Invited talk

Interaction of π-electron systems with magnetic surfaces

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The density functional theory provides a framework with predictive power that can be used to describe organic-metal hybrid systems in a realistic manner. In this respect, ab initio studies elucidate how the subtle interplay between the electrostatic, the weak van der Waals and the strong chemical interactions determine the geometric, electronic and magnetic structure of hybrid organic-metal interfaces. More precisely, the interaction between the π-like electronic cloud of organic materials with the magnetic states of a metal influences the (i) spin-polarization, (ii) magnetic exchange coupling, (iii) magnetic moments and (iv) their orientation at the hybrid interfaces. In this talk I will briefly summarize how first-principles calculations (i) provide the basic insights needed to interpret surface-science experiments and (ii) are a key tool to design novel materials with tailored properties that can be integrated in carbon-based spintronic devices.

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Invited talk

Novel Wave Function Approaches to both Extended and Finite Correlated Molecular Systems

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A prerequisite requirement of treating molecular spintronic systems is first being able to adequately treat the (sometimes large number of) strongly correlated degrees of freedom present in the system. In this regard, we will describe some of the techniques we are working on, in order to push quantum chemical wave function-based techniques to these larger systems, by introducing a novel stochastic algorithm in Fock space. This is also extended to spin-gaps, and heavy relativistic systems within a four-component framework, allowing for up to 50 explicit correlated degrees of freedom to be treated.

A second requirement, to extend the approach towards transport in spintronic devices, is to couple the system to a wider external environment. This has been tricky to do within wave function theory, and the dominant approach in recent years has been within Green function techniques, primarily Dynamical Mean Field Theory (DMFT). We will show how the accuracy and scope of DMFT can be systematically approached within a wave function setting, allowing for numerous benefits, including an algebraic, finite-sized mapping from the original system, and the admission of cheap, wave function-based solvers. This seamlessly merges wave function theory and the strong-coupling embedding theory of DMFT in a systematically improvable fashion.

Mechanically-tunable charge transport in ferrocene-based molecular junctions

María Camarasa-Gómez[1], Daniel-Hernangómez-Pérez[1], Giacomo Lovat[2], Michael S. Inkpen[2,] Latha Venkataraman[2], Ferdinand Evers[1]

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Ferrocene derivatives are well-known organo-metallic compounds [1]. Inspired by recent scanning-tunneling break junctions measurements, we present a density functional theory (DFT) based quantum transport (non-equilibrium Green's function formalism - NEGF) study. Our results suggest that ferrocene-derived species show interesting quantum interference properties. For example, we find mechanically-tunable (Fano-type) resonances related to the metal core d-states. These anti-resonances can change the conductance at the Fermi level by orders of magnitude in a relatively controlled manner.

In the second part, we present a self-consistent DFT-NEGF implementation for FHI-aims [2] building on the AITRANSS package [3]. Further, we propose how to extend this scheme in order to incorporate spin-orbit coupling effects in non-periodic systems. The goal of this extended self-consistent scheme will be to address, from first-principles, current induced forces on local magnetic moments. A specific goal will be to calculate spin-orbit torques [4-7].

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Invited talk

Multiconfigurational electronic structure methods applied to spin anisotropy and excited state deactivation

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The excellent price-quality ratio of density functional theory (DFT) makes this computational scheme often the best choice to study phenomena related to magnetic interactions in systems with unpaired electrons. However, there are several cases where the intrinsic monodeterminantal character of Kohn-Sham DFT severely hinders the correct description of the electronic structure. Typical examples are the transition metal complexes with (nearly) degenerate ground states or electronically excited states in spin crossover systems. In this contribution, we will focus on how multiconfigurational second-order perturbation theory can be used to describe magnetic anisotropy in mono- and dinuclear complexes and to what extent these calculations can help to understand the mechanisms for deactivation of excited states in systems that show light-induced magnetism.
After giving a short background on the technical details of the computational methods, an ab initio procedure will be presented to extract magnetic anisotropy parameters such as the axial and rhombic zero-field splitting, g-tensor, and the magnetic axes frame. Results are compared to experimental data and the validity of the commonly used model Hamiltonians will be checked [1]. The second part will be dedicated to the detailed description of the decay mechanism of the excited singlet state in Fe(II)-trisbipyridine. This complex has been studied in great detail in many experiments resulting in some partially contradictory interpretations concerning the fate of the excited state. Our calculations apparently resolve these issues and give an interpretation of the experimental data that is probably valid for a large variety of transition metal complexes with light-induced magnetic properties [2,3].

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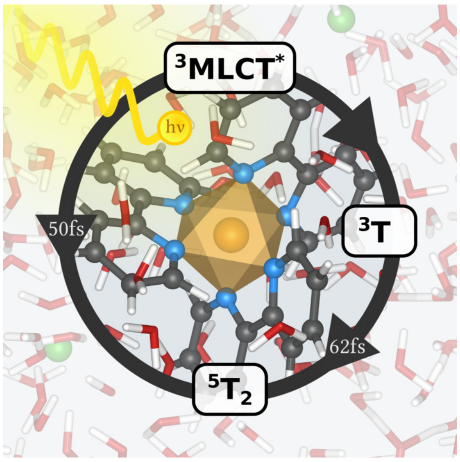

Schematic representation of the two different deactivation pathways for the excited state in Fe(II)-polypyridyl complexes.

Apparent Reversal of Molecular Orbitals Reveals Entanglement

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Scanning Tunnelling Microscopy (STM) is an excellent technique to study and manipulate matter at the nanoscale, as for example single molecules deposited on metallic surfaces. Simultaneous acquisition of spectral and spatial information about the molecule is achieved by scanning with the tip and sweeping the bias voltage across the junction. In carefully designed junctions, several electronic eigenstates of the molecule - the molecular orbitals - can be clearly identified and visualized. Moreover, most intriguing effects in single molecule transport originating from quantum interference [1] or electron correlation [2] leave their fingerprint in STM experiments.

In this talk I will address the frontier orbital sequence of individual dicyanovinyl-substituted oligothiophene molecules. On NaCl/Cu(111), the molecules are neutral, and the two lowest unoccupied molecular orbitals are observed in the expected order of increasing energy. On NaCl/Cu(311), where the molecules are negatively charged, the sequence of two observed molecular orbitals is reversed, such that the one with one more nodal plane appears lower in energy. These experimental results, in open contradiction with a single-particle interpretation, are explained by a many-body theory [3] predicting a strongly entangled doubly charged ground state.

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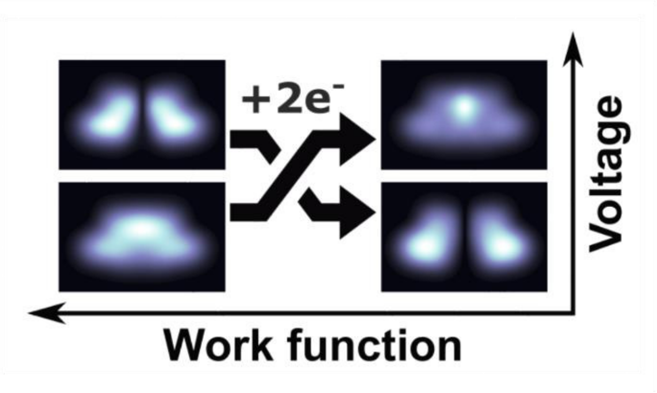

Figure Apparent reversal of the order of the lowest molecular orbitals of a dicyanovinyl-quinquethiophene upon variation of the substrate work function.

Invited talk

Spin interactions, excitations and fluctuations in magnetic adatoms and small clusters from first-principles

Manuel dos Santos Dias[1], Julen Ibañez-Azpiroz[2], Mohammed Bouhassoune[1], Stefan Blügel[1],
Hung The Dang[3], Benedikt Schweflinghaus[1], and Samir Lounis[1]

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Single atoms are the smallest possible magnets, of interest for fundamental physics and of great promise for technological applications. When assembled on a surface, their properties can be probed and manipulated via scanning tunneling microscopy (STM) and inelastic scanning tunneling spectroscopy (ISTS). However, the theoretical description is challenging, due to the interplay between the reduced dimensionality, the interactions driving the magnetism, and the coupling to the surface. Furthermore, an accurate description of the low-energy physics due to the spin-orbit interaction and external magnetic fields is essential.

We have recently developed a hierarchical theoretical approach to the static and dynamics properties of surface-supported magnetic nanostructures. The materials-specific information is supplied by density functional theory (DFT), which gives access to ground-state magnetic properties and magnetic interactions. The dynamics of the magnetic moments follows from time-dependent DFT (TDDFT), accounting for the impact of the surface electrons on the spin dynamics. The final level of theory addresses many-body effects, either through many-body perturbation theory (MBPT) or by solving a multi-orbital Anderson impurity model with quantum Monte Carlo, yielding realistic inelastic transport spectra.

In this talk I will present an overview of these theoretical methods while focusing on concrete physical systems: magnetic adatoms and small clusters on metallic surfaces, such as Cu(111) or Pt(111), in close connection with the available experimental information. Different magnetic adatoms on the same surface have very different static and dynamic properties [1-3], which influence their magnetic stability via zero-point spin fluctuations [4-6], while their tunneling spectra are only adequately described in MBPT [7-9]. The interactions between magnetic adatoms depend not only on their separation but also on their arrangement with respect to the surface, leading to widely different properties of apparently similar clusters [10-12]. I conclude by discussing the possible shortcomings and future research directions.

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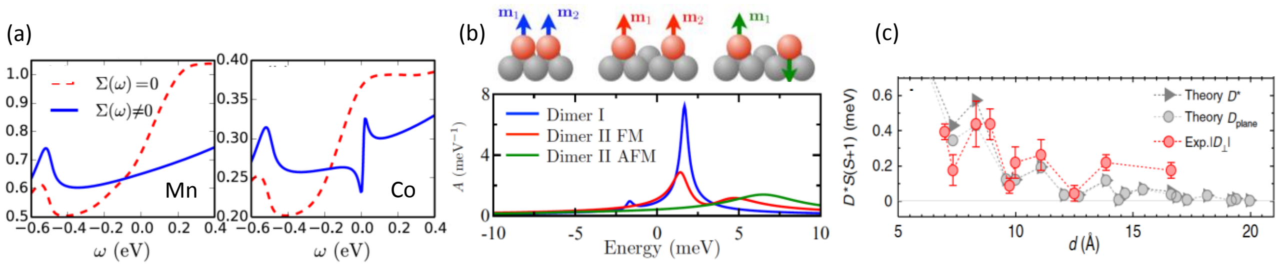

Theory of nanoscale systems. (a) On Cu(111), a Co adatom shows a Fano profile in ISTS, while a Mn adatom is featureless. (b) Fe dimers on Cu(111) in different arrangements display very different spin excitation characteristics. (c) Fe dimers on Pt(111) experience the chiral Dzyaloshinskii-Moriya interaction.

Invited talk

Charge transport in graphene nanoribbons: ab-initio simulations and model studies of strong correlations

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Transport properties of graphene nanoribbons have attracted a considerable attention ever since the advent of graphene. Indeed, they offer an exiting laboratory to study many fundamental aspects of transport physics. This talk is discussing three recent and partially striking examples. (i) Graphene nanoribbons functionalized with hydrogen exhibit a local current flow, which is strongly inhomogeneous. In particular, the local currents exhibit a pronounced tendency to form eddies with current densities exceeding the average by orders of magnitude. [1] (ii) The chemical environment of carbon atoms, which bind to hydrogen, is highly asymmetric. As a consequence, the spin-orbit interaction is locally enhanced and spin-flip scattering is significant in transport processes. [2] (iii) Very narrow ribbons (oligoacenes) exhibit an unusual band-structure with a linear (“Dirac-like”) crossing at incommensurate wavevectors. As a consequence, the transmission of oligoacene wires is non-monotonous. In fact, with increasing wire length, N, it is expected to exhibit very strong oscillations with period larger than 10 unit cells. [3]

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Invited talk

The relation between the electric current and magnetic interactions in molecular junctions

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Utilizing the possibility to electrically and thermally control the magnetic exchange, Figs. 1 (b) – (e), interactions between localized magnetic moments [1,2], we here present results regarding the charge and heat transport properties in dimer comprising, for example, paramagnetic molecules, see Fig. 1 (a) for schematics. We consider both charge, Fig. 1 (f), and heat, Fig. 1 (g), transport under non-equilibrium conditions imposed using voltage bias and temperature difference across the junction [3]. Generic properties for both transport quantities are reduced currents in the magnetically active regime compared to the inactive, or, paramagnetic, and efficient current blockade in the anti-ferromagnetic regime. In contrast, while the charge current is about an order of magnitude larger in the ferromagnetic regime, compared to the anti-ferromagnetic, the heat current is efficiently blockaded there as well [3]. This disparate behavior of the heat current is attributed to current resonances in the ferromagnetic regime which counteract the normal heat flow. It can also be noted that the temperature difference has a strongly reducing effect of the exchange interaction, which tends to destroy the magnetic control of the transport properties. The upside of the weakened exchange interaction is a possibility to tune the system into thermal rectification, for both the charge and heat currents.

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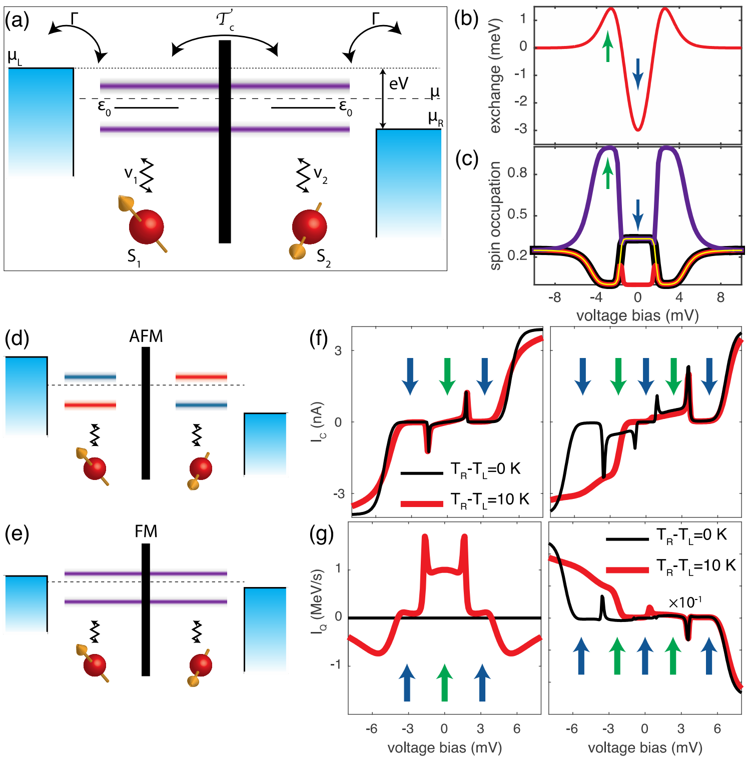

Invited talk

Density matrix renormalization group (DMRG) based methods for strong correlation and spin-state problems

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The density matrix renormalization group (DMRG) [1] applied to the full Coulomb Hamiltonian [2, 3] and post-DMRG methods have shown very promising advances in the accurate description of the electronic structure and properties of molecules with strong correlation, in particular of transition metal complexes.

This contribution will present an overview of DMRG and post-DMRG correlated methods and techniques such as second-order perturbation theory with Cholesky decomposition of two-electron integrals [4] and matrix product state interaction [5] which allow for a quantitative description of energies, spin densities[6, 7] and other properties of open-shell and other strongly-correlated systems such as heavy element compounds, spin-crossover complexes and complexes with non-innocent ligands. Moreover, wavefunction entanglement information [8] obtained from a DMRG wavefunction and its application to automated active orbital space selection in multiconfigurational methods [9] will be discussed.

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Invited talk

SU(2) x SU(2) Kondo effect in carbon nanotubes

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Entangled spin and orbital degrees of freedom in many-body systems are at the hearth of the Kondo effect. In particular, carbon nanotubes offer the possibility to study the emergence of the Kondo entanglement by tuning electron correlations with a gate voltage. In this case, we demonstrate that the combination of Coulomb interaction, spin-orbit coupling, and valley mixing results in a particular selection of the inelastic virtual processes contributing to the Kondo resonance at low temperatures. This effect is dictated by conjugation properties of the underlying carbon nanotube spectrum at zero and finite magnetic field. The analytic theory is developed by using the Keldysh effective action approach to the non-equilibrium Kondo problem. The main results are finally compared to experiments by the group of K. Kobayashi (Osaka University) and they are found to well reproduce all observations.

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Invited talk

Inchworm Quantum Monte Carlo for real-time dynamics

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We present real-time inchworm quantum Monte Carlo results for single-site dynamical mean field theory on an infinite coordination number Bethe lattice. Our numerically exact results are obtained on the L-shaped Keldysh contour and, being evaluated in real-time, avoid the analytic continuation issues typically encountered in Monte Carlo calculations. Our results show that inchworm Monte Carlo methods have now reached a state where they can be used as dynamical mean field impurity solvers and the dynamical sign problem can be overcome. As non-equilibrium problems can be simulated at the same cost, we envisage the main use of these methods as dynamical mean field solvers for time-dependent problems far from equilibrium.

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Invited talk

Accelerating discovery of new spin crossover materials with machine learning and alternative DFT approaches

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Accurate prediction of spin-state ordering in open-shell transition-metal (TM) catalysts is necessary for functional materials. Semilocal approximations in density functional theory (DFT), such as the generalized gradient approximation (GGA), suffer from delocalization error that causes them to overstabilize low spin states. Descriptions of energetics and bonding are often improved by introducing a fraction of exact exchange (e.g., erroneous low-spin GGA ground states are instead correctly predicted as high-spin with a hybrid functional). Nevertheless, comparison to high-level quantum chemistry (e.g., CASPT2) has revealed that the optimal functional varies across reaction coordinates and with ligand chemistry in transition metal complexes[1,2]. We have also shown that spin splitting and its sensitivity to incorporation of exact (i.e., Hartree-Fock) or higher-rung (i.e., meta-GGA) exchange can be predicted based on knowledge of the geometric and electronic structure of the spin states being compared[2-4]. We have trained artificial neural network (ANN) machine-learning models to predict spin state ordering within 3 kcal/mol of DFT energetics in a matter of seconds as well as the sensitivity of those predictions to varying the functional[4]. I will discuss how we have used these ANN models in conjunction with genetic algorithms to discover new spin-crossover complexes from thousands of candidate molecules in seconds[5]. Time permitting, I will also describe how we have revisited DFT+U-style model-Hamiltonian functional corrections to semi-local DFT to instead aim to recover conditions that eliminate delocalization error without increasing static correlation error[6].

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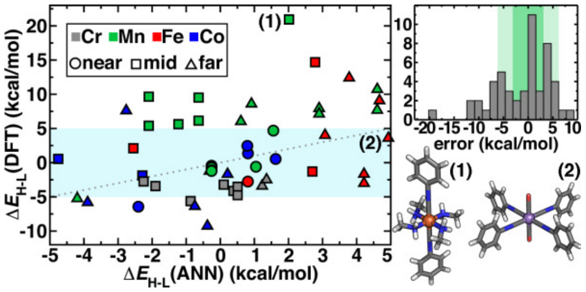

Figure 1 Example of spin-state ordering prediction with an ANN vs. DFT calculations.

Invited talk

Theory of Chiral Induced Spin Selectivity

Per Hedegård[1], Sakse Dalum[1]

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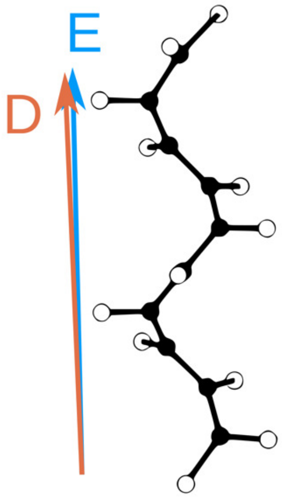
[2] *Affiliation*

We present a comprehensive theory of the CISS effect. The Büttiker-Onsager relation is generalized and it reveals that close attention needs to be paid to the precise experimental setup. Spin-orbit coupling, though weak for organic molecules, is the essential physical ingredient. We further discuss the dependence on size of molecule and temperature.



Invited talk

Chemical approaches to the Kondo effect

Marc Philipp Bahlke[1], Carmen Herrmann[1]

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The Kondo effect is a highly interesting manifestation of strong electron correlation, which results in a zero-bias conductance anomaly for spin-polarized adorbates on metal surfaces, owing to the formation of a singlet state below a certain temperature. This temperature can be controlled not only by the chemical nature of adsorbate atoms and metal substrate, but also by other chemical variations of the adsorbate, such as the number of ligands [1] (see also Figure 1). These variations may cause, e.g., changes in adsorbate—surface distances [2] or changes in the electronic interaction between unpaired adsorbate spins and substrate. Our goal is to gain insight into the relationships between such chemical modifications and Kondo properties, employing density functional theory (DFT) and DFT++ techniques [3].

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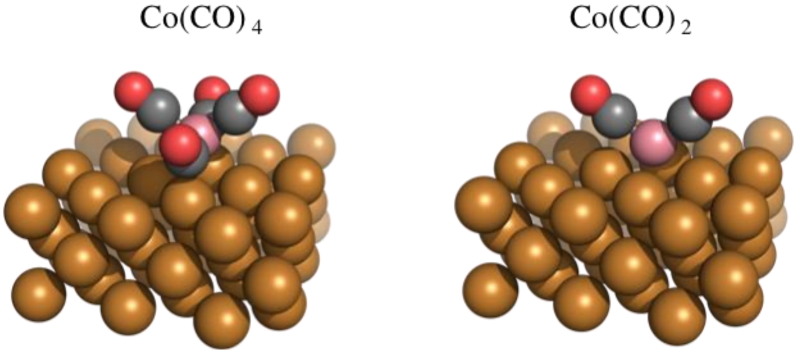

Figure 1: $Co(CO)_4$ and $Co(CO)_2$ molecules on Cu(100) as obtained from density functional theory (PBE).

Invited talk

Transport signatures of complex nanoscale magnets from NanoDMFT

David Jacob[1,2]

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Nanoscale magnets can now be built by depositing magnetic atoms or molecules on conducting substrates and be probed by transport spectroscopy using a scanning tunneling microscope (STM). This offers the unique possibility to study the interaction of single spins with their environment, the interaction between spins, and the emergence of collective behavior. Their electronic, magnetic and transport properties are often strongly affected by electronic correlations, leading e.g. to Coulomb blockade, Kondo effect and inelastic spin flip excitations. At the same time atomistic details also play a crucial role in determining the properties of nanoscale magnets. Thus in order to gain a profound understanding of these often very complex systems and to predict their properties, it is necessary to rely on *ab initio* calculations that take into account the atomistic details of the actual device.

However, electronic correlations are notoriously difficult to account for in density functional theory (DFT) methods. The NanoDMFT method [1,2] combines DFT based quantum transport calculations with more advanced many-body methods, namely impurity solver techniques and Dynamical Mean-Field Theory (DMFT), for treating the dynamic correlations originating from the strongly interacting electrons in open d- or f-shells of transition metal or rare earth elements. Using the NanoDMFT method it is possible to describe the Kondo effect and spin-flip excitations in the *equilibrium* spectral function of nanoscale magnets. In order to compute the transport characteristics requires in principle to solve the many-body problem out of equilibrium, which is computationally very demanding, and in practice limited to 1-2 correlated orbitals [2]. Instead one can make use of approximations for calculating the low-bias differential conductance spectra. While the zero-bias anomaly in the STM spectra due to Kondo effect is very well described within the *phase coherent approximation* [1], inelastic spin-flip excitations are not properly described. On the other hand, the *ideal STM limit* [5,6] yields a good description of the step features associated with inelastic spin-flip excitations in the STM spectra, but neglects quantum interference effects in the tunneling that ultimately determine the actual lineshape of the Kondo zero-bias anomaly [6]. A faithful description of both phenomena in the STM spectra of nanoscale magnets can be obtained by combination of both approaches. The approach is applied to investigate the case of complex spin formation in the case of an Fe porphyrin molecule on the Au(111) surface [7].

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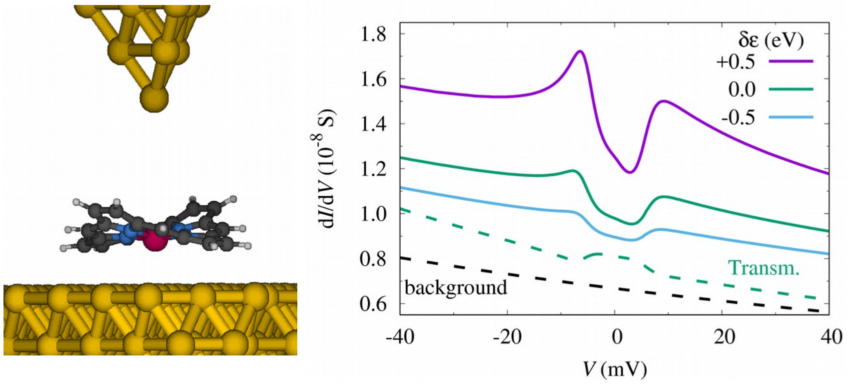

Figure (from Ref. 6). Left: Atomistic model of Fe porphyrin molecule on Au (111) substrate probed by an STM tip. Right: Calculated dI/dV spectra in the ideal STM limit (full lines), and in the phase coherent approximation (dashed green line).

Invited talk

Manifestations of a coherent Kondo lattice formed in adatoms

Richard Korytár

Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic

Nano-scale and molecular systems offer new realizations of correlated phenomena in the Coulomb blockade regime. In the first part, I will discuss a molecular pseudo-Kondo peak, which reveals a subtle low-energy scale of the molecule. In the second part I will explore the route of a bottom-up construction of a Kondo lattice, formed e.g. from ad-atom chains on a surface. Many-body calculations allows to address diverse real-space aspects of the chain, such as: overlapping Kondo clouds, long-range mediated hybridization and Fermi surface effects. The onset of heavy fermions in these systems will be discussed. The results provide a satisfactory explanation of the recent STM measurements [1].

[1] Real-space manifestations of coherent screening in atomic scale Kondo lattices, *in preparation,* 2018 M. Moro-Lagares, R. Korytár, M. Piantek, R. Robles, N. Lorente, J.I. Pascual, M.R. Ibarra and D. Serrate

Invited talk

Steady-State Density Functional Theory: from Differential Conductances to Many-Body Spectral Functions

Stefan Kurth[1,2,3]

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We present a formalism within the framework of density functional theory (DFT) to describe electronic transport through correlated systems in the steady state which uses the density on the junction and the steady current as basic variables [1]. In this formalism, called i-DFT, both density and current of the interacting system can be reproduced through a fictituous non-interacting system, the Kohn-Sham system, which features two exchange-correlation (xc) potentials. Both xc potentials, a local xc potential and an xc contribution to the bias, are universal functionals of the basic variables. For weakly coupled junctions the xc potentials exhibit steps in the density-current plane which are shown to be crucial to describe Coulomb blockade at finite bias.

A recent parametrization [2] of the xc potentials for the single-impurity Anderson model correctly incorporates both the Kondo and Coulomb blockade regimes, i.e., both zero and finite temperature. This parametrization allows for calculation of currents and differential conductances at arbitrary bias and temperature at negligible numerical cost but with the accuracy of sophisticated renormalization group methods.

The proposed formalism can also be used to extract the many-body spectral function of an interacting many-electron system within a DFT framework in a two-step procedure [3]. The first step is a standard DFT calculation for the ground state of the system. In the second step we employ i-DFT in a special setup which may be viewed as an idealized scanning tunneling microscope (STM): one of the electrodes serves as a probe (``STM tip") weakly coupled to the system. In the limit of vanishing coupling, the system is restored to quasi-equilibrium and the normalized finite-bias differential conductance yields the exact equilibrium many-body spectral function. Using i-DFT to calculate the differential conductance, we derive an exact relation expressing the interacting spectral function in terms of the Kohn-Sham one. We illustrate our scheme by application to non-trivial model systems.

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Invited talk

Nanospintronics and quantum thermodynamics in molecular magnets

G. Lefkidis and W. Hübner

Technische Universität Kaiserslautern and Research Center OPTIMAS, Box 3049, 67653, Kaiserslautern, Germany

As current computer technology advances rapidly, the conventional semiconductor-based technologies are slowly reaching their physical limits with respect to both size and speed. Therefore, for future nanoscale functional devices it becomes increasingly important to search for alternative ideas. One promising road is to use the spin degree of freedom as information carriers (spintronics) and to combine it with ultrafast optical control (nano-spintronics).

In this talk I will first introduce some fundamental ideas needed for the quantum chemical calculations and the logic functionalization of magnetic molecules and nanoclusters [1]. The first-principles separation of laser-induced spin and charge dynamics benefits from the strong electronic correlations in magnetic materials [2]. The Λ process represents a mechanism which allows for the rapid optical manipulation of the magnetic state of realistic molecules bypassing slow dynamical degrees of freedom.

Based on these concepts I will show that the molecular spins can be exploited as input and output bits in a variety of laser-driven, logical processes, going far beyond simple information storage. The systems considered here are realistic and mostly synthesized molecules (Fig. 1). As main examples of functionalities on magnetic molecules I will address the implementation of Boolean logic (AND, OR, and XOR gates), the spin-SHIFT register, as well as the ERASE operation by breaking time-reversal symmetry. Additionally, I will briefly mention some new concepts such as mechanically controlled spin dynamics [3], the inclusion of the molecular rotation, as well as the which-path interference, in which the final state of the spin reveals the path followed during the spin-transfer process [4]. Finally, I will show how including temperature can both lead to nano-heat engines and give rise to new spin-related phenomena [5].

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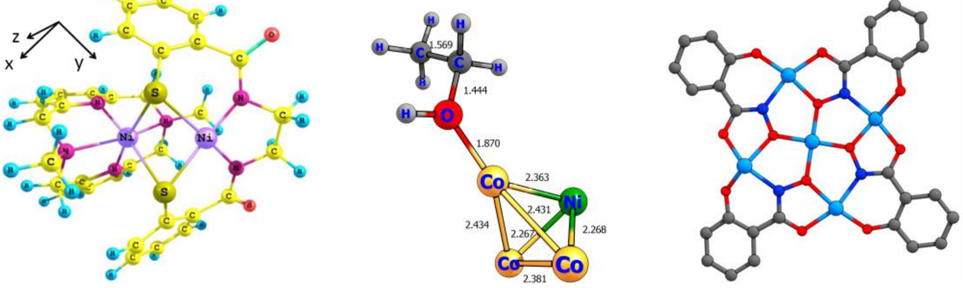

Figure 1. Some molecular magnets: Left: $[Ni^{II}_2(L\text{-}N_4Me_2)(emb)]^+$. Middle: $[Co_3Ni]^+EtOH$. Right: $(HNEt_3)_2Cu^{II}[12\text{–}MC_{Cu^{II}N(Shi)}\text{–}4]$.

Invited talk

Modelling quasiparticle excitations of adsorbates on 2D materials

Johannes Lischner[1]

[1]*Imperial College London (UK)*

I will discuss the electronic structure of adsorbed atoms and molecules on doped graphene.
First, I will demonstrate that F4-TCNQ molecules on doped graphene exhibit tunable charge and spin states as well as electron correlation effects. I will show that a model which captures doping dependent image charge interactions between the graphene and the molecule describes the experimentally measured renormalization of the LUMO energies. Next, I will discuss the properties of linear chains of F4-TCNQ molecules on graphene and show that the observed charge ordered ground states can be described using an extended Hubbard model with screened Coulomb interactions. Finally, I will argue that graphene with heavy adatoms, such as thallium, is an unlikely candidate for a quantum spin Hall insulator.

Invited talk

Spin-flip scattering off spin chains, molecules and single adsorbates

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Spin-flip scattering is at the core of spin transport. Elastic spin-flip scattering gives rise to Kondo peaks in differential conductance and inelastic scattering produces steps at the inelastic thresholds. Elastic and inelastic processes can appear simultaneously. In systems with rich spectra of magnetic excitations, both features can be found. This is the case of spin chains. A combination of Fe and Mn atoms leads to steps and peaks in the differential conductance, but this combination takes place under special combinations of Fe and Mn atoms, revealing the importance of spin entanglement and when it takes place [1]. The environment is obviously of great importance at determining spin properties. Nickelocene molecules present very different magnetic signals in their conductance properties depending on the degree of coupling to the electrodes [2]. At large electrode coupling, transport is driven in the out-of-equilibrium regime, and the Kondo signal presents clear non-equilibrium aspects [3], see the below figure.

References:

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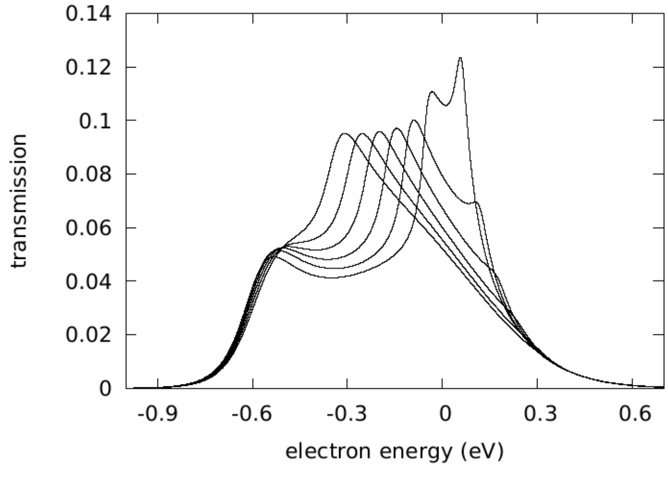

Figure. Transmission through a S=1 atom strongly coupled to two electrodes computed for 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 V between the two electrodes.

Invited talk

Spin Dynamics and Electron Transport from Time-Dependent Density Functional Calculations

Juan E. Peralta

Department of Physics, Central Michigan University, Mount Pleasant, MI, USA

In this talk, I will show two approaches based on real time time-dependent density functional theory (TDDFT) calculations for the simulation of magnetic and open systems. The first approach is based on a time-dependent extension of noncollinear spin density functional theory and allows for for the simultaneous propagation of charge and magnetization in closed molecular systems. For this we employ a second-order Magnus propagator combined with an efficient predictor-corrector scheme that allows us to treat large molecular systems over long simulation periods.[1] The method is benchmarked against the low-frequency dynamics of the lnear H–He–H molecule where the magnetization dynamics can be modeled by the simple classical magnetization precession given by a Heisenberg–Dirac-van Vleck Hamiltonian. Furthermore, the magnetic exchange couplings of the bimetallic complex $[\mathrm{Cu(bpy)(H_2O)(NO_3)2(\mu\text{-}C_2O_4)}]$ (BISDOW) are extracted from its low-frequency spin precession dynamics showing good agreement with the coupling obtained from ground state energy differences. A second approach is based on the direct propagation of the driven Liouville von Neumann[2] equation for the simulation of many-electron (open) quantum systems out-of-equilibrium. This approach allows us to simulate the transient current and find stationary solutions of molecular complexes placed between explicit leads subject to an energy bias. I will show some preliminary proof-of-concept calculations on hydrogen chains and compare with other methodologies.

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Invited talk

Charging in a single-molecule junction: Tunable magnetoresistance and reorganisation energy

Mats Persson and coworkers[1], Cyrus F. Hirjibehedin and coworkers[2], Gerhard Meyer and coworkers[3]

[1] *SSRC/Dep. of Chemistry, Univ. of Liverpool, UK*
[2] *London Centre for Nanotechnology, UCL, UK*
[3] *IBM Research – Zurich, Rüschlikon, Switzerland*

In this talk, we will cover both tunable magnetoresistance [1] and Marcus reorganisation energy [2] associated with charging in a single-molecule junction.

We observe magnetically sensitive negative differential resistance (NDR) in a single-molecule junction arising from resonant tunneling and charging of an iron phthalocyanine (FePc) molecule on a single layer of copper nitride on a copper surface,. The effective shift of the NDR with magnetic field is enhanced by the inherent voltage division across the two asymmetric tunnelling barriers, and this allows for the creation of novel magnetoresistance phenomena. Furthermore, the size of the enhancement can be controlled by tuning the asymmetry of the tunneling barriers, which can be modified by making physical or chemical changes to the junction by using different thin insulators or molecules.

We measured the hole reorganization energy caused by the charging of a single naphthalocyanine (Npc) molecule adsorbed on top of an insulating sodium chloride film supported by a copper substrate. Our method revolves around detecting single-electron transfer processes, based on the single-charge sensitivity of an atomic force microscope. Our results are corroborated by density functional theory calculations, in which the metal support of the multilayer film is treated implicitly in a perfect conductor model. The experimental method can be extended to other insulating films as well as other adsorbates, different charge state transitions. The ability to measure reorganization energies at the atomic scale is indispensable to quantify and predict single-electron transfer processes between molecules on insulating films and, in turn, tune and manipulate their energy transfer rates.

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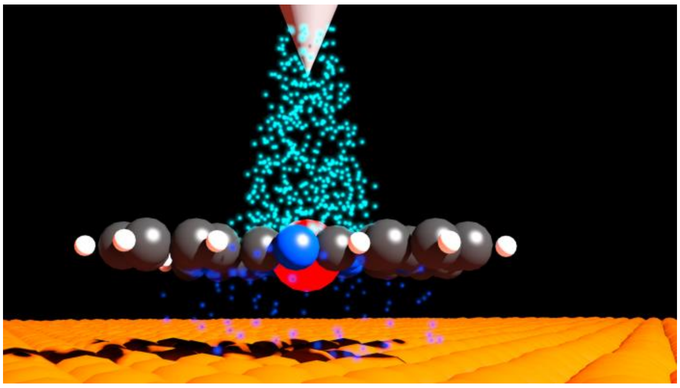
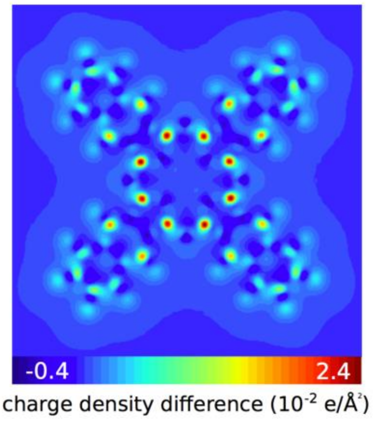


FePc/Cu_2N/Cu molecular junction



Hole charge distribution of Npc/NaCl/Cu

Invited talk

Electron transport through spin crossover molecules. Inspections from wavefunction theory

V. Robert[1], S. Vela[1], M. Vérot[2], E. Fromager[1]

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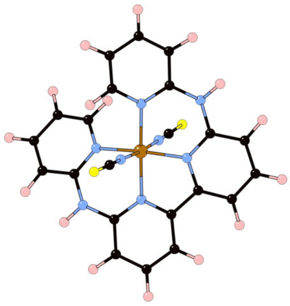
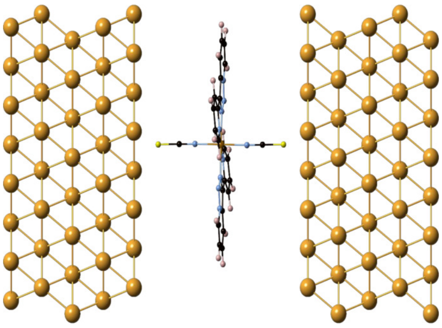
[2] Laboratoire de Chimie, Ecole normale supérieure de Lyon-France

Generally, the conductance through molecular junctions is computationally evaluated using the shapes and energies of the frontier molecular orbitals. To go beyond this one-electron picture, a theoretical approach has been recently developed by some of us to describe the electron transport using N-electron states [1]. The proposed methodological framework allows for the multi-configurational representation of the junction states, and has been designed to describe uncoherent, sequential transport within the weak-coupling regime. It is based on the solution of the Master Equation and, thus, on the balance between the different transfer rates describing the electron hopping from/to the junction and the left and right electrodes.

With a molecular spintronic goal in mind, we will discuss on the application of this perspective to study electron transport through a Fe(II)-based spin crossover (SCO) compound ($Fe(bapbpy)(NCS)_2$, see Figure left). To this purpose, we have used CASPT2 calculations to obtain the wavefunctions of states details and the energy of the full low-energy states of the neutral, anionic and cationic LS- and HS-structures, required in the description of the transfer rates. Then, the resulting states have been expanded by means of the Clebsch-Gordan coefficients to obtain the wavefunction of all the degenerate (2S+1) microstates, which allows us to rigorously explore the spin polarized transport originated in the junction [2].

We will discuss on the resulting I/V curves, and on the importance of the proper description of the spectroscopy of the junction by including all M_S states and even some of the excited states that lie within the bias window.





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Invited talk

Room Temperature Magnetoresistance in Single-Molecule Devices

Eliseo Ruiz[1]

[1] *Departament de Química Inorgànica i Orgànica and Institut de Química Teòrica i Computacional, Universitat de Barcelona, Diagonal 645, 08028 Barcelona, Spain*

This presentation is devoted to a combined theoretical and experimental study of transport properties in single-molecule devices. Conductance through mononuclear complexes deposited on a gold substrate in contact with magnetic Ni STM tip have measured and non-equilibrium Green Functions method combined with DFT calculations have been employed to rationalize such results. Our first results provided a proof of concept strongly indicating that the STM conductance through Fe^{II} or Co^{II} complexes (that are also a spin-crossover system and a single-molecule magnet, respectively) changes one order of magnitude with the direction of the Ni tip magnetic field. Our study shows a theoretical analysis and the practical implementation through two-terminal devices using STM equipment to achieve the room temperature molecular-based spintronic nanodevices.[1,2] This study have been extended to similar complexes with other metal cations, Ni^{II} and Mn^{II} as well as to other family of complexes as those formed by metalloporphyrins (Co^{II} and Cu^{II}, see Figure 1) with thiol-pyridine axial anchoring groups. In this case, the coordination of the anchoring group plays a fundamental role in the transport properties

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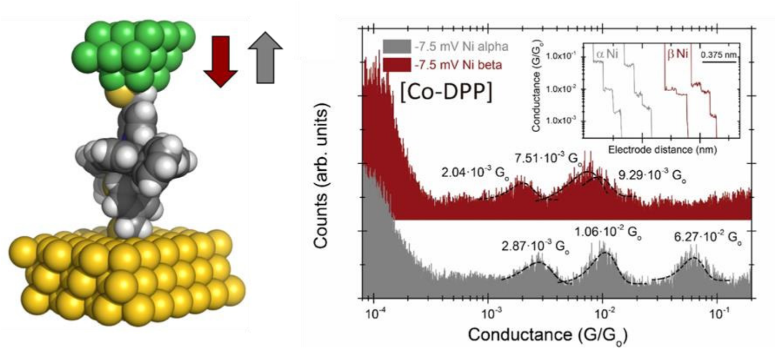

Figure 1. Single-molecule conductance histograms for the Co^{II} porphyrin complex with thiol-piridine axial ligands bridging between Au and both α-up spin polarized (gray) and β-down spin polarized (maroon) Ni electrodes.

Invited talk

STM investigation of molecules on surfaces: many-body quantum transport approach from level spectroscopy to Kondo

Dmitry A. Ryndyk[1]

[1] *Bremen Center for Computational Materials Science, Department of Physics, University of Bremen, Bremen, Germany*

I will discuss the theoretical and computational approaches for simulations of STM images and spectroscopy, in particular of molecules on metal and semiconductor surfaces. We developed and employed the density functional (DFT) and density functional tight-binding (DFTB) based atomistic approaches combined with the Green function and master equation quantum transport techniques [1], which offers a framework to consider a tip, molecule and surface as one integrated system and take into account the tip geometry, as well as various types of interactions inside molecules and between molecules and surfaces. Besides, within our framework the nonequilibrium many-body effects can be taken into account systematically. This new computational approach can be applied for investigations of finite-voltage effects and describe the higher molecular transport states. We implemented new methods in the DFTB$^+$XT computational package [2], based on the DFTB$^+$ source code [3,4]. It makes possible and convenient calculations for large-scale molecular nanosystems on metal surfaces. We work on the extension of the platform including the CP2K code to make available general DFT and semi-empirical Hamiltonians.

As an example, I will first consider the "HOMO/LUMO" spectroscopy of some organic molecules and conjugated polymers composed of alternating donor and acceptor repeat units, on the Au(111) surface, investigated experimentally by the group of F. Moresco at TU Dresden. The level spectroscopy is an efficient way to characterize the molecular structures and determine the actual conformations.

Then I want to show how our approach can capture the interaction effects, starting from elastic dephasing [5] towards the strongly correlated systems, including Coulomb blockade, local polaron and Kondo effects [6]. The link between atomistic models and many-body physics is convenient to formulate through the Hubbard like many-body models on top of the DFTB approach.

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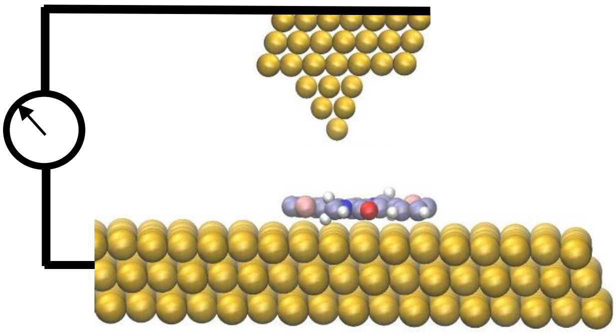

Invited talk

How to control the many-body effects of high-spin molecules

Giorgio Sangiovanni

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Am Hubland, 97074 Würzburg, Germany

Free isolated molecules get structurally as well as electronically remodeled by the presence of an atomic environment, such as a substrate or other molecules. The progresses in the understanding of this complex quantum mechanical influence are so rapid that an "on demand" microscopic control at the atomic scale is no longer considered an unreachable goal. Transition-metal phthalocyanine (TMPc) molecules are characterized by magnetic moments arising from electrons hosted by the *d*-orbitals at the transition-metal site. The screening from the conduction electrons leads to a, sometimes, controllable Kondo effect [1, 2]. In my talk I will present different ways of manipulating the magnetic moment of TMPc, discussing at which stage we currently are in the control of the corresponding many-body correlations. I will show recent scanning tunneling microscopy experiments and density functional theory (DFT) calculations and supplement the latter with full many-body continuous-time quantum Monte-Carlo calculations. The focus will be put on how the environment not only rearranges electronic levels or lifts orbital degeneracies, but how it can even be used to tune the strength of many-body interactions in single molecules.

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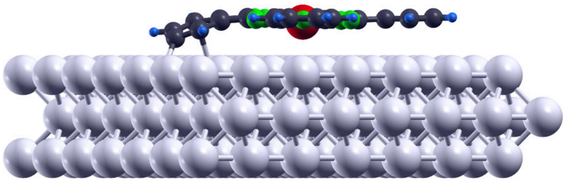

Figure. Side view of a dehydrogenated Manganese-phthalocyanine molecule on Ag(001) [2].

Invited talk

Phonon-induced spin relaxation relaxation in molecular magnets

Stefano Sanvito[1], Alessandro Lunghi[1], Federico Totti[2] and Roberta Sessoli[2]

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Single molecule magnets (SMMs) are molecules comprising only a handful of magnetic ions, which show some of the properties of bulk magnets and at the same time those of low-dimensional systems. These, for instance, include magnetic hysteresis together with quantum tunneling of the magnetization. A typical way to characterize the magnetism of SMMs is through relaxation experiments, where an ensemble of SMMs is polarized along the direction of an external field and then the relaxation of the magnetization is monitored in time. Surprisingly, many experiments measure a relaxation time considerably faster then what expected from the measured zero-field splitting (e.g. extracted from spin resonance), and such discrepancy usually increases with the strength of the anisotropy barrier. This surprising result collides with the most common SMMs design rules, which consist in engineering the ligand field of the magnetic ions so to increase the magnetic anisotropy or to increase the molecule total spin.

Here we demonstrate that spin-phonon coupling can account for such discrepancy and in particular that phonon dissipation is key to explain the under-barrier relaxation. Our calculations combine advanced post Hartree-Fock electronic structure theory with a master equation approach to the spin-dynamics. In particular we construct the spin-phonon Hamiltonian by first calculating the phonon spectrum via a finite difference method and then by mapping the spin-phonon matrix elements onto a giant spin Hamiltonian. This constructs a master equation, which now includes both diagonal and non-diagonal terms in the spin-state occupations. At this level also spin-spin interaction is taken into account and the many-body problem is solved by exact diagonalization over a truncated spin-Fock space. Crucially phonon dissipation is included in the model and it is treated through an appropriate temperature-dependent stochastic model [1].

The central result of our work is the demonstration that, in general, in the presence of spin-phonon coupling the relevant energy scale for spin relaxation is given by the lower-lying phonon modes interacting with the spin system. These provide a channel for the relaxation at energies lower than that needed to overcome the anisotropy barrier, hence producing a fast spin-decay mechanism. Importantly, such mechanism becomes dominant over the standard over-the-barrier relaxation process only for molecules presenting large zero-field split, a fact that calls for a redefinition of the design criteria for highly stable SMMs.

Our methodology is put to the test at the quantitative level for a class of Fe(II) molecules [2] presenting long spin lifetimes. In this case we find that the relaxation time has complex temperature behaviour, where different relaxation mechanisms dominate over different energy ranges (see Fig. 1) [1]. Furthermore we have been able to identify the phonon modes most relevant for the spin relaxation. These typically involve vibrations of the first coordination shell around the transition metal center, vibrations that affect strongly the spin-orbit interaction. Our work suggests several designing strategies for reducing the spin relaxation and thus for engineering long-living SMMs. For instance, although complicated to exploit in practice, a possible strategy may be that of modulating the spin excited state energy in order to obtain a non-resonant condition with the phonon spectrum.

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Invited talk

First-principles NEGF approach to ultrafast carrier dynamics

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We put forward a first-principle NonEquilibrium Green's Function (NEGF) approach to simulate the ultrafast carrier dynamics of molecular systems driven by attosecond laser pulses. The method can deal with ionizing fields and accounts for electron-electron repulsion through a many-body self-energy. We present a few recent applications to pump-probe optical spectra of atoms [1], charge separation in donor-acceptor complexes [2], charge migration in biological molecules [3] and time-resolved Auger decays [4]. If time permits, we discuss future perspectives and outlooks.

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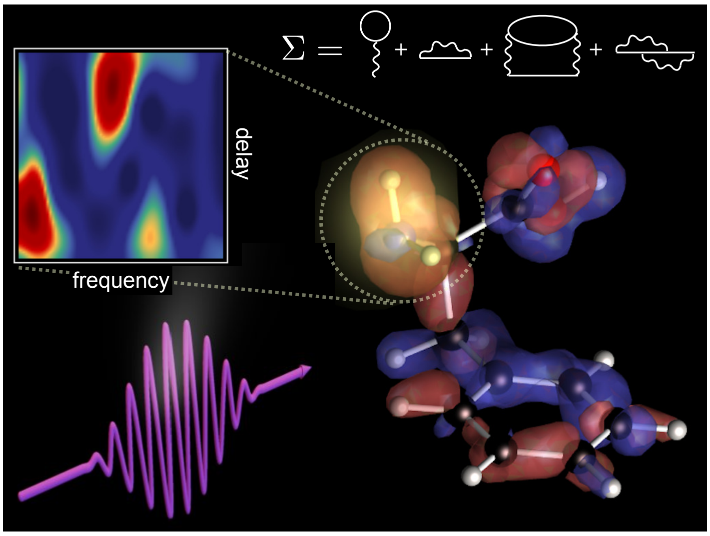

Invited talk

Diffusion quantum Monte Carlo for systems with spins

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Accuracy is a major challenge in calculations of spin systems. We will discuss recent developments using diffusion quantum Monte Carlo techniques to perform first principles calculations on systems with spins. We find that one can achieve quite high accuracy using these techniques, and will go over methods to use these accurate calculations to extract spin-only and coupled spin models.

Invited talk

Many body effects in transition metal molecular systems

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Phenomena that are connected to quantum mechanics, such as magnetism, transport, and the effect of impurity atoms and disorder, and their relation to material design and energy needs are important for almost every branch of the industry.

Density functional theory (DFT) was successful at making accurate predictions for many materials,in particular compounds which have a metallic behaviour. DFT combines high accuracy and moderate computational cost, but the computational effort of performing calculations with conventional DFT approaches is still non negligible and scales with the cube of the number of atoms.

A recent optimised implementation of DFT was however shown to scale linearly with the number of atoms (ONETEP), and opened the route to large scale DFTcalculations for molecules and nano-structures.

Nonetheless, one bottleneck of DFT and ONETEP, is that it fails at describing well some of the compounds where strong correlations are present, in particular because the computational scheme has to capture boththe band-like character of the uncorrelated part of the compound and the Mott-like features emerging from the local strongly correlated centres. A recent progress has been made in this direction by the dynamical mean-field theory (DMFT), that allows to describe the two limits (metal and insulator) in a remarkable precise way when combined with DFT.

The TO-lbox for Strongly Correlated Approaches for Molecules (TOSCAM) was recently implemented [1] in the ONETEP DFT code, and allows for linear scaling DFT combined with DMFT calculations.

We discuss its implementation and strategies to address the issues with linear scaling DFT combined with quantum solvers used in DMFT. We will discuss its recent application to heme, the kernel of haemoglobin. TOSCAM allowed to identify a low spin to high spin transition as a function of the Hund’s coupling, concomitant by an increase of the quantum entanglement at the transition. Extending the calculations to a thousand atoms for Myoglobin, this new methodology solves a long standing problem for ligand binding to myoglobin: the binding to O2 and CO is not reversible in DFT. This problem is solved when the local quantum effects in the Fe atomic d shell are properly treated. We will also present an application of the methodology to the case of hemocyanin, a di-copper system which is important for a large class of biological functions (and is in particular the respiration transport molecule of the horse shoe crab).

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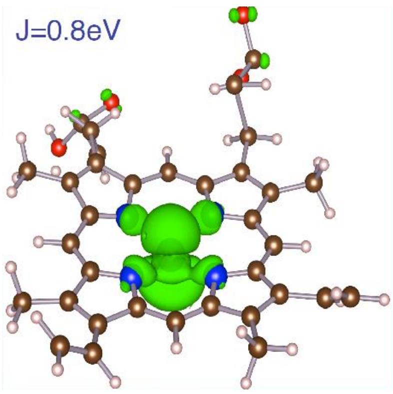

Figure 1. Homo real space electronic density as obtained by TOSCAM in the unligated Heme molecule. When the Hund’s coupling exchange J=0.8eV is included in the calculation, we observe a charge pinning at the Fe atom (central sphere). This affects in turn the binding of the Fe atom to ligands, such as CO and O2.

Invited talk

Numerical renormalization group investigations of magnetic impurities coupled to superconductors

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Recent advances in the fabrication of nanometer scale hybrid semiconductor-superconductor devices as well as in the scanning tunneling spectroscopy of adsorbate covered surfaces of superconductors have made possible very detailed experimental studies of the old problem of paramagnetic impurities in a superconducting host using local probes with very high energy and spatial resolution. At the same time, improved theoretical tools have been devised to reliably and accurately calculate the excitation spectra of the corresponding quantum impurity problems with gapped continuum electrons. These developments have enabled very stringent tests between experiment and theory. The results demonstrate the importance to describe the magnetic impurities as quantum objects with non-trivial internal dynamics due to the coupling to their environment.

I will review the application of the numerical renormalization group (NRG) to problems of this class: algorithmic developments such as the efficient discretization of the continuum of states, convergence properties, handling numerically demanding problems, and post-processing of the raw results. I will present some examples of successful modeling of complex experiments, e.g. double quantum dots, magnetic field effects, where semi-quantitative agreement was obtained. Finally, I will discuss the problem of a quantum impurity coupled to a mesoscopic superconductor with finite charging energy.

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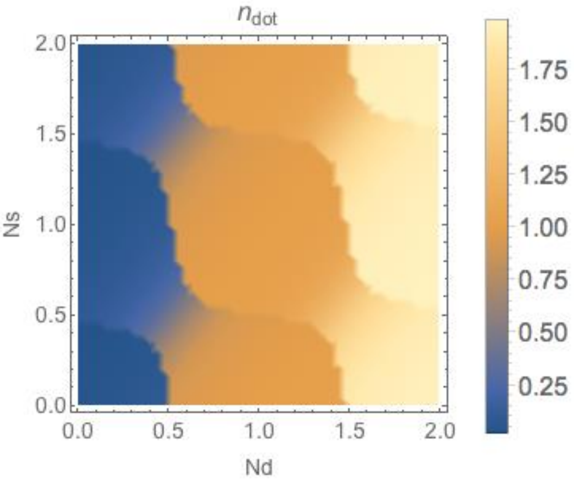

Figure: Charging diagram for a quantum dot coupled to a mesoscopic superconducting island.