

BOOK OF ABSTRACTS

8th Workshop on Time-Dependent Density-Functional Theory: Applications and Prospects

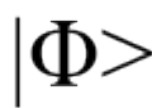
Benasque Center for Science “Pedro Pascual”
August 28th-30th 2018 (Benasque, Spain)



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multi-scale
modeling from
first principles



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PROGRAM

TUESDAY 28th

- 09:30 - 10:10 #1 **Ilya Tokatly**
Conserving approximations in cavity quantum electrodynamics
- 10:10 - 10:50 #2 **Carsten Ullrich**
(TD)DFT for systems with noncollinear spin: orbital-dependent xc functionals and their application to the magnetized Hubbard dimer

COFFEE BREAK

- 11:20 - 12:00 #3 **Ivano Tavernelli**
Quantum computing for quantum chemistry and physics
- 12:00 - 12:40 #4 **David Strubbe**
Density-functional perturbation theory for excited states from constrained DFT
- 12:40 - 13:10 #5 (Canceled)

LUNCH BREAK

- 15:00 - 15:40 #6 **Joachim Burgdörfer**
Dynamical correlations beyond TDDFT: time-dependent two-particle density matrix theory
- 15:40 - 16:20 #7 **Christine Isborn**
Improved Methods for Simulating Optical Spectroscopy of Dyes in Solution
- 16:20 - 16:50 #8 **Stefan Kurth**
Many-Body Spectral Functions from Steady-State Density Functional Theory

COFFEE BREAK

- 17:20 - 18:00 #9 **Esa Räsänen**
Scartronics: Quantum transport through chaos
- 18:00 - 18:40 #10 **Nicolas Tancogne-Dejean**
High-harmonic generation from solids and two-dimensional materials

WEDNESDAY 29th

- 15:30 - 16:10 #11 **Shunsuke Sato**
Applications of TDDFT in attosecond physics

- 16:10 - 16:50 #12 **Carlos Benavides**
Time evolution of the natural occupation numbers
- 16:50 - 17:20 #13 **Junhyeok Bang**
Coherent dynamics and dephasing-induced ultrafast charge transfer in van der Waals heterostructures

COFFEE BREAK

- 17:40 - 18:20 #14 **Pina Romaniello**
Many-Body Effective Energy Theory: photoemission at strong correlation
- 18:20 - 19:00 #15 **Eric Suraud**
On the inclusion of dissipative effects in clusters and molecules
- 19:00 - 19:30 #16 **Arjan Berger**
Optical spectra from first principles: fundamentals, functionals and numerics

- 19:30 - **POSTER SESSION**

THURSDAY 30th

- 09:30 - 10:10 #17 **Valerie Veniard**
Optical nonlinear processes in semiconductors: an ab-initio description
- 10:10 - 10:50 #18 **Ryan Requist**
TDDFT + exact factorization: performance of adiabatic functional approximations

COFFEE BREAK

- 11:20 - 12:00 #19 **Roi Baer**
Stochastic Methods for Electronic Structure and Dynamics
- 12:00 - 12:40 #20 **Johannes Lischner**
Tuning the electronic structure of 2d materials via defect engineering and twisting
- 12:40 - 13:10 #21 **Lara Román Castellanos**
Ab initio model for plasmonic hot electrons

LUNCH BREAK

- 15:00 - 15:40 #22 **Andre Schleife**
Charge states and time scales of electron-ion dynamics due to electronic stopping
- 15:40 - 16:20 #23 **Emmanuel Fromager**
Unified formulation of the fundamental and optical gap problems in density-functional theory for ensembles
- 16:20 - 16:50 #24 **Adrián Gómez Pueyo**

*Propagators for the time-dependent Kohn-Sham equations:
multistep, Runge-Kutta, exponential Runge-Kutta, and
commutator free Magnus methods*

COFFEE BREAK

17:20 - 17:50 #25 Peter Koval
*PySCF-NAO: an efficient and flexible implementation of linear
response time-dependent density functional theory with
numerical atomic orbitals*

17:50 - 18:20 #26 Fumiyuki Ishii (poster prize winner)
TBA

21:00 - **WORKSHOP DINNER**

1. Conserving approximations in cavity quantum electrodynamics

Ilya Tokatly

Ikerbasque - Basque Foundation for Science

In this talk I discuss general conservation laws and construction of conserving approximation in the MBPT and TDDFT approaches to cavity quantum electrodynamics (QED). I will start from the physical picture and the formal mathematical statement of the many-body problem for non-relativistic electrons strongly coupled to photon modes of a microcavity. Then I will derive the exact momentum/force balance equation in cavity QED and discuss its implications for the self-energy of MBPT and the xc potential of QED-TDDFT. Finally I show how to generalize the concept of Φ -derivability to construct approximations which ensure the correct momentum balance. As an explicit example of conserving approximation in QED-TDDFT I will consider a recently proposed electron-photon optimized effective potential.

2. (TD)DFT for systems with noncollinear spin: orbital-dependent xc functionals and their application to the magnetized Hubbard dimer

Carsten Ullrich

Department of Physics and Astronomy, University of Missouri

Noncollinear magnetism occurs in many systems and materials of practical interest, such as spiral ferromagnets or frustrated spin liquids. Apart from some recent exceptions, most existing density-functional approaches for noncollinear magnetism cannot account for magnetic xc torque effects. The consequences of this are not very well explored, which is in part due to the lack of exact benchmark results. Here, a new class of orbital-dependent xc magnetic fields is introduced within the Optimized Effective Potential (OEP) approach of DFT and linear-response TDDFT, treating correlation with the Singwi-Tosi-Land-Sjölander (STLS) method generalized to noncollinear spins. Systematic tests are performed for a very simple model system, the half-filled Hubbard dimer in an arbitrary magnetic field, with promising results for total energies, densities and magnetizations, especially in the weakly to moderately correlated regime. Comparison between the STLS and exact benchmark result shows that magnetic xc torques may be more challenging to approximate, in particular for strong correlation.

This work is supported by the Research Corporation for Science Advancement and by the US Department of Energy.

[1] C. A. Ullrich, arXiv:1805.06417 (submitted to Phys. Rev. B)

3. Quantum computing for quantum chemistry and physics

Ivano Tavernelli

IBM Research - Zurich, 8803 Rüschlikon, Switzerland

Quantum chemistry is definitely one of the most promising application areas of near-term quantum computers. The exponentially large Hilbert space of molecular systems can be efficiently mapped into the spin configuration space of available quantum computers offering a unique opportunity for the solution of interesting electronic structure problems with

unprecedented accuracy. To achieve this goal, new quantum algorithms need to be developed that are able to best exploit the potential of quantum speed-up [1,2]. While this effort should target the design of quantum algorithms for the future fault-tolerant quantum hardware, there is a pressing need to develop algorithms, which can be implemented in present-day non-fault tolerant quantum hardware with limited coherence times [3]. In this talk, we will discuss: (i) ways to derive efficient trial wavefunctions based on known quantum chemistry solutions (like e.g., Moller-Plesset perturbation theory and Unitary Coupled Cluster), (ii) schemes to map states to available quantum computer architectures, (iii) procedures to reduce the overall circuit depths in quantum chemistry calculations and experiments, and (iv) extensions for the calculation of additional properties including electronic excited states. These methods will be applied to a set of model systems (e.g., the Hubbard model) and molecules.

[1] B.P. Lanyon et al, Nature Chem. 2, 106 (2010).

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4. Density-functional perturbation theory for excited states from constrained DFT

David Strubbe

University of California Merced

Constrained DFT (cDFT) is a crude but computationally cheap approach for modeling excited states, in which non-equilibrium occupations are assigned to the Kohn-Sham states. Despite the availability of more sophisticated approaches, cDFT remains useful in contexts such as charge-transfer excitations, thermalized excited electron populations in solids, and TDDFT for excited-state absorption. Within ordinary DFT, vibrational and dielectric linear-response calculations have become routine with density-functional perturbation theory (DFPT), which needs only the occupied states. This technique works at zero temperature or with an effective temperature described through a smearing function, and can be used in both static and TDDFT calculations. However, the formalism has not been available for calculation of states with arbitrary occupations, as can arise in the cDFT description of excited states. I derive a simple modification to extend DFPT to arbitrary fractional occupations and show example applications for systems with non-equilibrium occupations.

6. Dynamical correlations beyond TDDFT: time-dependent two-particle density matrix theory

Joachim Burgdörfer

Institute for Theoretical Physics, Vienna University of Technology

Describing time-dependent many-body systems where correlation effects play an important role remains a major theoretical challenge. The ab-initio simulation of dynamical correlations, for example particle-particle correlations in the break-up of many-body systems, requires approaches beyond mean-field descriptions. The full solution of the full N-body Schrödinger equation is still prohibitive for large systems due to the unfavourable exponential (or factorial) scaling with the number of degrees of freedom.

The present time-dependent two-particle density matrix (TD-2RDM) approach aims at bridging the gap between descriptions based on the reduced one-particle density $\rho(r,t)$ such

as TDDFT or mean-field models on one end and the full wavefunction based N-particle description on the other. As a hybrid between the one-body density and the full wavefunction, the 2RDM contains the complete information on two-particle correlations but still scales polynomially with particle number. Contraction consistency and N-representability constraints explicitly accounted for the present TD2RDM theory are key to achieve accurate and stable propagation of non-equilibrium dynamics. We benchmark our approach for N-fermion systems by a comparison with multi-configurational time-dependent Hartree-Fock (MCTDHF) results for the harmonic spectra of many-electron atoms. First numerical results indicate that the TD-2RDM is well-suited to describe the non-linear many-body response and to reveal the influence of electron correlation effects.

7. Improved Methods for Simulating Optical Spectroscopy of Dyes in Solution

Christine Isborn

School of Natural Sciences, University of California Merced

Optical spectra are essential tools for identifying molecules, characterizing their ground and excited states, and learning about how they interact with their environment. Theory can provide complementary information to optical spectra by giving electronic and atomistic detail about the system, but accurately modeling spectra is not a trivial task. Often, simulations ignore all specific-solvent interactions, solvent-induced inhomogeneous broadening, and the vibronic coupling between states. This talk will present recent work from my group towards modeling accurate shapes of solution-phase absorption spectra, including accounting for temperature-dependent non-Gaussian inhomogeneous broadening effects, vibronic transitions, and short- and long-range solute-solvent interactions.

8. Many-Body Spectral Functions from Steady-State Density Functional Theory

Stefan Kurth and David Jacob

Univ. of the Basque Country UPV/EHU and IKERBASQUE, Basque Foundation for Science, and Donostia International Physics Center (DIPC)

A scheme is proposed to extract the many-body spectral function of an interacting many-electron system within the framework of density functional theory (DFT) in a two-step procedure [1]. The first step is a standard DFT calculation for the ground state of the system. In the second step we employ the recently proposed steady-state DFT formalism (i-DFT) [2] which allows one to calculate the steady current through a nanoscopic region coupled to two biased electrodes in a special setup. In this setup, which may be viewed as an idealized scanning tunneling microscope (STM), one of the electrodes serves as a probe ("STM tip"). In the limit of vanishing coupling to the tip, 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, one can 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 such as the single Anderson impurity model.

[1] D. Jacob, S. Kurth, Nano Lett. **18**, 2086 (2018)

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9. Scartronics: Quantum transport through chaos

Esa Räsänen

Tampere University of Technology, Finland

A quantum scar is a striking visualization of quantum mechanical suppression of classical chaos. A scar is a track of an enhanced probability density in a quantum eigenstate. This track corresponds to a short unstable periodic orbit of the corresponding chaotic classical system. Recently, a new type of quantum scarring was discovered in two-dimensional (2D) quantum wells perturbed by local “bumps” in the potential. These scars stem from the classical resonances in the unperturbed system and from the local nature of the perturbations. It was demonstrated that the geometry and the orientation of the scars are controllable with a magnetic field and a focused perturbative potential, respectively.

Here we show that quantum scars can be exploited to propagate quantum wave packets with extreme fidelity. The combination of coherent transport through the scars and their controllability opens up a path into “scartronics” in nanoscale quantum systems. We report the development of transport scheme and discuss also the possibilities in the many-electron case within time-dependent density-functional theory.

10. High-harmonic generation from solids and two-dimensional materials

Nicolas Tancogne-Dejean

Max-Planck Institute for the Structure and Dynamics of Matter, Hamburg

Recently the strong-field electronic dynamics in solids have received a lot of attention, in particular due to the experimental observation of high-harmonic generation in solids. The dynamics associated with strong fields requires a non-perturbative description of the electronic dynamics. One possible way of describing this dynamics by ab initio methods is to use real-time time-dependent density functional theory (TDDFT).

In this talk, we discuss how we use TDDFT to model the strong-field electronic dynamics in solids, using the real-space real-time code Octopus. This approach allows us to gain a deep insight on the underlying physical mechanism, in both bulk materials and quasi two-dimensional materials, and is shown to yield quantitative agreement with experimental results.

11. Applications of TDDFT in attosecond physics

Shunsuke Sato

Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany

Thanks to the recent progress of laser technologies, real-time electron dynamics have been investigated in atoms and molecules over the past few decades. Recently, the real-time observation technique has been further applied to solid-state materials, and nonequilibrium electron dynamics have been investigated towards future applications. However, reflecting the complex electronic structure of solid-state materials, it is often hard to directly interpret the experimental results. The first-principles simulation based on TDDFT is a powerful tool to describe such complex electron dynamics and to provide microscopic insight into such

ultrafast phenomena.

In this work, we combine our TDDFT first-principles simulation and the recent attosecond experimental technique to investigate laser-induced nonequilibrium electron dynamics in diamond [1] and GaAs [2]. As a result, we found that the laser-induced intraband motion of electrons strongly modifies the transient optical property of the materials in the sub-femtosecond time-scale in both resonantly and off-resonantly driving conditions. In the talk, we would like to further discuss our recent progress about transition metals.

[1] M. Lucchini, S. A. Sato, A. Ludwig, J. Herrmann, M. Volkov, L. Kasmi, Y. Shinohara, K. Yabana, L. Gallmann, U. Keller Science 353, 916 (2016).

[2] F. Schlaepfer, M. Lucchini, S. A. Sato, M. Volkov, L. Kasmi, N. Hartmann, A. Rubio, L. Gallmann, U. Keller, Nature Physics 14, 560 (2018).

12. Time evolution of the natural occupation numbers

Carlos Benavides

Martin-Luther-Universität Halle-Wittenberg

Reduced density matrix functional theory (RDMFT) is based on the Gilbert theorem, which asserts that the ground-state wave function can be written as a functional of the one-body reduced density matrix. Since RDMFT accounts for fractional natural occupation numbers, it captures quite well static (strong) electron correlation (unlike DFT, RDMFT correctly predicts the insulating behavior of Mott-type insulators). Yet the time-dependent extension of RDMFT suffers from various shortcomings. Chief among them, the current status of the theory does not allow the fermionic occupation numbers to evolve in time. It is known that this deficiency is connected to the failure of RDMFT to account for relative phases at the level of the two-body reduced density matrix. Based on recent results on fermionic exchange symmetry, we propose a new equation for the time evolution of the fermionic occupation numbers.

13. Coherent dynamics and dephasing-induced ultrafast charge transfer in van der Waals heterostructures

Junhyeok Bang, Han Wang, Yiyang Sun, Liangbo Liang, Damien West, Vincent Meunier, and Shengbai Zhang

Korea Basic Science Institute

The physics of charge transfer across interface is an important foundation for new device concepts and applications. In contrast to conventional heterostructures where a strong interfacial coupling is essential to charge transfer, van der Waals (vdW) heterostructures are expected to have a weak coupling, and hence inferior for optoelectronic applications. The recent experimental observation of the ultrafast hole transfer from MoS₂ to WS₂ is thus both exciting and puzzling. Using time-dependent density functional theory molecular dynamics, we find the coherent motion of excitons at the interface leading to plasma oscillations associated with optical excitation. By constructing a simple model of the vdW heterostructure, we show that there exists an unexpected criticality of the oscillations.

Interaction with phonon bath dephases the quantum-mechanical coherence, and can lead to classical charge transfer state within a timescale of 100 fs. Application to the MoS₂/WS₂ heterostructure yields good agreement with experiment, showing ultrafast charge transfer.

14. Many-Body Effective Energy Theory: photoemission at strong correlation

Pina Romaniello

Laboratoire de Physique Théorique, Université de Toulouse, CNRS, UPS, France and European Theoretical Spectroscopy Facility (ETSF)

In this talk we focus on the spectral function, which determines, for example, photoemission spectra, and which cannot be obtained in a straightforward way from simple physical quantities such as the density, and on the regime of strong electron correlation, which is difficult to treat by standard methods [1,2]. We present a recently derived many-body effective energy theory that can describe photoemission in strongly correlated systems [3]. With the example of bulk NiO, we show that our theory yields a qualitatively correct picture both in the antiferromagnetic and paramagnetic phases, contrary to mean-field methods, in which the paramagnet is incorrectly described as a metal.

[1] S. Di Sabatino, J.A. Berger, L. Reining, and P. Romaniello, J. Chem. Phys. 143, 024108 (2015)

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15. On the inclusion of dissipative effects in clusters and molecules

Eric Suraud

Laboratoire de Physique Théorique, Université Paul Sabatier

Mean field provides an essential starting point to understand the dynamics of numerous many-body systems ranging from nuclei to molecules, clusters and nano structures. Beyond structural or low energy properties, the analysis of dynamical processes, especially beyond the linear response domain requires the account of correlations beyond mean field, especially incoherent ones. The topic has been widely explored in nuclear dynamics with major efforts devoted to the development of semi-classical approximations, leading to Boltzmann type kinetic equations [1]. Recent developments in laser technology now allow to analyse in some detail the response of clusters and molecules in short intense laser fields which typically lead to dissipative effects, beyond mean field. Semi-classical approaches have also been explored in the field [2] but are restricted to simple metals at sufficiently high excitations, which represents a strong limitation. There is thus a growing interest in the inclusion of dissipative features in current mean field theories in the case of electronic systems. An underlying mean field theory is here provided by Density Functional Theory (DFT) in its simplest Local Density Approximation (LDA), which is recognized as a robust and flexible approach for such systems, at least at moderate excitations [2,3].

We discuss in the present work some extensive studies we have led to include incoherent correlations on top of Time Dependent LDA or Time Dependent Hartree Fock (TDHF) approaches which represent archetypical approaches in the time domain. We briefly discuss available methods such as Trajectory Surface Hopping [4] and Time Dependent Current Density Functional Theory [5]. We next propose two alternative routes. We propose a

quantum Relaxation Time Ansatz (RTA) providing an approximate quantum kinetic treatment [6] and a stochastic extension of mean field, known as Stochastic TDHF [7]. The RTA has allowed us to access realistic laser irradiation scenarios and study the impact of dissipation on electron emission in moderate size clusters. The STDHF approach is much richer but still at a more schematic level because of the computational cost. We have explored it in simple molecular systems and been able to analyse its capabilities in detail [8,9]. We have also developed an averaged version thereof which opens the door to applications in realistic systems [10].

- [1] Y. Abe, S. Ayik, P-G. Reinhard and E. Suraud, Phys. Rep. 275 (1996) 49
- [2] Th. Fennel et al., Rev. Mod. Phys. 82 (2010) 1793
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- [4] J. M. Escartin et al, J. Chem. Phys. 137 (2012) 234113
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- [10] L. Lacombe et al, J. Phys. B 49 (2016) 245101

16. Optical spectra from first principles: fundamentals, functionals and numerics

Arjan Berger
University of Toulouse

The prediction of optical spectra of materials from first principles is a major challenge. In this talk I will discuss recent advances in the modelling of these spectra using time-dependent (current-)density-functional theory (TD(C)DFT). The scope of this talk will range from fundamental to numerical issues.

In particular I will discuss: 1) the problem of multiple solutions [1,2] 2) a recent dynamical exchange-correlation functional that can accurately describe the spectra of metals, semiconductors and insulators [3,4]. 3) numerical pitfalls and how to avoid them [5,6]

I will illustrate the above points by showing optical spectra calculated within TDDFT and TDCDFT..

References

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17. Optical nonlinear processes in semiconductors: an ab-initio description

Valérie Vénier

Laboratoire des Solides Irradiés, Ecole Polytechnique, CNRS, CEA-DRF-IRAMIS,
Université Paris Saclay, Palaiseau, France

A deep understanding of the non-linear optical properties of solids is crucial for the improvement of devices (frequency doubling for instance). In addition, it offers the possibility to search for new materials with very specific properties. Among these processes, an important role is played by Second Harmonic Generation (SHG). In this process, two photons are absorbed by the material and a photon, with twice the energy of the incoming photons, is emitted. In recent years, it has become a highly effective non-invasive technique for characterizing materials, thanks to its particular sensitivity to system symmetries.

While SHG can only be observed when the material is submitted to an intense light, such as the one provided by lasers, there is however some cases where it is possible to observe nonlinear optical processes with moderate light intensity, such as the electro-optic effect. This process corresponds to a change of the refractive index in a medium using a dc-electric field and has attracted particular interest for the development of optoelectronic devices. It is often not counted among the nonlinear optical effects since the change is proportional to the applied optical electric field. However, it may be seen as a second-order polarization and then described by a second-order susceptibility. Following the same idea, a similar phenomenon happens also for SHG, corresponding to a second harmonic response in the presence of a dc-field, called “Electric Field Induced Second Harmonic” (EFISH) and described in terms of a third-order polarization.

18. TDDFT + exact factorization: performance of adiabatic functional approximations

Ryan Requist

Max Planck Institute of Microstructure Physics, Halle (Germany)

Including beyond-Born-Oppenheimer effects in ab initio molecular dynamics simulations is a costly enterprise. To make this feasible in large systems, we combine time dependent density functional theory with the exact factorization of the electron-nuclear wave function [Abedi Maitra Gross PRL 105, 123002 (2010)]. The conditional electronic density $n_R(r,t)$ and nuclear wavefunction can be determined by self-consistently solving a time-dependent Kohn-Sham equation and the exact nuclear Schrodinger equation. The nonadiabatic exchange-correlation potential, as well as the potential energy surface driving the nuclei, are functionals of $n_R(r,t)$. We use a model driven-proton-transfer process to evaluate the viability of approximating these functionals with the adiabatic extension of a beyond-Born-Oppenheimer ground state functional. There are some notable differences with respect to electron-only TDDFT, yet we show that for slow driving the adiabatic-extension approximation accurately accounts for beyond-Born-Oppenheimer effects.

19. Stochastic Methods for Electronic Structure and Dynamics

Roi Baer

Fritz Haber Center for Molecular Dynamics and Institute of Chemistry, The Hebrew
University of Jerusalem

I will discuss two topics concerning stochastic approaches to electronic structure. First, for

open-system time-dependent density functional theory (TD-DFT): the development of a stochastic approach for evolving in real time non-interacting Fermions in open quantum systems under the influence of a Boson bath. The method is based on the unraveling procedure of the Lindblad equation and uses a Hubbard-Stratonovitch transformation to remove the bath-induced electron-electron interaction. Next, I will discuss stochastic density functional theory for warm dense matter using finite temperature Kohn-Sham DFT (FT-KS-DFT). The complexity scales as $\mathcal{O}(N^3 T^{-1})$ to be contrasted with the $\mathcal{O}(N^3 T^3)$ scaling of deterministic approaches, where N is the system size and T is the temperature. I will show equations of state as well as conductance calculations.

20. Tuning the electronic structure of 2d materials via defect engineering and twisting

Johannes Lischner
Imperial College, London

I will discuss two approaches for modifying the electronic structure of 2d materials. First, I will show how charged defects give rise to shallow bound states in semiconducting transition-metal dichalcogenides. Interestingly, the character of the lowest-lying impurity states depends sensitively on the defect charge – both its sign and magnitude. Then, I will discuss twisted bilayer graphene which has attracted considerable attention in recent months because of the experimental observation of significant electron correlation effects and even unconventional superconductivity. These findings are explained using advanced electronic structure methods based on the renormalization group.

21. Ab initio model for plasmonic hot electrons

Lara Román Castellanos
Imperial College London

When light impinges on a metallic nanoparticle, localised surface plasmons can be excited. These are the result of the collective behaviour of conduction electrons that oscillate coupled to an electromagnetic field. The energetic electrons generated after the decay of the plasmon are of great interest due to its potential applications in nanoplasmonic devices. Previous approaches have calculated hot-electron properties using a classical description of the plasmon. We propose a first-principles model where the optical properties of the nanoparticle are calculated using linear response density functional theory. In this model, the plasmon is described as a linear superposition of electron-hole pairs. After the excitation, the plasmon decays producing energetic electrons. We describe the plasmon decay using Fermi's golden rule, where the matrix element has been derived from many-body perturbation theory. This approach allows us to calculate hot-carrier distributions for different nanoparticle sizes and discuss the limitations of semiclassical approaches.

22. Charge states and time scales of electron-ion dynamics due to electronic stopping

Andre Schleife
University of Illinois at Urbana-Champaign

Energetic-particle radiation is of high technological interest for applications, since as a result of the irradiation, damage occurs and ultimately determines materials properties. In particular, swift heavy ions are known to either exacerbate or mitigate damage. At the same time, high-energy projectiles significantly drive the electronic system of the target out of equilibrium, rendering standard atomistic simulations based on the Born-Oppenheimer approximation no longer valid. Purposefully controlling the modification of a material using radiation, however, necessarily relies on a detailed, quantitative understanding of fundamental interactions between particle radiation and target material that occur over multiple length and time scales.

To this end, Ehrenfest molecular dynamics and real-time time-dependent density functional theory have recently been shown to successfully describe electronic stopping during the early stages of radiation damage for light projectiles. Here we extend this picture towards electronic stopping for heavy ions, i.e., for silicon projectiles traversing silicon bulk crystals. We found a pronounced dependence of electronic stopping on the initial charge state of the projectile ion, which was not observed for light projectiles. Our analysis shows that this can be explained by accounting for dynamics of charge equilibration in the target, and we explicitly study the influence of the impact parameter as well as contributions of core and valence electrons. From our simulations we demonstrate that off-channeling trajectories as well as semi-core electrons are needed for a direct comparison to experiment.

At the same time, knowledge of non-equilibrium electron-ion physics becomes crucial, since directly after excitation by the projectile ion, the electronic system of the target is in a highly excited, non-thermalized state. It is currently not well understood whether and how non-thermalized excited carriers, as well as thermalized hot carriers, affect atomic diffusion. In order to achieve a quantitative description, we propose a parameter-free first-principles simulation framework that bridges time scales from ultrafast electron dynamics directly after impact, to atomic diffusion in the presence of hot electrons. We then apply this framework to magnesium oxide under proton irradiation and compare the migration barrier of an oxygen vacancy in the presence of (i) non-thermalized hot electrons, (ii) thermalized Fermi-distributed electrons, and (iii) an ionized oxygen vacancy. We show evidence for enhanced diffusion under non-equilibrium conditions, hinting at a novel hot-electron mediated diffusion mechanism. Our quantitative simulations show that this mechanism strongly depends on the projectile-ion velocity, opening the possibility of turning it on or off, e.g. by varying the kinetic energy of the particle radiation, and observing its impact at a specific depth in the target.

23. Unified formulation of the fundamental and optical gap problems in density-functional theory for ensembles

Emmanuel Fromager

Laboratoire de Chimie Quantique, Institute of Chemistry, University of Strasbourg, France.

While the fundamental gap is obtained from N -, $(N-1)$ - and $(N+1)$ -electron ground-state energies, the optical gap is, on the other hand, defined as the difference between the N -electron first-excited and ground-state energies. For non-interacting electrons, these two gaps are simply equal to the HOMO-LUMO gap. In (real) interacting electronic systems, they differ from the Kohn-Sham HOMO-LUMO gap by the so-called derivative discontinuity (DD) contribution. The latter can be interpreted as a jump in the exchange-correlation potential when crossing an integral number of electrons [1] (for the fundamental gap) or when exciting from the ground to the first excited state [2] (for the optical gap). Modelling such DDs is one of the most challenging task in density-functional theory (DFT).

Interestingly, the optical gap problem can be reformulated in DFT for ensembles, thus providing an exact expression for the DD in terms of the weight assigned to the first excited

state and the corresponding ensemble exchange-correlation energy [3]. In this presentation, I will show that a similar in-principle-exact theory, referred to as N-centered ensemble DFT, can be derived for the fundamental gap problem [4]. While conventional DFT-based approaches consider grand canonical ensembles consisting of either (N-1)- and N-electron or N- and (N+1)-electron systems, N-centered ensemble DFT extracts informations from (N-1)-, N- and (N+1)-electron ground states, hence the name "N-centered". I will then explain how the theory can be generalized in order to extract the ionization potential and the electron affinity separately. As an illustration, the theory will be applied to the Hubbard dimer [4,5,6]. If time permits, I will finally show how instructive such a generalization can be regarding the calculation of individual excited-state energies in DFT.

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24. Propagators for the time-dependent Kohn-Sham equations: multistep, Runge-Kutta, exponential Runge-Kutta, and commutator free Magnus methods

Adrián Gómez Pueyo
University of Zaragoza

Although the Kohn-Sham equations are Schrödinger-like in their form, this set of equations is non-linear due to the dependence of the Hamiltonian on the electronic density. We examined various integration schemes for the time-dependent Kohn-Sham equations and discussed some of their exact properties, in particular their symplectic structure. Four different families of propagators are considered, specifically the linear multistep, Runge-Kutta, exponential Runge-Kutta, and the commutator-free Magnus schemes. We analyzed their performance in terms of cost-versus accuracy. The clear winner, in terms of robustness, simplicity, and efficiency is a simplified version of a fourth-order commutator-free Magnus integrator.

25. PySCF-NAO: an efficient and flexible implementation of linear response time-dependent density functional theory with numerical atomic orbitals

Peter Koval
Donostia International Physics Center

We present an algorithm and its implementation to calculate the properties of electronic excitations in molecules and clusters from first principles, using a time-dependent density functional theory (TDDFT). The algorithm assumes the use of some localized functions as a basis set to represent the spatial degrees of freedom. It relies on an iterative computation of the induced density according to the Dyson-like equation for the linear response function. The current implementation is built upon so-called numerical atomic orbitals. It is suitable for a wide variety of the density functional theory (DFT) software. In this work, we demonstrate TDDFT calculations starting from preceding DFT runs with SIESTA, GPAW and PySCF

packages, while a coupling with the other DFT packages such as Fireball and OpenMX is planned. The mentioned packages are capable of performing ab initio molecular dynamics simulations, and the speed of our TDDFT implementation makes feasible to perform a configuration average of the optical absorption spectra. Our code is written mostly in Python language allowing for a quick and compact implementation of most numerical methods and data-managing tasks with the help of NumPy/SciPy libraries and Python intrinsic constructs. Part of the code is written in C and Fortran to achieve a competitive speed in particular sections of the algorithm. Many parts of the current algorithm and implementation are useful in other ab initio methods for electronic excited states, such as Hedin's GW, Bethe-Salpeter equation and DFT with hybrid functionals. Corresponding proof-of-principles implementations are already part of the code.

26. First-principles study of anomalous thermoelectric effects

Fumiyuki Ishii
Kanazawa University, Japan

We are interested in how to achieve much higher thermoelectric (TE) conversion efficiency by effectively manipulating electron-spin degree of freedom. As one possibility, we have been studying anomalous thermoelectric effect, the contribution of the anomalous Hall conductivity (AHC) in TE power. Previously, we have shown quite large effect of AHC in a skyrmion crystal model [1]. What we target here is anomalous thermoelectric effect in magnetic half-Heusler alloys, the anomalous Nernst effect (ANE), heat-to-electricity conversion in transverse direction. ANE is driven by an effective magnetic field originating from topology of wavefunctions which induced by spin-orbit coupling or spin chirality as we found in skyrmion crystal model [1]. In this study, we have performed first-principles computations [2] on half-metallic half-Heusler compounds and found that the crystal-momentum component of effective magnetic field generate large ANE [3]. This behavior was clearly understood by the energy-dependent anomalous Hall conductivity.

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