

## CPP 22: Focused Session: Frontiers of Electronic Structure Theory - Non-equilibrium Phenomena at the Nano-scale III (original: O, joined by CPP)

Time: Tuesday 10:30–13:15

Location: TRE Ma

**Topical Talk**

CPP 22.1 Tue 10:30 TRE Ma  
**Ultrafast relaxation dynamics of Hubbard nanoclusters** —  
 ●MICHAEL BONITZ<sup>1</sup>, SEBASTIAN HERMANN<sup>1</sup>, CHRISTOPHER HINZ<sup>1</sup>, and DENIS LACROIX<sup>2</sup> — <sup>1</sup>Institut für Theoretische Physik und Astrophysik, CAU Kiel, Leibnizstr. 15, 24098 Kiel — <sup>2</sup>IPN Orsay, 15 Rue Georges Clemenceau, 91406 Orsay

With the growing availability of intense short-pulse radiation sources it becomes possible to drive interacting many-particle or few-particle systems out of equilibrium in a controlled way. The subsequent relaxation and equilibration dynamics is still poorly understood. From a theory point of view these processes are complicated due to the simultaneous dynamics of the occupation functions and of binary correlations. The problem becomes even more complicated when the system has finite size and is spatially inhomogeneous [1]. The Hubbard model is a prototype for treating correlation effects in condensed matter or molecular systems fully including finite size and inhomogeneity effects. We, therefore, concentrate on the relaxation dynamics of small 1D, 2D and 3D Hubbard clusters that contain from a few to several hundred electrons. We observe a complex multi-stage relaxation behavior that depends on the external excitation, on the coupling strength and on the geometry of the system. In this talk we present results from two complementary theoretical approaches: first, from nonequilibrium Green functions where we apply the Generalized Kadanoff Baym ansatz [1] and, second, from a stochastic mean field approach.

[1] K. Balzer, and M. Bonitz, “Nonequilibrium Green’s Functions Approach to Inhomogeneous Systems”, *Lect. Notes Phys.* **867** (2013)

CPP 22.2 Tue 11:00 TRE Ma  
**Exact adiabatic approximation in TDDFT** — ●JEIRAN JOKAR and NICOLE HELBIG — Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

The use of functionals from static density functional theory in an adiabatic way in a time-dependent framework is known to cause various problems due to the resulting exchange-correlation kernel being frequency independent. In order to isolate the effects which are due to the adiabatic approximation we calculate the exact static potential for two electron systems. Before using this potential in an adiabatic way in a time propagation we need to ensure that the potential is well defined also at those parts of space where the density is small as they might become more populated at a later time. We use the exact adiabatic approximation to describe Rabi oscillations, i.e. the oscillation between the ground state and an excited state when a monochromatic laser with a frequency close to the resonance is applied.

CPP 22.3 Tue 11:15 TRE Ma  
**Real-time propagation of coupled Maxwell-Schrödinger and time-dependent Kohn-Sham-Maxwell systems** — ●RENÉ JESTÄDT<sup>1</sup>, HEIKO APPEL<sup>1</sup>, and ANGEL RUBIO<sup>1,2</sup> — <sup>1</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — <sup>2</sup>NanoBio Spectroscopy group and ETSEF, Universidad del País Vasco, San Sebastián, Spain

Based on the Riemann-Silberstein vector of the electromagnetic field, we formulate Maxwell’s equations in a symplectic spinor representation similar to the Dirac equation. This spinor representation allows us to use standard unitary propagation techniques developed for the Schrödinger equation [1] also for Maxwell’s equations and simplifies a coupled solution of Maxwell’s and Schrödinger’s equations. To illustrate our approach, we present the real-time evolution of atomic systems embedded in optical waveguides and dielectric nanostructures. The coupling of Maxwell’s equations to the time-dependent Kohn-Sham equations is a basic ingredient for the development of a time-dependent density functional theory formulation of quantum electrodynamics [2]. As an extension of our work on coupled Maxwell-Schrödinger systems, we show first steps of an implementation of Maxwell’s equations coupled to the time-dependent Kohn-Sham equations in the first principles real-space real-time code octopus [3].

[1] A. Castro et al., *J. Chem. Phys.* **121** (2004).

[2] M. Ruggenthaler, F. Mackenroth, and D. Bauer, *Phys. Rev. A* **84**, 042107 (2011); *I. Tolkatly, Phys. Rev. Lett.* **110**, 233001 (2013).

[3] X. Andrade et al., *J. Phys. Cond. Mat.* **24** (2012).

CPP 22.4 Tue 11:30 TRE Ma  
**Nonlinear optics by means of the dynamical Berry phase: Application to second- and third-harmonic generation** — ●CLAUDIO ATTACALITE<sup>1</sup> and MYRTA GRUNING<sup>2</sup> — <sup>1</sup>Univ. Grenoble Alpes/CNRS, Institut Neel, F-38042 Grenoble, France — <sup>2</sup>School of Mathematics and Physics, Queen’s University Belfast, Belfast BT7 1NN, Northern Ireland, UK

We present a real-time approach to study nonlinear optical properties in Condensed Matter systems that is especially suitable for crystalline solids. The equation of motions and the coupling of the electrons with the external electric field are derived from the Berry phase formulation of the dynamical polarization. Many-body effects are introduced by adding single-particle operators to the independent-particle Hamiltonian. Specifically we include crystal local field effects, renormalization of the energy levels and excitonic effects. The approach is validated by calculating the second and third harmonic generation of bulk semiconductors. Finally we present second-harmonic generation spectrum of h-BN or MoS2 monolayers and show that correlation effects double the signal intensity at the excitonic resonances with respect to the contribution from independent electronic transitions.

References: [1] Nonlinear optics from ab-initio by means of the dynamical Berry-phase <http://arxiv.org/abs/1309.4012> [2] Second Harmonic Generation in h-BN and MoS2 monolayers: the role of electron-hole interaction <http://arxiv.org/abs/1310.7459>

**15 min. break**

CPP 22.5 Tue 12:00 TRE Ma  
**Accurate Correlation Energies from Adiabatic Time-Dependent Density Functional Theory with Renormalized Kernels** — ●THOMAS OLSEN<sup>1</sup> and KRISTIAN S. THYGESEN<sup>2</sup> — <sup>1</sup>Universidad del País Vasco — <sup>2</sup>Center for Atomic-scale Materials Design (CAMD), Technical University of Denmark

We demonstrate the accuracy of electronic correlation energies obtained from the adiabatic connection and Time-Dependent Density Functional Theory (TDDFT) using a non-empirical renormalized gradient-corrected exchange-correlation kernel. The method can be viewed as a natural step beyond the Random Phase Approximation (RPA) and captures the short-range correlation effects which are poorly described in RPA. In particular, we show that for molecules and solids the renormalized kernel gives a four and five fold improvement in binding energies respectively when compared to RPA. We also consider examples of barrier heights in chemical reactions, molecular adsorption and graphene interacting with metal surfaces, which are three examples where RPA has provided highly accurate results. In these cases, our novel kernel provides results that are of equal quality or even slightly better than RPA, with a similar computational cost. We finally note that the renormalization procedure can be applied to any known semi-local exchange-correlation functional and thus defines an entire new class of adiabatic non-local functionals for ground state calculations within TDDFT.

CPP 22.6 Tue 12:15 TRE Ma  
**Low scaling algorithm for the random phase approximation** — ●MERZUK KALTAK, JIRI KLIMEŠ, and GEORG KRESSE — University of Vienna, Computational Material Physics

The computationally most expensive step in conventional RPA implementations is the calculation of the independent particle polarizability  $\chi$ . We present an RPA algorithm that calculates  $\chi$  using the Green function  $G$  in real space and imaginary time. The systematic construction of optimized time and frequency grids for  $G$  is obtained by means of solving a fitting problem. Furthermore a non-uniform discrete Fourier transform between the two grids is introduced, which converges exponentially. We show that the usage of the Green function approach in combination with the optimized grids can be used for the calculation of the RPA correlation energy for large systems.

CPP 22.7 Tue 12:30 TRE Ma  
**Long range correlation energy from coupled atomic response functions** — ●ALBERTO AMBROSETTI and ALEXANDRE TKATCHENKO — Fritz Haber Institut der MPG, Faradayweg 4-6 14195 Berlin, Ger-

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Electron correlation is an elusive and ubiquitous energy contribution that arises from transient collective electron fluctuations. Its reliable (accurate and efficient) modeling is central to the correct description of cohesive, structural, and response properties of molecules and solids. In this regard, the main challenge is to model the long-range correlation energy beyond (semi-)local density-functional approximations. Here we propose a very efficient method to compute the long-range correlation energy for non-metallic molecules and solids within a density functional theory framework, by using coupled atomic response functions (ARF). Extending the recent MBD method [1], we separate the coupling between ARFs into short and long range, allowing for a seamless many-body treatment of weakly and strongly polarizable systems. Thorough benchmarking on large data sets including small molecules (S22, S66x8), large supramolecular complexes (S12L), molecular crystals (X23) and bulk graphite shows consistently good agreement with high level theoretical and experimental reference binding energies (within the order of 6%). The uniform accuracy for molecules and solids represents a strong validation of our method, and further confirms the importance of modeling the truly collective nature of the long-range correlation energy. [1] A. Tkatchenko et al. PRL **108** 236402 (2012).

CPP 22.8 Tue 12:45 TRE Ma

**The exact Hohenberg-Kohn functional for a lattice model** — •TANJA DIMITROV<sup>1</sup>, HEIKO APPEL<sup>1</sup>, and ANGEL RUBIO<sup>1,2</sup> — <sup>1</sup>Fritz-Haber-Institut der MPG, Berlin, Germany — <sup>2</sup>NanoBio Spectroscopy group and ETSF, Universidad del País Vasco, San Sebastián, Spain

Standard local exchange-correlation and semi-local functionals in ground-state density functional theory are known for their shortcomings in describing correct charge transfer, dissociation energies of molecular ions, and barriers of chemical reactions [1,2]. To understand the failures of approximate functionals and to gain insight into the behavior of the exact functional, we investigate the exact solution of the many-body Schrödinger equation for a lattice model. Using exact diagonalization, we explicitly construct the exact Hohenberg-Kohn functional and the mapping from densities to wavefunctions. Besides the normal inter-system derivative discontinuity widely discussed in

the density-functional theory community, we observe a new feature of the exact functional in the low-density limit. This "intra-system derivative discontinuity" resembles the inter-system derivative discontinuity, but is within the system (work in progress [3]). The description of many physical phenomena linked to charge-transfer processes (both in the static and dynamical regimes) require a proper account of this "intra-system derivative discontinuity".

[1] A. J. Cohen et al. Science **321**, 792 (2008).

[2] P. Mori-Sanchez et al., Phys. Rev. Lett. **100**, 146401 (2008).

[3] T. Dimitrov, H. Appel, A. Rubio to be published

CPP 22.9 Tue 13:00 TRE Ma

**Incorporating static correlation effects into density functional theory** — NEKTARIOS N. LATHIOTAKIS<sup>1</sup>, •NICOLE HELBIG<sup>2</sup>, NIKITAS I. GIDOPOULOS<sup>3</sup>, and ANGEL RUBIO<sup>4,5</sup> — <sup>1</sup>Theoretical and Physical Chemistry Institute, NHRF Athens, Greece — <sup>2</sup>Peter-Grünberg Institut, Forschungszentrum Jülich, Germany — <sup>3</sup>Department of Physics, Durham University, United Kingdom — <sup>4</sup>Nano-Bio Spectroscopy group, Universidad del País Vasco and DIPC, San Sebastian, Spain — <sup>5</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

We present a novel idea that builds on the knowledge acquired in Reduced density matrix functional theory (RDMFT) to construct a density-functional scheme which accurately incorporates static and left-right correlation effects. At the same time, the new scheme preserves the high quality of a density functional description at the equilibrium and keeps the computational costs at an acceptable level comparable to the costs when using hybrid functionals. Within this scheme the natural orbitals, i.e. the eigenfunctions of the one-body density matrix, are constrained to be solutions of a single-particle Schrödinger equation with a local effective potential. This provides a natural way to connect an energy eigenvalue spectrum to the natural orbitals. This energy spectrum is found to reproduce the ionization potentials of different atoms and molecules very well. In addition, the dissociation limit of diatomic molecules is well described without the need to break any spin symmetry, i.e. this attractive feature of RDMFT is preserved. The present scheme can be easily implemented in all first principles codes for electronic structure calculations.