects. We have studied this dependence for $[Pt_2I(S_2CCH_3)_2]_n$ wires, both experimentally and theoretically. Experimentally, we find an exponential increase of resistance with length. For nanoribbons, made by many molecular chains, such an increase can be explained by the decreasing probability of finding nondefective chains in the ribbon [3]. For individual molecular chains, however, this increase suggests a model of Anderson localization of coherent states, in a chain of weakly dispersive defects, similar to that found in nanotubes [4].

Theoretically, we have modeled nanoribbons as a lattice of low-resistivity chains, interrupted by highresistance defects, and weakly coupled to other parallel chains. Such a model reproduces the observed dependence with ribbon length and width [3]. For few- or single-molecule chains, we study an alternative model of weak defects. Using density functional theory, we study different possible defects, extracting hopping and overlap matrices to calculate the conductance of a whole chain, with randomly placed defects.

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Friday June 17

Quantum transport properties across different chemical decorations in layered materials

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New materials with greater capabilities are a key component in the strategy to further the performance of current electronic devices. Of the limited available base options, light element layered materials are among the most promising solutions for high-performance charge transport with low heat dissipation. But the small or the absence of an electronic band gap in materials such as graphene prevents the creation of an on-to-off switch, hindering their integration in today's electronics. Within this setting, and motivated by prospects of integrating layered compounds into electronic devices to reduce consumer power consumption, I will describe how various types of chemical modifications and structural disorder in bilayer graphene [1], double-walled nanotubes [2], as well as some new 2D materials such as black phosphorus [3] and silicene [4] can enlarge the small or non-existing electronic band gaps while preserving a good charge mobility. I will discuss the required chemistry criteria for each material, which are obtained using a combination of electronic-structure and quantum transport computational methods at the micro-meter scale, to select the type of external defect and stoichiometry for achieving specific transport profiles.



Figure 1: Defected bilayer graphene yields homogeneous transport profiles across different chemical modifications.

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CONTRIBUTED TALK

First principle semiclassical conductivity and quantum transport in graphene with resonant scatterers: the case of H and F adatoms and of carbon atom vacancies

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The outstanding electronic and mechanical properties of graphene are unavoidably affected by the presence of a variety of possible defects in realistic samples. Atomic-scale defects such as charge scatterers, adatoms and carbon atom vacancies are typically introduced during the fabrication process and largely impact on its charge and spin transport properties. In this context neutral impurities which form resonant scattering centers have attracted much attention in the last few years, and considered to be important scatterers limiting electronic mobility [1,2].

Here, we analyze the effect of neutral defects on the transport properties of graphene, evaluating from *first principles* the cross section of resonant scatterers like H and F adatoms, and single C atom vacancies. The conductivity of two dimensional graphene with the above neutral impurities is calculated in the semi-classical limit where coherence is assumed to be lost between two scattering events, using a DFT-NEGF approach [3,4] on several defective graphene channels of different width and length. Quantum transport at and close to the Dirac point is further analyzed, and the same universal behavior is proved to exist for the intrinsic resistance of the defective transport channels, irrespective of the scatterer considered.

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INVITED TALK Modeling magnetism of single molecules: from electronic structure to spin-flip spectroscopy

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Magnetic molecules and single-molecule magnets in particular have attracted a lot of interest due to their capability to store magnetic information, offering a high storage density, promising stability and fast spinmanipulation [1]. Information about the magnetic properties of ensembles of these molecules is available through a series of experimental techniques, from variable-temperature magnetic susceptibility, to infrared spectroscopy, neutron scattering or electron paramagnetic resonance [2]. In addition, spin-flip spectroscopy provides a direct access to spectroscopic information of single molecules deposited on a substrate [3]. Density functional theory (DFT) calculations yields valuable theoretical information of these objects, but it is not especially suited to treat the low-energy magnetic properties. By contrast, spin models offer detailed information of the magnetic properties which can be directed compared with experiments, but they lack of the predictive capability of DFT since they rely on phenomenological parameters. Here we show that by combining DFT and electronic or spin models one can extract magnetic properties such as the magnetic susceptibility. We illustrate the treatment with Co-benzene magnetic clusters where we predict a non-collinear magnetization [4]. In addition, we show that the transport properties can very often be studied by using a generalized Anderson model. In particular, we demonstrate that cotunneling is the leading mechanism that accounts for the spin-assisted inelastic conductance observed in adsorbed Co-phthalocyanine molecules [5].



Figure 1: Contour plot of the average magnetic susceptibility of a (CoBc)₃ molecule versus applied magnetic field and temperature (in units of the uniaxial magnetic anisotropy parameter D).

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INVITED TALK Many-body correlations in STM single molecule junctions

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The electronic structure and the transport characteristics of single molecule junctions are strongly influenced by many-body correlations. Some of their fingerprints have been theoretically predicted [1,2] others clearly observed in STM experiments [3,4] both at the spectral and topographical level. We consider here a copper phthalocyanine (CuPc) molecule on an insulator coated substrate and demonstrate the non-equilibrium tip induced control of the molecular spin state. We find that, under the condition of energetic proximity of manybody neutral excited states to the anionic ground state, the system can undergo a population inversion towards these excited states. The resulting state of the system is accompanied by a change in the total spin quantum number [5]. Experimental signatures of the crossover are the appearance of additional nodal planes in the topographical STM images as well as a strong suppression of the current near the center of the molecule. The robustness of the effect against moderate charge conserving relaxation processes has also been tested.



Figure 1: Simulation of the spin map of a Cu-Phthalocyanine as a function of tip position. At specific tip positions a low to high spin transition on the molecule is triggered by the external bias across the junction and is accompanied by population inversion towards excited molecular states.

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CONTRIBUTED TALK Tunable competition between Kondo effect and spin-orbit interaction in a single molecule

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The Kondo effect and the spin-orbit interaction (SOI) play important roles to determine the magnetism of a single molecule. On metallic substrate, the local magnetic moment of a molecule is screened by the substrate conduction electron, which gives rise to a sharp peak (Kondo resonance) at the Fermi level in the differential conductance (dl/dV). The SOI splits the degenerate states with spin magnetic quantum number S_z into multiple fine structures (SO splitting), which causes magnetic anisotropy. The competition between the Kondo effect and the SO splitting results in exotic physics [1], but is not sufficiently understood yet.

In this study, we investigate the above competition, focusing on iron phthalocyanine (FePc) on Au(111). Bulk FePc molecules take S=1 triplet state consists of the unpaired electrons in Fe d_z^2 and degenerate d_{zx}/d_{yz} orbitals. The SO splitting induces the in-plane magnetic anisotropy and energy gap opens between S_z =0 and S_z =±1, which suppresses the Kondo resonance. On the contrary, a clear Kondo resonance appears in the dl/dV spectrum measured by scanning tunneling spectroscopy (STM) in FePc/Au(111) [2,3]. We modeled this system by an extended two-orbital and two-channel Kondo model and analyzed by using the numerical renormalization group technique [4]. We found that the strong renormalization of the SO splitting by two-channel Kondo screening enables to form the Kondo resonance. With reducing the Kondo coupling, the Kondo resonance formation is hampered by the SO splitting and the gap structure in the dl/dV spectrum develops instead of the Kondo resonance peak structure. The reduction of the Kondo coupling can be achieved by changing the Fe atom position. We realized this by STM experiments [4]. As the STM tip approaches to the Fe ion in FePc/Au(111), the spectral shape and the width of the dip in the dl/dV spectrum is changed, which is rationalized by the transition from the Kondo-effect-dominant state to the SO-splitting-dominant state.

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CONTRIBUTED TALK Electron transport simulations in the Kondo regime

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When magnetic atoms and molecules are brought into contact with metals the electron-electron interaction leads to the appearance of the correlated Kondo state at low temperatures. In this talk we will outline the methodological approach to evaluate the conductance of such systems from first principles, which is implemented in the Smeagol electron transport code [1]. In particular, we integrate the Density Functional Theory (DFT) with the continuous time quantum Monte Carlo (CTQMC) and the Numerical Renormalization Group (NRG) impurity solvers. We will present results of simulations for STM and break junction experiments that investigated stable radical molecules [2,3]. These molecules correspond to spin half molecular magnets. Finally we will briefly mention how the method has been extended to treat solid state devices, such as metallic heterostructures, within the Dynamical Mean Field Theory (DMFT) [4].



Figure 1: DFT transmission function (T0) compared to the DFT+CTQMC coherent (Te) and total, i.e. coherent+incoherent (T_{total}) transmission function for a spin ½ magnetic molecule between gold electrodes.

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Posters

POSTER Diamondoid-based molecular devices and their electronic transport properties

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In this work, we deal with the electronic transport properties across small diamond-like nanostructures, the diamondoids [1], in a gold nanogap. In our diamondoid-based devices, a small diamondoid is placed in between the two gold electrodes of the nanogap. The diamondoids are covalently bonded to the gold electrodes through two different molecules, a thiol group and a N-heterocyclic carbene [2] molecule. The transport properties of the diamondoid-based molecular device are evaluated with respect to these two binding possibilities and the size of the diamondoid. We also investigate the influence of doping the diamondoids leads to a considerable increase of the electron transmission across the device. We show the asymmetric feature of the IV curve applying the positive and negative bias which indicates the diode like property resulting in rectification within a very small range of bias voltages. In all cases, the efficiency of the device was manifested and is discussed in view of novel nanotechnological applications. In view of these applications, our results reveal a pathway to tune the electronic transport properties of diamondoid-based molecular devices by selectively choosing their structural characteristics.



Figure 1: The setup for the transport calculations: N-doped di-thiol tetramantane embedded inside a gold nano-gap.

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POSTER Direct Au-C contacts based on biphenylene for single molecule circuits

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Understanding the fundamental mechanisms governing charge transport in metal-molecule-metal systems represent an essential step towards gaining control over single molecular applications. The contacts between metal and molecule strongly influence the electronic and conducting properties of molecular junctions [1]. Here we use Density-Functional Theory (DFT) and Non-Equilibrium Green's Functions (NEGF) to calculate the conductance of a biphenylene-based molecule with different chemical linkers between Au electrodes. Direct Au-C metal-molecule bonds were shown to be strong and highly-conducting [2,3]. We choose to study this molecule since it is expected that, at the gold surface, the biphenylene molecule forms stable Au-C bonds by breaking its relatively weak C-C bond. In this adsorption geometry the benzene rings are almost perpendicular to the surface. We then consider several linker groups at the other end of the molecule, which are contacted by a Au tip. In particular, we study pyridine (-C5H5N), amine (-NH2), methyl-sulfide (-SCH3) nitrile (-CN) and Au-C links and calculate the electronic and conducting properties across each of these junctions.

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POSTER Characterization of chemically synthesized nanocomposites obtained by methylpyrrole and/or pyrrole with ZrO2 nanopowder

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The polypyrrole/ZrO₂ (PP/ZrO₂), poly(methylpyrrole)/ZrO₂ (PMP/ZrO₂) and poly(methylpyrrole-copyrrole)/ZrO₂ (poly(MP-co-P)/ZrO₂) nanocomposites has been successfully prepared via a facile chemical polymerization method. Nanopowders (ZrO₂) were successfully coated with polymer through 'in-situ' chemical oxidative polymerization of pyrrole according to the procedure described elsewhere [1, 2]. X-ray diffraction analysis provides structural information. The pattern of nanocomposites (PP/ZrO₂, PMP/ZrO₂ and poly(MP-co-P)/ZrO₂) shows the corresponding broad peak with polymer and nanopowders. UV-vis and FTIR studies showed that the ZrO₂ particles affect the quinoid units along the polymer backbone and indicate strong interactions between ZrO₂ and quinoidal sites of organic material. The thermal degradation behavior of polymer in the nanocomposites has been investigated by thermogravimetric analysis. The weight loss suggests that the polymer chains in the nanocomposites are more thermally stable than pristine polymer. The electrochemical behavior of the polymers extracted from the nanocomposites has been studied by cyclic voltammetry. Good electrochemical response has been observed for polymer grown into nanoparticles, the redox processes indicates that the polymer obtained in these conditions is electroactive.

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POSTER When can the Landauer formalism reproduce time-dependent transport?

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Capturing electron transport events across molecular junctions subject to time-dependent forces or a fluctuating environment usually requires employing explicitly time-dependent techniques, such as TD-NEGF method [1], that effectively solve the time-dependent Schrödinger equation. Nevertheless, it is often desirable to approximate the time-dependent transport with steady-state techniques such as the Landauer formalism [2] by supposing that, even in the presence of time-dependent forces, the transport across the junction is in steady-state at each instant of time during the dynamics. Recently, the validity of this often-used strategy has been called into question in the context of simulations of transport through DNA in a solvent that indicate that the steady-state approximation can offer a qualitatively wrong description of the dynamics [3]. While the steady-state approach is clearly not expected to be quantitative under all modeling conditions, the practicality of the approach makes it desirable to understand the regime in which it can safely be used to model time-dependent transport phenomena.

In this work, we determine well-defined limits in which the time-dependent transport characteristics of molecules subject to a fluctuating environment can be quantitatively captured via the Landauer approach. To do so, we consider a two-level junction subject to correlated noise and contrast the time-dependent transport that results from an exact TD-NEGF method with that generated by supposing that the system is at steady-state at each instant in time. The global agreement between the two strategies is quantified by examining differences in the average currents obtained via the two methods. In turn, the ability of the steady-state approach to capture the TD-NEGF current at each instant of time is quantified by investigating the same-time correlation function of the currents obtained via the two methods. This criteria can be employed to establish an effective modeling strategy for time-dependent transport for molecules in interaction with a fluctuating environment.



Figure 1: Two level model with correlated noise.

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POSTER Electrons and phonons in phagraphene

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Recently, various carbon allotropes with sp^2 and sp^3 hybridization were predicted theoretically and some are candidates to show Dirac's cones [1-3]. Here we study the electron and phonon properties of one of these new allotropes of two-dimensional carbon called phagraphene, consisting of rings with 5, 6 and 7 atoms (Figure 1a) [4]. This stable structure is energetically relatively close to graphene compared to other allotropes of carbon due to its sp^2 hybridization and dense atomic packing. The existence of a Dirac cone distorted in the first Brillouin zone of this structure was shown by both density functional theory (DFT) and tight-binding calculations [4].

Our investigations are based on DFT as implemented in SIESTA [5]. Electron and phonon band structures (Figure 1b,c) and density of states are computed with a finite difference scheme using Inelastica [6]. With TranSIESTA [7] we further explore electronic transport through interfaces between phagraphene and graphene (Figure 1d).



Figure 1: a) Phagraphene structure in a 3×3 repetition of the 20-atom unit cell, b) Electron band structure revealing a Dirac cone at the Fermi energy, c) Phonon band structure, d) Example of an interface structure between phagraphene and graphene for transport studies.

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POSTER Artaios – a transport code for post-processing quantum chemical electronic structure calculations

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Driven by the idea of using molecules as electronic building blocks, the understanding of electron transport in molecular junctions is an important field of research. The state-of-the-art theoretical framework to investigate electron transport in the coherent regime is the Landauer–Imry–Büttiker approach [1].

We present our post-processing program Artaios [2], which is based on the Landauer approach in combination with the Green's function method [3]. Several quantum chemical electronic structure codes can be interfaced, or alternatively simple Hückel-type Hamiltonians can be post-processed. The program is capable of decomposing the transmission into local contributions (see Figure 1). The subsystem molecular orbitals can be obtained by solving the subsystems secular equations. Additionally, the program offers the possibility of calculating local spins by the Mayer local spin analysis scheme and Heisenberg exchange-spin coupling constants with a Green's function approach [4].

We incorporated several features to make user interaction as easy as possible: An easy-to-use define script can be used to setup and run transport calculations, and the program can be extended to read the output of other quantum chemistry codes.



Figure 1: Local transmissions through a meta-substituted phenyl ring at energies of -6.02 eV (left) and -7.04 eV (right).

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POSTER

Molecular rectifier composed of DNA with high rectification ratio enabled by intercalation

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The predictability, diversity and programmability of DNA make it a leading candidate for the design of functional electronic devices that use single molecules, yet its electron transport properties have not been fully elucidated. This is primarily because of a poor understanding of how the structure of DNA determines its electron transport. Here, we demonstrate a DNA-based molecular rectifier constructed by site-specific intercalation of small molecules (coralyne) into a custom-designed 11-base-pair DNA duplex. Measured current–voltage curves of the DNA-coralyne molecular junction show unexpectedly large rectification with a rectification ratio of about 15 at 1.1 V, a counter-intuitive finding considering the seemingly symmetrical molecular structure of the junction. A non-equilibrium Green's function-based model – parameterized by density functional theory calculations – revealed that the coralyne-induced spatial asymmetry in the electron state distribution caused the observed rectification. This inherent asymmetry leads to changes in the coupling of the molecular HOMO–1 level to the electrodes when an external voltage is applied, resulting in an asymmetric change in transmission.



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POSTER Will it conduct?

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In a recent paper [1], we have theoretically investigated the electronic properties of neutral and n- doped dangling bond (DB) quasi-one-dimensional structures (lines) in the Si(001):H and Ge(001):H substrates [2,3] with the aim of identifying atomic-scale interconnects exhibiting metallic conduction for use in on-surface circuitry. Whether neutral or doped, DB lines are prone to suffer geometrical distortions or have magnetic ground-states that render them semiconducting. However, from our study we have identified one exception – a dimer row fully stripped of hydrogen passivation. Such a DB-dimer line shows an electronic band structure which is remarkably insensitive to the doping level and, thus, it is possible to manipulate the position of the Fermi level, moving it away from the gap. Transport calculations demonstrate that the metallic conduction in the DB-dimer line can survive thermally induced disorder, but is more sensitive to imperfect patterning. In conclusion, the DB-dimer line shows remarkable stability to doping and could serve as a one-dimensional metallic conductor on *n*-doped samples.



Figure 1: Relaxed configuration of two different types of 1D lines on the Si/Ge(001):H substrate- color shows height of atom (black-red-orange- yellow-white). With the addition of one electron the "zigzag" pattern (A-B) undergoes distortion while the "dimer" pattern (C-D) retains its geometric and electronic structure (not shown).





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POSTER Electron-vibration signatures in transport characteristics of graphene nanoribbons

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Electron transport was recently measured across graphene nanoribbons (GNRs) suspended between a metal surface and the tip of a scanning tunneling microscope [1]. Such lift-off experiments of GNRs from the surface open the question about propensity rules of vibrational scattering for the traversing electrons in small GNR structures.

We performed first-principles simulations of inelastic electron tunneling spectroscopy (IETS) of long pristine and defective armchair and zigzag nanoribbons under a range of charge carrier conditions [2]. For the armchair ribbons we find two robust IETS signals around 169 and 196 mV corresponding to the D and G modes of Raman spectroscopy as well as additional fingerprints due to various types of defects in the edge passivation. For the zigzag ribbons we show that the spin state strongly influences the spectrum and thus propose IETS as an indirect proof of spin polarization.



Figure 1: (a) Generic setup for an armchair GNR with a suspended part (blue shaded region) bridging semiinfinite regions in which the ribbon is thought to be in contact with a metal substrate (red shaded region) not explicitly included in the simulation. (b) Computed IETS signal for the pristine armchair GNR as a function of the dynamical region (green shaded area). Adapted from [2].

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POSTER Probing changes in local dipole moments of non-covalently functionalized carbon nanotubes

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Non-covalent functionalization of carbon nanotubes (CNTs) is a useful strategy to modify and control the nanotube's electronic and transport properties, rendering them promising building blocks for designing nanoelectronic and optoelectronic devices [1].

In this work, we study the supramolecular interactions between CNTs and (among others) photoswitches using Kohn–Sham density functional theory (see Figure 1). To further clarify the involved chemical gating mechanisms, we will also present a generalized approach for the calculation of local electric dipole moments for fragments of molecular or supramolecular systems within the theory of atoms-in-molecules [2], and a new implementation in the program GenLocDip [3]. As origin-independence is achieved by relying on only few internal reference points, our approach is particularly suitable for fragments of large systems (e.g., molecules on surfaces) and may help to understand various phenomena in nanoscience, such as solvent effects on the conductance of single molecules in break junctions or the interaction between the tip and the adsorbate in atomic force microscopy.



Figure 1: Left: Schematic illustration of non-covalent functionalization of a carbon nanotube field-effect transistor. Right: Photoreactivity of diarylethene photoswitches. The photoswitches' dipole moments are indicated as red arrows pointing towards the negative part (δ –).

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POSTER Scanning tunneling microscopy current from localized basis orbital density functional theory

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We present a method capable of calculating elastic scanning tunneling microscopy (STM) currents from localized atomic orbital density functional theory (DFT) using the Siesta code. To overcome the poor accuracy of the localized orbital description of the wave functions far away from the atoms, we propagate the wave functions, using the total DFT potential. From the propagated wave functions, the Bardeen's perturbative approach provides the tunneling current. To illustrate the method we investigate carbon monoxide adsorbed on a Cu(111) surface and recover the depression/protrusion observed experimentally with normal/CO-functionalized STM tips. The theory furthermore allows us to discuss the significance of s- and p-wave tips.



Figure 1: Comparison of the calculated constant height STM image at 5.0 Å, computed by means of a) the propagated, and b) Siesta wave functions. Bottom panel shows the cross sections along the dashed lines.

POSTER Hopping conduction and inelastic effects in molecular wires via Buttiker probes

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We explore in-detail the Landauer-Buttiker probe (LBP) technique, a simple approach that can be used to simulate electronic conduction in molecular wires. With this technique, we can phenomenologically incorporate thermal/environmental effects at trivial additional cost while replicating key physical features of conduction [1]. To demonstrate the utility of the method, we recreate experimental conditions and semiquantitatively recover prior results to provide mechanistic information. Our simulations recover the following behavior: (i) exponential decay of conductance with molecular length, characteristic of the tunneling (superexchange) mechanism, transitioning to Ohmic-like conduction in long wires, (ii) a "Kramers-like" turnover in bath-assisted transport with respect to dephasing strength, (iii) thermal activation at high temperature, and (iv) significant fragility of on-resonance, finite bias conductance to dephasing. We also demonstrate the flexibility of the method by implementing memory (non-Markovian) effects through a structured environment.

We further extend the LBP technique into the high-bias regime and examine the role of inelastic effects on the operation of tunneling diodes [2]. We conclude that the environment has a negative impact on device efficiency, but that even with significant environmental interaction, the operation remains robust. Finally, we thoroughly explore the intrinsic differences between elastic and inelastic (dissipative) scattering methods in the near and on-resonance regimes [3], and comment on their appropriateness for simulations of molecular electronics.



Figure 1: Tunneling-hopping turnover of the conductance with finite dephasing strength.

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POSTER Speeding up G₀W₀ implementation

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Hedin's GW approximation (GWA) is a well established method of calculating the one-particle spectrum of electronic excitations. It provides a good starting point for the calculation of electron transport and optical excitation properties. A non-self-consistent version of GWA (so-called one-shot GW or G_0W_0) can be formulated via a one-particle Hamiltonian $\hat{a} \in$ " the fact which simplifies the computational burden significantly. This simplification practically does not reduce the value of ab-initio predictions, especially when G_0W_0 calculation is started from a closely related Hartree-Fock (HF) ground state. However, even simplest G_0W_0 calculation remains much more cumbersome than density-functional theory (DFT) or HF calculations due to the presence of so-called screened interaction (SI). From the other hand, the G_0W_0 calculations of large organic molecules and molecular crystals provide a valuable information as the quality of the electronic-structure predictions is comparable with the quantum-chemistry methods based on many-electron wave functions [1].

Recently, we realized several calculations within GWA including G_0W_0 , self-consistent GW, quasi-particle GW, all starting from the output of the DFT package SIESTA [2]. Due to an exclusive usage of real-space in representation of SI and an optimal product basis for representing SI, we were able to formulate a method with asymptotically $O(N^3)$ computational complexity, where N is number of atoms [3,4]. In this contribution, we discuss the recent advances in the method development of GWA. We are concerned now mostly with a practical walltime of execution of G_0W_0 calculation. This walltime can be drastically reduced i) using a contour deformation technique, ii) the availability of Lehmann representation for the non-interacting Green's function G_0 , iii) special product basis set optimized for the calculation of Fock-like operators. Moreover, for moderately large molecules containing several dozens of atoms, the runtime can be significantly reduced resorting to the $O(N^4)$ methods of computing the SI.

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POSTER Electrical resistance of metal-graphene edge-contacts

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Understanding the properties of electrical contacts between bulk materials, like metals, and nanoscale structures is very important for their use in a wide variety of nanotechnology applications. Particularly, contacts of bulk metals with graphene might be of relevance in fields like electronics and spintronics. While conventional graphene-metal surface contacts have been studied extensively, graphene-metal edge-contacts are a rather new construct. Various studies demonstrate the advantages of edge-contacts over surface contacts [1,2]. However, regarding the influence of the metal on the conductance properties of edge-contacts, contrary conclusions are reached: although simulations indicate that the contact resistance for graphene-metal edge-contacts is of the same order of magnitude for different metals [2], experiments reveal a strong metal dependence [1]. To explore the origin of the differences in the reported contact resistances, we carry out transport calculations using density functional theory (DFT) ombined with a non-equilibrium Green's functions (NEGF) approach, as implemented in the TranSIESTA code. Different metals, as well as different graphene edge conformations and passivations are considered. Our results, besides clarifying the above mentioned discrepancies, will offer insights towards control of the conductance properties of graphene-metal contacts deviating from ideal interfaces.

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POSTER Currents from field-driven leads in molecular junctions: the directional photo-electric effect

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The study of molecular junctions and the electronic transport through them combines theoretical and experimental efforts in aim to understand these complex non-equilibrium systems and to possibly utilize them in new technological applications. A main technical difficulty that stands in our way to understand these systems regards the dynamics time scale of the electronic and nuclear motion which is still far from the time scale in which standard tools for measuring the system operate. It is therefore desired to develop a new measurement tool that would be able to probe the molecular dynamics. One approach to such new measurements is to drive molecular junctions with external electromagnetic fields.

In this work we re-derived the theory of photo assisted transport through molecular junctions on the basis of the time-independent scattering theory for time-dependent Hamiltonians. General transport formulas for field driven leads are obtained beyond some of the limitations of Tien&Gordon's formula[1]. The new formulas are tested and compared to numerical simulations for model junctions. We studied the effect of the field's parameters on the current for ac-fields and for periodic pulses and predict a "directional photo-electric effect" with promising applications, where not only the magnitude, but also the direction of photo-assisted currents can be controlled by the driving field at a given static bias voltage, see Fig.1.



Figure 1: Photo-induced current versus field's intensity (a), for a two level molecule in a model junction, demonstrating a change of the current sign with the external field parameters.

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POSTER Simulation of charge transport in self-assembled monolayers for applications in field-effect transistors

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We study charge transport through self-assembled monolayers (SAMs), which are used in field-effect transistors [1,2], employing a combination of molecular-dynamics simulations, semiempirical electronic structure calculations [2] and Landauer transport theory. In particular, we investigate SAMs consisting of multifunctional molecules, where the active Π -system is linked to a flexible insulating alkyl-chain. Discussing the dependence of the transport properties on the layer composition and morphology, we find a close relation between the transport characteristics and the structural and electronic properties of the SAM [3]. For selected systems, we analyze pathways for efficient charge transport by examining local currents in the molecular layers [4]. The pathways are compared to those obtained using Metropolis Monte Carlo (MC) path searches [5]. In order to study the time-dependence of the preferred electron paths, we consider snapshots of a system selected at different times of the MD simulations. To further examine the influence of fluctuations on the transport properties, we utilize a time-dependent approach to charge transport based on time-dependent nonequilibrium Green's function (NEGF) theory [6]. This also allows for a more complete theoretical treatment, including dephasing processes.



Figure 1: Transmission path through C60 SAM.

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POSTER Time-dependent density-functional approach for exciton binding energies

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Optical processes in insulators and semiconductors, including excitonic effects, can be described in principle exactly using time-dependent density-functional theory (TDDFT). Ullrich and co-workers [1,2] adapted the Casida equation formalism for molecular excitations to periodic solids, which allows to obtain exciton binding energies in a direct way. However, in this type of calculations the problem always arises from the lack of proper long-range behavior of the exchange correlation kernels in general (xc). One of the kernels proposed to overcome this issue is the well known semi-empirical Long Range Kernel (LRC) $fxc(r,r')=-\alpha/|r-r'|$ but its integrable singularity at r=r' as well as the slow decaying rate, need special attention particularly for periodic solids.

Recently, Sundararaman and Arias [3] developed an original method based on the Minimum Image Convention (MIC) [4] in which Coulomb type interactions are truncated on Wigner-Seitz super-cells for the calculation of exchange energies. We have implemented this numerical scheme for the direct calculation of exciton binding energies of various small- and large-gap semiconductors, as the earlier mentioned Casida formalism, resembles Fock type exchange integrals. We show preliminary results.

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POSTER Accurate classical force field for non-reactive metal-molecule interactions

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Metal-molecule interactions play a determining role in molecular electronics experiments. Accurately capturing such interactions is essential in realistic simulation of state-of-the-art experiments. In particular, to obtain the statistical distribution of single-molecule events that occur in break-junction experiments, it is necessary to develop accurate and computationally inexpensive strategies that capture these essential interactions. In this paper, we introduce a transferable classical force field (FF) for non-reactive metalmolecule interactions that achieves the accuracy of high-level electronic structure methods at the cost of a classical FF computation. Specifically, the FF is composed of van der Waals (vdW) interactions, an image-charge electrostatic potential and a short-range component, and consist of just two adjustable parameters per atom type-metal pair. The simplicity of the approach is achieved by adapting recent developments [1,2] in the accurate description of vdW interactions using DFT into a classical FF. In this way, the vdW component of the FF is obtained from first-principles, and only the short-range part of the adsorption curve needs to be captured by adjustable parameters. An initial parameter set is developed via the class of planar conjugated molecules physisorbed on Au(111) shown in Figure 1. The force field is demonstrated to reproduce the adsorption profile of this class of molecules within 0.05 eV of the one obtained via DFT+vdW methods. This force field can be employed in the classical molecular dynamics simulation of the formation and evolution of molecular junctions.



Figure 1: Three conjugated molecules adsorbed on Au(111) surfaces used for the development of the classical FF. The molecules are (A) Benzene, (B) Diindenoperylene, and (C) Perylene-3,4,9,10-tetracarboxylicdianhydrid (gold atoms are in pink, carbon in black, oxygen in red, hydrogen in light-gray).

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POSTER Modeling of excitons in bulk rutile and the pentacene monolayer on TiO₂ (110)

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We modeled bulk rutile and the full monolayer of pentacene adsorbed on rutile TiO_2 (110) with density functional theory and computed their optical properties by solving a parametrized Hamiltonian that include the electron-hole interaction and the matter-field coupling. In bulk TiO_2 we include quadrupole and magnetic dipole matrix elements that we find necessary to reproduce the experimental line shape of the Γ -point exciton. Density functional theory modeling of the pentacene monolayer on TiO_2 (110) reveals a lying down, head-to-tail configuration of the molecules, with new localized states appearing in the band gap. The computed optical response shows charge transfer excitations directly from the molecular HOMO to the first TiO_2 conduction bands. Exciton wave functions and binding energies are shown to be highly dependent on the dielectric screening used in the calculation.

POSTER Modeling elastic charge transfer times including the effect of structural fluctuations at hybrid organic-semiconductor interfaces

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Realistic descriptions of charge transfer processes at hybrid organic-semiconductor interfaces for photovoltaic applications take into account the atomic motions of adsorbates and substrates at finite temperatures. Here we present an extension of our first-principles scheme [1,2] for the extraction of elastic linewidths to model the effects of such structural fluctuations. Based on snapshots obtained from Car-Parinello molecular dynamics simulations at room temperature [3], we set up geometries in which dye molecules at interfaces are attached to a semi-infinite TiO₂ substrate. We compute elastic linewidths using a Green's function method [1]. This effectively introduces the coupling to a continuum of states in the substrate. In particular we investigate the system of isonicotinic acid on rutile(110) at the level of semi-local density functional theory. We perform multiple calculations of linewidths and peak-positions associated with the adsorbate's frontier orbitals for different geometric configurations to obtain a time-averaged analysis of such physical properties. To test our theoretical model we compare our results to previously conducted core-hole clock experiments [4]. For this comparison it is necessary to include the excitonic effect in the simulation of the electronic structure. We systematically assess structural parameters affecting the interfacial charge transfer and investigate the dependence of the extracted elastic lifetimes on the relative alignment between adsorbate and substrate states.

This project has received funding from the European Union's Seventh Framework Programme under grant agreement no. 607323 [THINFACE].

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POSTER Application of dephasing models to molecular wires

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We present the application of a phenomenological dephasing models based on a Non Equilibrium Green's Function formulation of electron-phonon interactions in the elastic limit. The model is applied on model hamiltonians representative of oligomers and pi-stacked wires or in combination with the Density Functional Tight Binding based DFTB+NEGF code [1,2]. We show that the processes trigerred by dephasing such as transport regime transitions, suppression of localization and diffusive transport are captured, but we will also discuss the limitations of such a simplified model. At the DFTB level, we present simulation on Quantum Interference (QI) cross-conjugated molecular wires [3]. We demonstrate a modulation of QI effects compatible with experiments and confirm the robustness of QI signatures with respect to dephasing. An analysis of the spatial localization of the dephasing process reveals that both the QI and the dephasing process are localized in the AQ region, hence justifying the general robustness of the transmission temperature dependence in different AQ based systems. The implementation in the open source library libNEGF ans possible applications are also discussed [4].

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POSTER Plasmonic response of metallic nanojunctions driven by single atom motion: quantum transport revealed in optics

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The correlation between transport properties across sub-nanometric metallic gaps and the optical response of the system is a complex effect that, similarly to the near-field enhancement [1], is determined by the fine atomic-scale details of the junction structure. Using ab initio calculations, we present here a study of the simultaneous evolution of the structure and the optical response of a plasmonic junction as the particles forming the cavity, two Na₃₈₀ clusters, approach and retract. Atomic reorganizations are responsible for a large hysteresis of the plasmonic response of the system, which shows a jump-to-contact instability during the approach process and the formation of an atom-sized neck across the junction during retraction. Our calculations show that, due to the quantization of the conductance in metal nanocontacts, atomic-scale reconfigurations play a crucial role in determining the optical response. We observe abrupt changes in the intensities and spectral positions of the plasmon resonances, and find a one-to-one correspondence between these jumps and those of the quantized transport as the neck cross-section diminishes. These results point out to an unforeseen connection between transport and optics at the atomic scale, which is at the frontier of current optoelectronics.



Figure 1: Left panel: Evolution of the resonances in the imaginary part of the polarizability as a function of the junction size. Due to the spontaneous formation of a metal neck across the nanojunction, we can observe a characteristic charge transfer plasmon (CTP) mode all the way up to ~30 Å nominal separations. The inset shows the electric current flowing through the junction (at the frequency of the CTP resonance), and the evolution of the cross-section of the neck. There is a one-to-one correspondence between the jumps observed in the current, in the neck cross-section and in the far-field optical response of the plasmonic cavity. Right panels: Structure of the system at the separations indicated as (a), (b) and (c) in the left panel. Imaginary part of the induced electronic charge distribution at the CTP resonance frequency for each of the configurations is also plotted (different colors indicate charge accumulation and charge depletion).

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POSTER Multi-scale modeling of spin transport in organic semiconductors

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Since the discovery of magnetoresistance in organic spin-valves [1], organic spintronics has been an active area of research. Organic semiconductors (OSC) show great potential for applications in next generation electronic devices due to their weak spin-orbit coupling and hyperfine interactions which leads to much longer spin life times when compared to their inorganic counterparts.

In this work, we present our development based on the VOTCA [2] toolkit for charge transport of a multi-scale modeling framework for spin transport in bulk organic materials.

By combining several techniques e.g. molecular dynamics, density functional theory and kinetic Monte Carlo, we are able to study spin transport by including thermal effects, magnetic and electric field effects in realistic morphologies of amorphous organic systems. We apply our multi-scale approach to investigate the spin transport in amorphous Alq3 [Tris(8-hydroxyquinolinato)aluminum] and address the underlying spin relaxation mechanism in this system as a function of temperature.



Figure 1: Realistic morphology of an amorphous Alq3 sample used to calculate the charge and spin dynamics.

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POSTER Electronic transport in B-N substituted bilayer graphene nanojunction

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We investigated a suspended bilayer graphene [1] where the bottom/top layer is doped by boron/nitrogen substitutional atoms. By using density functional theory calculations, we found that at high dopant concentration (one B-N pair every 32 C atoms) the electronic structure of the bilayer does not depend on the B-N distance but on the relative occupation of the bilayer graphene sub-lattices by B and N. The presence of the dopants and the consequent charge transfer establish a built-in electric field between the layers, giving rise to an energy gap [2].

We further investigated the electronic transport properties using the TranSIESTA code [3], which combines the non-equilibrium Green's function (NEGF) technique with DFT. We found that intra-layer current is weakly influenced by the presence of these dopants while the inter-layer one is enhanced for biases allowing an easy tunneling between layers. In order to study the role played by the dopants on the inter-layer current, we also consider a $\hat{a} \in \hat{c}$ eshingle $\hat{a} \in \hat{c}$ nano-junction where the contact is made by overimposing the terminations of two semi-infinite H-terminated graphene layers. The contact region is hence constituted by partial overlap of doped graphene flakes. In this case the electron current can only flow from one graphene layer to the other, overcoming an energy barrier represented by the vacuum region in between the two flakes. This system breaks the left-right symmetry and can behave like a p-n nano-junction.



Figure 1: Eigenchannels at the Fermi level for the doped "shingle" nano-junction (left panel) and for the corresponding undoped case (right panel). The applied bias is -1.5 V.

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POSTER Temperature effects on orthorhombic GeS

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Group IV chalcogenides such as GeS, SnS, SnSe and GeSe, possess layered crystalline structures that resemble the one of black phosphorus (BP). In contrast to BP, they possess band gaps that cover the energy window from 0.9 to 1.7 eV which make them attractive for a number applications. For instance, recently SnSe has been proposed as an promissory material for thermoelectric applications as high figure of merit (ZT >2) have been found, at specific conditions of temperature and crystal orientation [1]. In addition, GeS and SnS the largest band gap among the chalcogenides, possess promising features as absorber materials and could be integrated in the design of high efficient photovoltaic cells [2]. Thus, the correct understanding of temperature on the electronic and optical properties of these chalcogenides is necessary to provide further insights regarding their applicability in photovoltaics.

In this work, we study the temperature effects on the electronic and optical properties of orthorhombic GeS. The temperature effects on the electronic states are treated in an ab-initio way within the Many-Body Perturbation Theory (MBPT) framework. There, the electron-phonon coupling which is composed by the first and second order Taylor expansion in the nuclear displacement, is treated perturbatively. Our results indicates a zero-point energy motion of ~ 36 meV. In addition, by combining the electron-phonon linewidth with the excitonic effects, we are able to study the optical absorption at finite temperatures. Our results for optical absorption are compared with ellipsometric measurements showing excellent agreement.

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POSTER Switching the conductance of graphene-molecule junctions by proton transfer

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The possibility of using single molecule junctions as components of nanoelectronic devices has motivated intensive experimental and theoretical research on the conductance properties of these systems. Recently, it has been suggested that it is possible to switch the conductance of a molecular junction by means of a proton transfer reaction triggered by an external electrostatic field [1,2]. Specifically, it has been shown that a molecular bridge, which exhibits two tautomeric forms with different conductance, can realize the "on" and "off" states of the switch. An external electrostatic field can be used to control the state of the junction in a reversible way. In this contribution, we analyze the detailed mechanism of the switching process in a molecular junction that uses graphene as material for the electrodes. Using density functional theory, we characterize the reaction path of the concerted and step-wise proton transfer processes and analyze how these different theory and the non-equilibrium Green's function method [3] show the different conductance properties of the two states of the switch (see Fig. 1) and explain how they emerge from the electronic structure of the molecule.



Figure 1: Current-voltage characteristics for the different junctions investigated (the two insets at the top show the low and high conducting forms of the molecular bridge).

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