# CPP 26: Frontiers in Electronic-Structure Theory - Focus on Electron-Phonon Interactions II (joint session O/HL/CPP/DS)

Time: Monday 15:00–17:30 Location: GER 38

CPP 26.1 Mon 15:00 GER 38

**Satellites in optical and loss spectra** — •Pier Luigi Cudazzo — Faculty of Science, Technology and Communication, RU Physics and Materials Science, Campus Limpertsberg, Université du Luxembourg, 162 A, avenue de la Faïencerie, L-1511 Luxembourg

Coupling of excitations leads to intriguing effects on the spectra of materials. We propose a cumulant formulation for neutral electronic excitations which opens the way to describe effects such as double plasmon satellites or exciton-exciton and exciton-phonon coupling. Our approach starts from the GW plus Bethe-Salpeter approximation to many body perturbation theory which is based on a quasiparticle picture, and it adds coupling of excitations through a consistent inclusion of dynamically screened interactions. This requires to consider scattering contributions that are usually neglected. The result is formulated in a way that highlights essential physics, that can be implemented as a post processing tool in first principles codes, and that suggests which kind of materials and measurements should exhibit strong effects. This is illustrated using a model.

CPP 26.2 Mon 15:15 GER 38

**The XPS limit within the one-step model of photoemission: temperature and photon energy effects** — •Laurent Nicolaï[1], Vladimir Strocov[2], Juraj Krempaský[2], Federico Bisti[2], Jürgen Braun[3], Hubert Ebert[3], Charles Fadley[4], Ajith Kaduwela[5], Nicholas Pike[6,7], Matthieu J. Verstraete[7], and Ján Minár[1] — [1]Univiversity of West Bohemia, Plzeň, Czech Rep. — [2]Paul Scherrer Institut, Villigen, Suisse — [3]Ludwig-Maximilians-Universität, Germany — [4]Berkeley, California, USA — [5]University of California, USA — [6]University of Oslo, Norway — [7]Université de Liège & European Theoretical Spectroscopy Facility, Belgium

Angle-Resolved Photoemission Spectroscopy (ARPES) is the method of choice for characterising the electronic structure of a given material. A complete understanding of the experimental spectra requires theoretical analyses as well. However, the development of theoretical tools in order to reproduce experimental conditions remains, to this day, a challenge. Using the one-step model of photoemission[1] as implemented in the SPRKKR package[2], our calculations incorporate temperature- and phonon energy-dependent effects via inclusion of both bulk[3] and surface phonons. We also investigate the photon energy range over which the Angle-Integrated PhotoEmission (AIPES) spectra can be compared to the corresponding Weighed Density of States (WDOS).

[1] Braun, Rep. Prog. Phys. 59, 1267-1338 (1996), [2] H. Ebert, D. Ködderitzsch and J. Minár, Rep. on Prog. in Phys. 74, 096501 (2011), [3] L. Nicolaï and J. Minár, AIP Conf. Proc. 1996, 020033 (2018)

CPP 26.3 Mon 15:30 GER 38

**Ab Initio Linear and Pump-Probe Spectroscopy of Naphthalene Crystals** — •Alan Lewis[1] and Tim Berkelbach[2,3] — [1]MPSD, Hamburg, Germany — [2]Columbia University, New York City, USA — [3]Flatiron Institute, New York City, USA

Linear and non-linear spectroscopies are powerful tools used to investigate the energetics and dynamics of electronic excited states of both molecules and crystals. While highly accurate ab initio calculations of molecular spectra can be performed relatively routinely, extending these calculations to periodic systems is challenging. Here, we present calculations of the linear absorption spectrum and pump-probe two-photon photoemission spectra of the naphthalene crystal using equation-of-motion coupled-cluster theory with single and double excitations (EOM-CCSD). Molecular acene crystals are of interest due to the low-energy multi-exciton singlet states they exhibit, which have been studied extensively as intermediates involved in singlet fission. Our linear absorption spectrum is in good agreement with experiment, predicting a first exciton absorption peak at 4.4 eV, and our two-photon photoemission spectra capture the behavior of multi-exciton states, whose double-excitation character cannot be captured by current methods. The simulated pump-probe spectra provide support for existing interpretations of two-photon photoemission in closely-related acene crystals such as pentacene.

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**All-electron real-time TDDFT implementation with Ehrenfest molecular dynamics** — •Ronaldo Rodrigues Pela[1,2] and Claudia Draxl[1,2] — [1]Institut für Physik and IRIS Adlershof, Humboldt-Universität zu Berlin, Berlin, Germany — [2]European Theoretical Spectroscopy Facility (ETSF)

Linearized augmented planewaves with local-orbitals (LAPW+lo) are arguably the most precise basis set to represent Kohn-Sham states. When employed within real-time time-dependent density functional theory (RT-TDDFT), they promise ultimate precision achievable for exploring the evolution of electronic excitations in time scales ranging from attoseconds to picoseconds. In this work, we present the implementation of RT-TDDFT in the full-potential LAPW+lo code exciting [1]. For relaxing the nuclear degrees of freedom, we include Ehrenfest molecular dynamics [2]. We benchmark our implementation by analyzing the electric current density and the ion dynamics of Si, C, SiC, and two dimensional BN under the exposure to laser pulses. We compare our results with those obtained using the octopus code [3] and find a satisfactory level of agreement.

**References**

[1] A. Gulans et al. J. Phys.: Condens. Matter **26**, 363202 (2014).
[2] G. Kolesov et al. J. Chem. Theory Comp. **12**, 466 (2015).
[3] X. Andrade et al. Physical Chemistry Chemical Physics **17**, 31371 (2015).

CPP 26.5 Mon 16:00 GER 38

**Ab initio study of nonradiative recombination for defects in MoS2 via multiphonon emission** — •Simone Manti[1], Lukas Razinkovas[2], Audrius Alkauskas[2], and Kristian Thygesen[1] — [1]Computational Atomic-scale Materials Design (CAMD), Department of Physics, Technical University of Denmark, Kongens Lyngby, Denmark — [2]Center for Physical Sciences and Technology (FTMC), Vilnius, Lithuania

Carrier capture at point defects determines the lifetime of charge carriers and is therefore a very important process for both electronic and opto-electronic devices. The general theory of nonradiative recombination via the so-called multiphonon emission is rather well established, but most studies to date have mainly focused on the description in bulk materials. In this work, we investigate nonradiative carrier capture for a prototypical 2D material, molybdenum disulphide MoS2. Multiphonon emission is governed by (i) electron-phonon coupling between the band edge states and defect states and (ii) the change in the defect geometry upon carrier capture. Our results provide a preliminary description for nonradiative electron capture at sulphur vacancies in monolayer MoS2. In particular, we reveal the important role of the Jahn-Teller effect on the capture process.

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**Phonon-induced electronic relaxation in a strongly correlated system: the Sn/Si(111) ($\sqrt{3} \times \sqrt{3}$) adlayer revisited** — •Peter Kratzer and Maedeh Zahedifar — Faculty of Physics, University Duisburg-Essen

The ordered adsorbate layer Sn/Si(111) ($\sqrt{3} \times \sqrt{3}$) with coverage of one third of a monolayer is considered as a realization of strong electronic correlation in surface physics. Our theoretical analysis shows that electron-hole pair excitations in this system can be long-lived, up to several hundred nanoseconds, since the decay into surface phonons is found to be a highly non-linear process. We combine first-principles calculations with help of a hybrid functional (HSE06) with modeling by a Mott-Hubbard Hamiltonian coupled to phononic degrees of freedom. The calculations show that the Sn/Si(111) ($\sqrt{3} \times \sqrt{3}$) surface is insulating and the two Sn-derived bands inside the substrate band gap can be described as the lower and upper Hubbard band in a Mott-Hubbard model with U=0.75eV. Furthermore, phonon spectra are calculated with particular emphasis on the Sn-related surface phonon modes. The calculations demonstrate that the adequate treatment of electronic correlations leads to a stiffening of the wagging mode of neighboring Sn atoms; thus, we predict that the onset of electronic correlations at low temperature should be observable in the phonon spectrum, too. The deformation potential for electron-phonon coupling is calculated for selected vibrational modes and the decay rate of an electron-hole excitation into multiple phonons is estimated, sub-

stantiating the very long lifetime of these excitations.

CPP 26.7 Mon 16:30 GER 38

**Spectral properties of the interacting homogeneous electron gas** — •Tommaso Chiarotti[1], Nicola Marzari[1], and Andrea Ferretti[2] — [1]Theory and Simulation of Materials (THEOS), and National Centre for Computational Design and Discovery of Novel Materials (MARVEL), École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland — [2]Centro S3, CNR–Istituto Nanoscienze, 41125 Modena, Italy

Despite its simplicity, the interacting homogeneous electron gas (HEG) is a paradigmatic test case in the study of the electronic structure of condensed matter. Beside being a model for valence electrons in simple metals, it also provides the basic ingredients for key electronic-structure theories. Here, we propose to study it with many-body perturbation theory (MBPT) using one shot, partial self-consistent, and full self-consistent GW, and analyze the description of its spectral function. For this, a novel numerical implementation of MBPT for the 3D non-relativistic HEG has been developed, with a special focus on the treatment of the full-frequency dependence of the Green's function and self-energies. Results for a broad range of densities (going from $r_s$ from 1 to 10) are presented with particular attention to the calculated density-of-states and the spectral potential.

CPP 26.8 Mon 16:45 GER 38

**Multipole Polarizabilites of Positronium and Its Interaction with Atoms and Molecules** — •Jorge Charry, Dmitry Fedorov, and Alexandre Tkatchenko — University of Luxembourg, 1511 Luxembourg, Luxembourg

Positron – the antiparticle of the electron – has many intriguing fundamental properties and it is also useful in many applications for probing matter. Besides electron-positron annihilation, metastable states of atomic and molecular systems involving binding between electrons and positrons are of great interest [1]. In addition, electrons and positrons can form positronium (Ps) atoms and even larger clusters. The polarization of positron by a residual ion is one of possible mechanisms for the formation of bound states for positron-based chemistry [2]. An accurate description of the polarizability of Ps and its bound state with atoms and molecules is essential to understand such interactions. Here, we extend the direct transition-matrix approach, proposed by Kharchenko to determine the multipole polarizabilities of the hydrogen atom [3], to the case of finite nuclear mass. The obtained analytical results, which are in agreement with our numerical calculations performed by means of the molecular orbital based method [4], show that Ps has unique properties in comparison to other normal atoms. Our results shed light into the fundamental interactions between matter and antimatter. [1] Gribakin *et al.*, Rev. Mod. Phys. **82**, 2557 (2010); [2] Bromley and Mitroy, J. Phys.: Conf. Series **199**, 012011 (2010); [3] Kharchenko, Annal. Phys. **355**, 153 (2015); [4] Reyes *et al.*, Int. J. Quant. Chem. **119**, 1 (2019)

CPP 26.9 Mon 17:00 GER 38

**Energy gap closure of crystalline molecular hydrogen with pressure** — •Vitaly Gorelov[1], Markus Holzmann[2,3], David M. Ceperley[4], and Carlo Pierleoni[5,1] — [1]Maison de la Simulation, CEA-Saclay, Gif-sur-Yvette, France — [2]Univ. Grenoble Alpes, CNRS, LPMMC, Grenoble, France — [3]Institut Laue-Langevin, Grenoble, France — [4]Department of Physics, University of Illinois Urbana-Champaign, USA — [5]Department of Physical and Chemical Sciences, University of L'Aquila, L'Aquila, Italy

We study the gap closure with pressure in Phases III and IV of molecular crystalline hydrogen. Nuclear quantum and thermal effects are considered from first principles with Coupled Electron Ion Monte Carlo. The fundamental electronic gaps are obtained from grand-canonical Quantum Monte Carlo methods properly extended to quantum crystals. Nuclear zero point effects cause a large reduction in the gap ($\sim 2eV$). As a consequence the fundamental gap closes at 530GPa for ideal crystals while at 360GPa for quantum crystals. Since the direct gap remains open until ∼450GPa, the emerging scenario is that upon increasing pressure in phase III (C2/c-24 crystal symmetry) the fundamental (indirect) gap closes and the system enters into a bad metal phase where the density of states at the Fermi level increases with pressure up to ∼450GPa when the direct gap closes. Our work partially supports the interpretation of recent experiments in high pressure hydrogen.

CPP 26.10 Mon 17:15 GER 38

**Using the powerful electronic structure theory to identify single photon emitters in h-BN.** — •Sajid Ali — CAMD, Department of Physics, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark

In recent years two-dimensional Van Der Walls material h-BN have gained a considerable interest due to the discovery of single photon emission (in both visible and UV region) from the colour centres in this material. This emission is bright, owing to the natural proximity of the centres to the surface, showing promise for high quantum efficiency applications, linearly polarized and strain tuneable. However, the exact chemical nature of the emitting centres is still unknown.

Here, we have performed first principle calculations to obtain observables that can be directly compared with electron paramagnetic resonance (EPR), Optically Detected Magnetic Resonance (ODMR), photoluminescence spectroscopy (PL) and Raman spectroscopy techniques performed on these h-BN emitters. We identify, based on the comparison of our calculations with the experimental data, the defect centres responsible for single photon emission from hexagonal boron nitride.