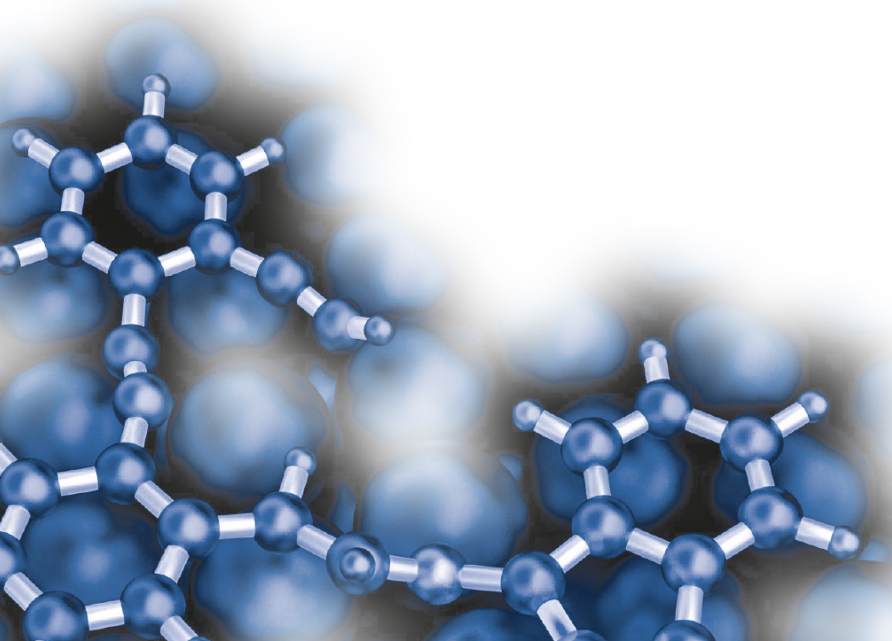Workshop on

Theoretical challenges:
simulating materials out of equilibrium

CFEL, Hamburg, June 1–3, 2016

ABSTRACT BOOKLET

Overview of Contributions

Optical control of collective phenomena in solids

Andrea Cavalleri
Max Planck Institute for the Structure and Dynamics of Matter

In this talk I will discuss how the nonlinear optical excitation of lattice vibrations [1] can be used to create new crystal structures [2] and to induce new properties in some complex solids with strongly correlated electrons. Specifically, I will discuss how in some cases one can control the specific bonds lengths and angles, change the electronic bandwidth and induce insulator-metal phase switching [3]. I will also discuss new experiments in which different modes are mixed nonlinearly, creating unconventional states in which the lattice is made to rotate and time-reversal invariance can be broken. Finally, I will reflect on the possibility of dynamically modulating the electronic properties and on the possibility of inducing incipient superconductivity at temperatures above the thermodynamic transition temperature [4,5,6].

[1] M. Först et al., *Nature Physics* **7**, 854–856 (2011).

[2] R. Mankowsky et al., *Nature* **516**, 71–73 (2014).

[3] M. Rini et al., *Nature* **449**, 72–74 (2007).

[4] D. Fausti et al., *Science* **331**, 189–191 (2011).

[5] W. Hu et al., *Nature Materials* **13**, 705–711 (2014).

[6] M. Mitrano et al., *Nature* **530**, 461–464 (2016).

Patterns, Correlations, and Causality in Big Data of Materials: Analytics for Novel Materials Discovery

Matthias Scheffler

Fritz Haber Institute of the Max Planck Society

Big data of materials are structured in a way that is typically not visible by standard tools. Furthermore, with respect to a certain (desired) property, the "chemical compound space", which contains a practically infinite amount of different materials, is very sparsely populated. Thus, a key issue in data-driven materials science is to find the proper descriptive parameters (descriptors) that identify the materials-property related structures of this huge space.

We will show that and how compressed sensing, originally designed for representing a complex signal in the lowest possible dimensionality, can select, out of a huge-dimensional space of potential descriptors (features), a low dimensional descriptor. Examples are crystal-structure and (meta)stability prediction and the prediction of the band gap of binary and ternary compounds.

By applying sensitivity analysis, supervised pattern discovery, and causal inference techniques, we discuss the causal relationship between the selected descriptors and the predicted physical properties.

We will also address how the recently establishes *NOMAD (novel materials discovery) Laboratory*, a European Center of Excellence (http://NOMAD-CoE.eu), will address these issues.

Some Theoretical Challenges from X-ray Free Electron Lasers

Massimo Altarelli
European XFEL

X-ray Free-electron Lasers (FEL's) have started operating since a few years. The salient features of these x-ray sources are the very short pulses, down to a few *fs* duration; the extremely high peak power, up to the ~100 *GW* range and beyond; the peak brilliance, exceeding that at the best synchrotron sources by many orders of magnitude. Experiments using these revolutionary sources open up new frontiers for x-ray physics, and a few examples shall be given to underline the most important aspects.

Both experimental observations and theoretical considerations show that interaction between FEL pulses and atomic, molecular and condensed matter takes place under conditions that are quite different from the usual. The intensity of the radiation field is in a regime where important non-linearities are expected and indeed observed. Phenomena familiar from laser physics at much longer wavelengths (multi-photon absorption processes, saturated absorption, sum-frequency generation, stimulated Raman scattering) are entering the x-ray domain. Modelling of these effects has been restricted to few-atoms systems or to semi-empirical methods. An ab-initio electronic structure description of these phenomena in the x-ray region for condensed matter systems is challenging; for example, the description of saturated absorption requires an accurate description of the probability of multiple excitation of core levels, of core level shifts, of radiation and Auger recombination rates.

At the same time, the very short duration of the pulses opens up the possibility to explore the dynamics of electronic and structural properties on an unprecedented time scale, well below the *ps* region. The challenges, but also the potential scientific payoff, for theoretical investigations of time-dependent properties are briefly described.

Stark control of electrons along nanojunctions

Ignacio Franco
University of Rochester

In a recent experiment, Schiffrin et al. demonstrated how a strong ($I\sim10^{13}$–10^{14} W/cm^2) non-resonant 4 fs laser pulse can be used to induce currents along gold-silica-gold nanojunctions [1]. Phenomenologically, these currents arise due to the nonlinear interaction of the junction with a laser pulse that has a low temporal symmetry. By varying the carrier envelope phase it is possible to vary the degree of time asymmetry of the incident radiation, and thus the direction and magnitude of the photoinduced current. The experiment marks a new frontier in the experimental laser control of electronic dynamics and is the fastest existing method for the generation of currents. However, since the photo-generated current depends on a highly non-equilibrium state of matter that has never been observed before, the microscopic origin of this rather spectacular effect is unclear and the subject of recent controversy. In this talk, I will discuss the feasibility of different possible mechanisms that have been proposed, and discuss simulations of the laser-induced transport along gold-silica-gold nanojunctions that clarify the microscopic origin of the effect.

[1] A. Schiffrin, T. Paasch-Colberg, N. Karpowicz, V. Apalkov, D. Gerster, S. Mühlbrandt, M. Korbman, J. Reichert, M. Schultze, S. Holzner, J. V. Barth, R. Kienberger, R. Ernstorfer, V. S. Yakovlev, M. I. Stockman, and F. Krausz, *Nature* **493**, 70–74 (2013).

Light-induced new states of matter in solids:
Prospects, concepts, and challenges

Michael Sentef
Max Planck Institute for the Structure and Dynamics of Matter

Controlling the properties of complex quantum materials with light is a tantalizing prospect. As an example, non-equilibrium driven systems offer the possibility to control their topology by the creation of Floquet-Bloch states, which can be probed with time-resolved spectroscopy. I will discuss basic concepts for the understanding and modeling of light-induced states as well as the challenges for theory and experiments.

Creating stable Floquet-Weyl semimetals by laser-driving of 3D Dirac materials

Hannes Hübener
Universidad del País Vasco

Periodic driving of many-body systems offers a platform to design Floquet states of matter with tunable electronic properties on ultrafast time scales. Here we show by first principles calculations how femtosecond laser pulses with circularly polarized light can be used to switch between Weyl semimetal, Dirac semimetal, and topological insulator states in a prototypical 3D Dirac material, Na_3Bi.

Ultrafast laser-induced demagnetisation of solids:
Understanding the mechanism with real-time TDDFT simulations

Eberhard Gross
Max Planck Institute of Microstructure Physics

TBA

Surface-hopping excited-state dynamics

Walter Thiel
Max-Planck-Institut für Kohlenforschung

Semiempirical quantum-chemical methods are well-established tools for computational studies of large molecules [1]. Methods with explicit orthogonalization corrections (OM1, OM2, OM3) offer better overall accuracy in standard statistical evaluations of ground-state properties as well as qualitative improvements for hydrogen bonding and conformational properties [2,3]. OMx-based studies of electronically excited states employ a general implementation of the GUGACI approach in a semiempirical framework which provides analytic gradients and nonadiabatic couplings. Comparisons with high-level ab initio benchmark data show that OMx/MRCI methods describe electronically excited states reasonably well [4]. They can thus be used in mixed quantum-classical dynamics to investigate fast nonradiative relaxation processes after photoexcitation. Numerous such surface-hopping dynamics studies have been carried out at the OM2/MRCI level in recent years [1], for example simulations on DNA bases in different environments, azobenzenes, molecular motors [5] and switches, GFP chromophores [6], and Schiff bases, covering both photophysical and photochemical processes.

The lecture will address the theoretical background of the OMx/MRCI surface-hopping methodology and present selected OM2/MRCI applications. Time permitting, it will also cover a nonadiabatic excited-state dynamics study on the bithiophene dimer using time-dependent density functional theory (TDDFT) to describe time-dependent excitonic effects in molecular aggregates [7]. The lowest excited states are found to be localized and unproductive in terms of charge separation. Productive high-energy charge-transfer (CT) states are populated within 50 fs during exciton deactivation, but they are short-lived ($\sim$100 fs) and quickly transfer their population to lower states. The TDDFT simulations offer molecular-level insights into ultrafast photoinduced charge separation potentially triggered by hot CT states in solid-state organic materials. They allow us to suggest design rules to increase hot exciton lifetimes, favoring the population of CT states as gateways for direct charge generation.

[1] W. Thiel, *WIREs Comp. Mol. Sci.* **4**, 145–157 (2014).

[2] P. O. Dral, X. Wu, L. Spörkel, A. Koslowski, W. Weber, R. Steiger, M. Scholten, W. Thiel, *J. Chem. Theory Comput.* **12**, 1082–1097 (2016).

[3] P. O. Dral, X. Wu, L. Spörkel, A. Koslowski und W. Thiel, *J. Chem. Theory Comput.* **12**, 1097–1120 (2016).

[4] M. R. Silva-Junior, W. Thiel, *J. Chem. Theory Comput.* **6**, 1546–1564 (2010).

[5] A. Nikiforov, J. A. Gamez, W. Thiel, M. Filatov, *J. Chem. Phys. Lett.* **7**, 105–110 (2016).

[6] X.-Y. Liu, X.-P. Chang, S.-H. Xia, G. Cui, W. Thiel, *J. Chem. Theory Comput.* **12**, 753–764 (2016).

[7] D. Fazzi, M. Barbatti, W. Thiel, *J. Am. Chem. Soc* **138** (13), 4502–4511 (2016).

Towards ab-initio Molecular Dynamics without Born–Oppenheimer Potential-Energy Surfaces

Guillermo Albareda
Universitat de Barcelona

The correlated motion of electrons and ions is a challenging problem yet one that is increasingly topical due to the advent of experimental techniques that allow visualizing the "molecular movie". Theoretical methods mostly rely on the Born-Huang expansion of the molecular wavefunction. Hence, the concepts of Born-Oppenheimer potential-energy surfaces (BOPES) and nonadiabatic couplings (NAC) arise naturally, suggesting the picture of a nuclear wavepacket evolving on many static BOPESs. This approach is, however, very expensive due to the computational costs associated to the calculation (and parametrization) of all BOPESs and NACs involved in the dynamics.

We propose an alternative approach to molecular dynamics based on the use of conditional wavefunctions [1]. The exact electron-nuclear dynamics is described by means of an ensemble of single, time-dependent, potential energy surfaces (CTDPESs) that drive each component of the total wavefunction. While keeping the theory at the full configuration level, this approach allows for the use of trajectory-based techniques to circumvent the calculation of the BOPESs and NACs, and allows drawing clear connections between different exact frameworks [2]. We have investigated features of the C-TDPESs in the presence of strong nonadiabatic couplings and proposed a universal mechanism for the explanation of quantum nonadiabatic effects [3]. The paradigm shift associated with the transition from the many static BOPESs to the single time-dependent potentials can open new avenues in the understanding of quantum dynamics. Furthermore, the combination of the CD approach with the inherent scalability of other techniques such as TDDFT could lead to a breakthrough in the efficiency of ab-initio molecular dynamics methods.
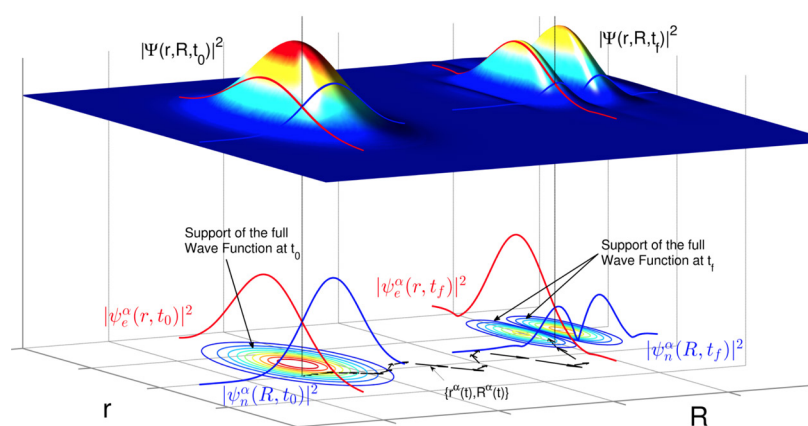
Figure: Schematic representation of the conditional wave function concept for a simple 2-dimensional scenario. The full probability density $|\Psi(r, R, t)|^2$ has been plot at two different times, t_0 and t_f together with the conditional probability densities $|\Psi(r, R^\alpha, t)|^2$ and $|\Psi(r^\alpha, R, t)|^2$ (in red and blue respectively) for a given trajectory $\left(r_1^\alpha(t), R_1^\alpha(t)\right)$.

[1] G. Albareda et al., *Phys. Rev. Lett.* **113**, 083003 (2014).

[2] G. Albareda et al., *J. Phys. Chem. Lett.* **6**, 1529 (2015).

[3] G. Albareda et al., arXiv:1512.08531 (2015).

Mechanical Non-equilibrium — Nanofriction

Erio Tosatti
SISSA, ICTP, and CNR-IOM Democritos

I plan to discuss, based on theory and simulations in our group, examples of nanofriction as a mechanical case of non-equilibrium. One question will be what information even such a non-invasive tool could reveal about phenomena that are going on inside the sliders or within an interposed lubricating film. The accent is on the physics and not on tribology, considering instances where friction and dissipation could anticipate experiments exploring some extreme frictional situations [1–3]; others where it could describe the frictional signature of phase transitions [4–10], or the effect of external perturbations such as electric fields [11], or else the effect of time-periodic amplitude modulations of the corrugation potential [12]. These and other examples [13–15] suggest that nanofriction and AFM dissipation could in some cases provide a sort of spectroscopic tool for the blind man.

[1] High temperature. T. Zykova-Timan, D. Ceresoli, E. Tosatti, *Nature Materials* **6**, 230–234 (2007).

[2] High speed. R. Guerra, U. Tartaglino, A. Vanossi, E. Tosatti, *Nature Materials* **9**, 634–637 (2010).

[3] High pressure. A. Vanossi, A. Benassi, N. Varini, E. Tosatti, *Phys. Rev. B* **87**, 045412 (2013); Y. Crespo et al., in preparation.

[4] Friction and phase transitions — model. A. Benassi, A. Vanossi, E. Tosatti, *Nature Communications* **2**, 236 (2011).

[5] Friction and phase transitions — SrTiO$_3$. M. Kisiel, F. Pellegrini, G.E. Santoro, M. Samadashvili, R. Pawlak, A. Benassi, U. Gysin, R. Buzio, A. Gerbi, E. Meyer, E. Tosatti, *Phys. Rev. Lett.* **115**, 046101 (2015).

[6] Phase transition in ion chains. A. Benassi, A. Vanossi, E. Tosatti, *Nature Comms.* **2**, 236 (2011).

[7] Depinning of adsorbed islands. N. Varini, A. Vanossi, R. Guerra, D. Mandelli, R. Capozza, E. Tosatti, *Nanoscale* **7**, 2093–2101 (2015).

[8] Frictional sliding of adsorbed island. M. Pierno, L. Bruschi, G. Mistura, G. Paolicelli, A. di Bona, S. Valeri, R. Guerra, A. Vanossi, E. Tosatti, *Nature Nanotechnology* **10**, 714–718 (2015).

[9] 2D Aubry frictional transition in colloidal monolayers. D. Mandelli, A. Vanossi, M. Invernizzi, S. V. Paronuzzi Ticco, N. Manini, E. Tosatti, *Phys. Rev. B* **92**, 134306 (2015).

[10] Spontaneous monolayer rotation affects friction. D. Mandelli, A. Vanossi, N. Manini, E. Tosatti, *Phys. Rev. Lett.* **114**, 108302 (2015).

[11] Ionic liquid lubricant in electric field. R. Capozza, A. Benassi, A. Vanossi, and E. Tosatti, *J. Chem. Phys.* **143**, 144703 (2015).

[12] Subharmonic Shapiro steps in sliding colloid monolayers. S.V. Paronuzzi Ticco, et al., *J. Phys. Cond. Matt.* **28** ,134006 (2016).

[13] Friction on nanotubes. M. Lucas et al., *Nature Materials* **8**, 876–881 (2009).

[14] Magnetic AFM dissipation. F. Pellegrini, G.E. Santoro, E. Tosatti, *Phys. Rev. Lett.* **105**, 146103 (2010).

[15] Mechanical dissipation by generation of phase slips in CDWs. M. Langer et al., *Nature Materials* **13**, 173–177 (2014).

Light-matter coupling in density-functional theory for quantum electrodynamics (I)

Michael Ruggenthaler
Max Planck Institute for the Structure and Dynamics of Matter

Recently, ground-state and time-dependent density-functional theory have been extended to include the interaction with photons from first principles. This so-called quantum-electrodynamical density-functional theory (QEDFT) treats light and matter on equal quantized footing and provides a bridge between high-energy physics, quantum chemistry, and quantum optics. QEDFT allows deriving numerically feasible approximations for a novel class of physical situations, where the matter and photon degrees of freedom are equally important.

In the first part of this sequence of presentations, we illustrate the basic ideas of how light-matter coupled quantum systems allow for a reformulation in terms of the charge current (of the particles) and the vector potential (of the photons). To find reasonable approximations to the unknown functionals we introduce an auxiliary uncoupled Kohn-Sham system with effective potentials. For the standard situation of cavity QED, i.e. dipole coupling, we present first approximations to the resulting effective potential that take the explicit coupling to the photons into account. We conclude this part with an outlook on field-theory, multi-mode and free-space problems.

Light-matter coupling in density-functional theory for quantum electrodynamics (II)

Heiko Appel
Max Planck Institute for the Structure and Dynamics of Matter
Fritz Haber Institute of the Max Planck Society

In the second part of our presentation of QEDFT, we illustrate effects that appear in the strong-coupling regime of matter with cavity photons. In particular, we show how Born-Oppenheimer surfaces are modified in the presence of the cavity, discuss photon bound states, and analyze polariton splittings in molecular absorption spectra. As illustrated in part (I), the density-functional approach to quantum electrodynamics is formally an exact framework. Here we show by inversion of the exact many-body solution of the time-dependent Schrödinger equation for a quantum dot system the exact time evolution of the effective potential of the Maxwell-Kohn-Sham system in QEDFT and analyze this in terms of a cavity Born-Oppenheimer approximation. We compare these exact results with the first approximate functional of QEDFT which is based on an optimized-effective-potential approach for the coupled matter-photon system. To go beyond model systems, we introduce a Riemann-Silberstein formulation of Maxwell's equations and present the first ab-initio real-time propagations of the coupled Maxwell-Kohn-Sham equations for molecular systems.

Orbital Magnetization

Raffaele Resta
Università di Trieste and CNR-IOM Democritos

Microscopic understanding of what orbital magnetization **M** *really is* started only in 2005–6. The macroscopic current density responsible for **M** in a magnetized large sample is localized near its boundary, and therefore is lost in the idealization of an unbounded crystal, as customary in condensed matter physics. The modern theory avoids addressing currents altogether, and provides an alternative expression in terms of the Hamiltonian and of the ground-state electron distribution.

The founding work of 2005–6 addresses crystalline systems and provides the **M** expression in terms of **k** integrals of Bloch-orbital matrix elements: these clearly refer to unbounded samples. More recent work addresses instead bounded samples in **r**-space and shows that the **M** value can be retrieved without accessing the boundary currents: knowledge of the Hamiltonian and of the electron distribution *in the bulk region* of the sample is enough. Remarkably, this applies to both insulators [1] and metals [2].

The modern theory provides **M** as the sum of two terms, both gauge invariant. The quantity actually measured in magnetic circular dichroism experiments is only one of the two terms, *not* the full **M** value [3].

[1] R. Bianco and R. Resta, Orbital magnetization as a local property, *Phys. Rev. Lett.* **110**, 087202 (2013).

[2] A. Marrazzo and R. Resta, Irrelevance of the boundary on the magnetization of metals, *Phys. Rev. Lett.* **116**, 137201 (2016).

[3] I. Souza and D. Vanderbilt, Dichroic f-sum rule and the orbital magnetization of crystals, *Phys. Rev. B* **77**, 054438 (2008).

Tensor Network Techniques and systems out of equilibrium

J. Ignacio Cirac
Max Planck Institute of Quantum Optics

Tensor networks can efficiently describe many-body quantum systems with local interactions in thermal equilibrium. However, as a consequence of the violation of the area law, they cannot describe their dynamics, in general. Still, they may provide useful information about several physical aspects of many-body systems out of equilibrium.

In this talk I will mention few of the applications of tensor networks related to that problem: the computation of quasi-constants of motion, and the characterization of many-body localized states.

Time-resolved ARPES from first principles and applications

Umberto De Giovannini
Universidad del País Vasco

Time resolved ARPES (angle-resolved photoemission spectroscopy) has emerged as a crucial tool to investigate quantum properties of materials driven out of equilibrium. An example is the observation of selective valley excitation in transition metal dichalcogenides. I will introduce the theory at the basis of our first-principles approach and illustrate its application on a selection of systems.

Optimal control of electron dynamics

Alberto Castro
ARAID Foundation and Universidad de Zaragoza

Optimal control theory (OCT) can be used in combination with non-equilibrium electron dynamics theories, and allows to find optimal Hamiltonian parameters (e.g. pulse shapes), capable of inducing a dynamical behavior of the electronic system that match a pre-defined objective. In this talk, I present the state-of-the-art in the theoretical and computational efforts in this field: the combination of OCT with time-dependent density-functional theory, the combination of OCT with first-principles molecular dynamics methods, and the application of these concepts to goals such as the ultra-fast photo-dissociation of molecules or the Coulomb explosion of clusters, the manipulation of the high harmonic generation spectra of atoms and molecules, and other possibilities.

Fingerprints of electron correlation in materials: understanding and predictions from electronic structure theory

Lucia Reining
École Polytechnique and European Theoretical Spectroscopy Facility

Electronic excitations determine the characteristics of materials all over science and technology, from photochemistry to radiation defects, from synchrotron experiments to cancer research. Theory and numerical modelling are valuable tools for the understanding and prediction of many of the important phenomena. During the last decades the field has evolved rapidly, but there are still many challenges. For example, some structures in the excitation spectra of interacting electrons, called quasiparticle peaks, can be directly related to excitations of independent electrons. Others, instead, such as satellites in the photoemission spectra of solids, cannot be understood in such a simple way. They are pure consequences of interaction and correlation, and they cannot be interpreted in a pure bandstructure picture. First principles calculations are in general very efficient in describing bandstructure, especially methods based on many-body perturbation theory such as the so-called GW approximation [1]. However, they often have difficulties to describe quantitatively, or even qualitatively, everything that goes beyond.

In this talk we will see what state-of-the art first principles calculations can today contribute to our understanding, focussing on the main ideas of the underlying theories, their conceptual and technical limitations, and useful comparisons with, and interpretation of, experiment.

We will show ways to go beyond currently used approximations, and we will discuss fingerprints of correlation in photoemission, inelastic x-ray scattering and optical spectra, making close connections between theory and experiment. Systems used for illustration will include models, simple metals and semiconductors, carbon nanostructures and transition metal oxides [2].

The results have been obtained in collaboration with many colleagues in the Theoretical Spectroscopy Group of the Laboratoire des Solides Irradiés and in the European Theoretical Spectroscopy Facility.

[1] L. Hedin, Phys. Rev. **139**, A796 (1965).

[2] see e.g. M. Guzzo et al., *Phys. Rev. Lett.* **107**, 166401 (2011) and *Phys. Rev.B* **89**, 085425 (2014); M. Gatti, G. Panaccione, and L. Reining, *Phys. Rev. Lett.* **114**, 116402 (2015); J. Zhou et al., *J. Chem. Phys.* **143**, 184109 (2015); P. Cudazzo et al., *Phys. Rev. Lett.* **116**, 066803 (2016).

Hamburg Photon Science Colloquium

Water: from ab-initio simulations to coarse grained models

Roberto Car
Princeton University

The unusual properties of water, including the thermodynamic anomalies of the liquid, the existence of more than one amorphous ice form, and the abnormal mobilities of the water ions, derive from the tetrahedral network of hydrogen bonds that hold the molecules together. Modern ab-initio simulations had to overcome major challenges to successfully predict the properties of ambient water from the basic molecular interactions and dynamics. These studies reveal features of the coupled dynamics of electrons and nuclei that would not be otherwise accessible.

Understanding the microscopic origin of the thermodynamic anomalies of liquid water has been a long-standing issue in this field. The behavior of metastable water at deeply undercooled conditions may hold the clue for resolving this issue. The very long times scales associated with the relaxation processes of the hydrogen bond network at undercooled conditions make these studies only feasible with coarse-grained models. Recent progress in this context will be presented.

The connections of theory, simulation, and experiment will be stressed throughout the lecture.