**MONDAY 9.00 – 10.30: K edges (part 1) John Rehr**

***John Rehr, Seattle, USA***

**Real-time and finite-temperature cumulant Green’s function approaches for excited states, x-ray spectra & thermodynamic properties**

Recently there has been considerable interest in the cumulant expansion for the one-electron Green's function [1], due to its success in treating many-body effects beyond the GW approximation. Here we discuss an extension based on a particle-hole cumulant to treat intrinsic and extrinsic losses and interference effects, including a real-time treatment for intrinsic charge-transfer excitations [2]. We also discuss the role of temperature using a finite temperature extension of the cumulant approach [3]. The method also yields thermodynamic properties including exchange-correlation energies and potentials, in good agreement with quantum-Monte Carlo calculations and fits to FT DFT functionals. \*Supported by DOE BES TCMP Grant DE-FG02-97ER45623.

[[1] Zhou JCP 143, 194109 (2015),](FXS/REHR1%20Zhou%20JCP%202015.pdf)[[2] Kas PRB 94, 035156 (2016)](FXS/REHR2%20Kas%20PRB%202016.pdf)*,* [[3] Kas. arXiv:1708.04126](FXS/REHR3%20Kas%20arXiv%201708.04126.pdf)

***David Prendergast, Berkeley, USA***

***Delphine Cabaret, Paris, France***

**Core-level spectra modelling using a DFT pseudopotential framework: from XAS to NRIXS**

A DFT-based pseudopotential approach, as developed in the XSpectra package of Quantum-Espresso [1-3], has proven its efficiency in the calculation of x-ray absorption spectra at numerous *K* edges for both electric dipole and quadrupole transitions [4,5]. This framework has been recently extended to the case of non-resonant inelastic scattering spectroscopy (NRIXS), which is becoming a promising tool to record spectra at *K* edges of low-*Z* elements, notably under extreme conditions. In this talk, I will show similarities and differences between XAS and NRIXS cross-sections, with a focus on the core-hole – electron interaction modelling.

[1] [Taillefumier PRB 66, 195107 (2002);](FXS/CABARET1%20Taillefumier%20PRB%202002.pdf)   
[2] [Gougoussis PRB 80, 075102 (2009);](FXS/CABARET2%20Gougoussis%20PRB%202009.pdf)    
[3] [Giannozzi JPCM 21, 395502 (2009)](FXS/CABARET3%20Giannozzi%20JCCM%202009.pdf)  
[4] [Cabaret PCCP 12, 5619 (2010)](FXS/CABARET4%20PCCP%202010.pdf)  
[5] [Nemausat PCCP 19, 6246 (2017)](FXS/CABARET5%20Nemausat%20PCCP%202017.pdf)

***Eric Shirley, NIST, USA*  
Exploration of local atomic geometry in perovskites**

We consider strontium, lead and barium-strontium titanate samples as a function of lattice distortions caused by epitaxial strain, vacancies, thermal motion of ions and/or phase transitions as a function of temperature.  Off-centering of the Ti ion within its oxygen cage mixes Ti 3d and 4p orbitals so that transitions of 1s electrons to eg-derived orbitals are enhanced by becoming dipole-allowed (E1) instead of just quadrupole-allowed (E2).  Other spectral features also appear to vary because of the off-centering, and these have been considered to be related to Ti 4p orbitals mixing with 3d orbitals on other sites.  We will investigate this concept and present a three-way comparison of three types of analysis that give insight into the off-centering: (1.) x-ray absorption near edge spectroscopy (XANES) measurements at the Ti 1s edge, (2.) Bethe-Salpeter calculations of the same, and (3.) density-functional calculations, for both ground-state calculations and finite-temperature ab initio molecular dynamics (AIMD).  This work is done in collaboration with Joe Woicik, Bruce Ravel, and Eric Cockayne of NIST, Steve Hellberg and Kris Andersen of NRL, and Keith Gilmore of ESRF.

***Keith Gilmore, ESRF, France***  
**A cumulant approach to including vibronic interactions in X-ray spectra**

Resonant inelastic X-ray scattering (RIXS) measurements now have sufficient energy resolution to reveal phonon contributions in a variety of systems. Recent experiments have mapped the ground- and excited-state potential energy surfaces of molecules [1] and determined the electron-phonon coupling strength in crystalline materials [2]. Particularly in the latter case, typical fitting of data with simplified models can lead to erroneous interpretations. It is preferable to develop first-principles methods for calculating the phonon contribution to RIXS spectra. Our initial efforts employ a cumulant formulation [3] for the vibronic contribution to the electron Green's function. The cumulant is constructed from molecular dynamics simulations or excited-state forces. Resulting X-ray photoemission and X-ray absorption spectra are in close agreement with experiment.

[1] [Schreck Sci. Rep. 6, 20054 (2016).](FXS/GILMORE1%20Schreck%20SR%202016.pdf)  
[2] [Johnston et al., Nat. Comm. 7, 10653 (2016).](FXS/GILMORE2%20Johnston%20NC%202016.pdf)  
[[3] Langreth. Phys. Rev. B 1, 471 (1970).](FXS/GILMORE3%20Langreth%20PRB%201970.pdf)

**MONDAY 11.00 – 12.40: K edges (part 2) Lars Pettersson**

***Lars Pettersson, Stockholm, Sweden***

**X-ray Spectroscopy Simulations of H-bonded Liquids**

The oxygen 1s core-hole life-time is long enough (~3.6 fs) that significant vibrational excitations take place in the internal OH bonds that the core-excited oxygen participates in. This results in significant life-time vibrational interference[1,2] or dynamical effects that redistribute intensity in the computed spectrum. We include these effects in a semi-classical approximation to the Kramers-Heisenberg formula by running classical core-hole-induced dynamics where it is essential to sample the zero-point quantum probability distributions of momenta and initial OH positions[3] . We have recently performed simulations of liquid methanol[4]. Here I will show how different aspects of H-bonding, initial conditions and, in the case of ethanol, also the internal conformation affect the computed spectrum. Extending to water we need significantly more trajectories since two OH groups must be sampled. I will discuss preliminary results from a search for structural criteria on simulated water that should be fulfilled in order to reproduce both x-ray absorption and emission spectra as well as the O-O radial distribution function of liquid water. In that case we employ our SpecSwap-RMC [5,6] multiple-data fitting technique.

[1] [Gelmukhanov CPL. 46, 133, (1977);](FXS/PETTERSSON1%20Gelmukhanov%20CPL%201977.pdf)

[2] [Ljungberg JCP 134, 044513 (2011)](FXS/PETTERSSON2%20Ljungberg%20JCP%202011.pdf);

[3] [Ljungberg PRB 82, 245115 (2010).](FXS/PETTERSSON3%20Ljungberg%20PRB%202010.pdf) [4] Ljungberg JCP 146, 134506, (2017); [5] [Leetmaa JPCM 22, 135001, (2010)](FXS/PETTERSSON5%20Leetmaa%20JPCM%202010.pdf);

[6] [Wikfeldt JCP 132, 104513 (2010).](FXS/PETTERSSON6%20Wikfeldt%20JCP%202010.pdf)

***Patrick Norman, Stockholm, Sweden***

**Response theory techniques to address X-ray spectroscopies with a focus on RIXS**

With the installation of the fourth-generation synchrotron facility MAX IV in Sweden and XFEL facilities around the world, the Knut and Alice Wallenberg Foundation has initiated a concomitant investment in the development of theory and simulation techniques. The resulting Consortium for Theoretical X-ray Sciences (CoTXS) initiative builds on the active collaboration and synergy between seven leading theoretical groups in Sweden with principal investigators P. Norman, I. Abrikosov, R. Lindh, O. Eriksson, L.G.M. Pettersson, Y. Luo, and H. Ågren. We will present recent advances in response theory, designed to address molecular systems under electronic resonance conditions and referred to as the complex polarization propagator (CPP) approach [1]. In the CPP formulation, electronic relaxation in the core-excited state becomes a matter of electron correlation as illustrated in studies employing the hierarchical sets of coupled cluster (CC) and algebraic diagrammatic construction (ADC) methods. The full propagator formulation of inelastic scattering matrix elements (the Kramer–Heisenberg– Dirac formula) has been derived in the ADC framework, which provides a response theory treatment of RIXS spectroscopy. The CPP approach is open-ended for extensions toward nonlinear X-ray spectroscopies.

[1] [Norman PCCP 13, 2051 (2011)](FXS/NORMAN1%20PCCP%202011.pdf)

***Barbara Brena, Uppsala, Sweden***

**K edge XAS and XPS of Molecules in Solvation and adsorbed on surfaces in a periodic approach**

I will present very recent results of the calculation of N K-edge absorption spectra and Photoemission spectra of triazine molecules in gas phase and adsorbed on a gold surface. We have simulated the absorption spectra by the N p partial density of states, calculated with half core hole in the Transition Potential Approach [1] . The calculations were performed with the Vasp code [2] and the projector augmented wave approach [3] . The main advantage of the periodic scheme in the present context is that the metal surface can easily be included in the calculations. We have also performed C1s Photoemission spectra calculations for Ru complexes in aqueous solution. In this case we have studied complexes containing a Ru atom with different oxidation number. In addition to the transition potential approach, we have also used ad hoc cut water clusters, computed by Monte Carlo simulations to account for the aqueous environment surrounding the complexes.

[1] [Triguero PRB 58, 8097 (1998](FXS/BRENA1%20Triguero%20PRB%201998.pdf)); [2] [Köhler PRB 70, 165405 (2004).](FXS/BRENA2%20Kohler%20PRB%202004.pdf) [3] [Kresse PRB 59, 1758 (1999).](FXS/BRENA3%20Kresse%20PRB%201999.pdf)

***Nick Besley, Nottingham, UK***

**The exchange-correlation functional in DFT calculations of XAS and XES spectra**

The calculation of X-ray absorption and X-ray emission spectra within the framework of time-dependent density functional theory (TDDFT) will be reviewed [1,2]. The dependence of the computed spectra on the nature of the exchange-correlation functional will be discussed and the use of short-range corrected and modified hybrid exchange-correlation functionals will be described [3]. The simulation of X-ray emission and resonant inelastic X-ray scattering spectra based upon Kohn-Sham DFT calculations will also be discussed [4] and the role of the exchange-correlation functional in these calculations will be explored.

[1] [Wadey JCTC 10, 4557 (2014)](FXS/BESLEY1%20Wadey%20JTCT%202014.pdf)

[2[] Besley JCTC 12, 5018 (2016)](FXS/BESLEY2%20JTCT%202016.pdf)

[3] [Besley PCCP 11, 10350 (2009)](FXS/BESLEY3%20PCCP%202009.pdf)

[4] [Hanson-Heine JCP 146, 094106 (2017)](FXS/BESLEY4%20Hanson-Heine%20JCP%202017.pdf)

***Niri Govind, PNNL Richland, USA***

**Core-Level Spectroscopies with Linear-Response and**

**Real-Time Time-Dependent Density Functional Theory**

This talk will focus on our recent developments geared towards studying core-level spectroscopies (pre and near-edge XANES) with linear-response and real-time TDDFT. This will be illustrated with applications to K-edge XANES of transition metal complexes in realistic environments combined with AIMD/MM simulations. I will also discuss our recent work on valence-to-core x-ray emission spectroscopy (VtC-XES) of transition metal complexes and solid-state transition metal compounds.

[1[] Lopata JCTC 7, 1344 (2011)](FXS/GOVIND1%20Lopata%20JCTC%202011.pdf) [2[] Lopata JCTC 8, 3284 (2012)](FXS/GOVIND2%20Lopata%20JCTC%202012.pdf) [3[] Lopata JCTC 9, 4939 (2013)](GOVIND3%20Lopata%20JCTC%202013.pdf) [4] [Fischer JCTC 11, 4294 (2015)](FXS/GOVIND4%20Fischer%20JCTC%202014.pdf) [5] [Zhang JCTC 11, 5804 (2015)](FXS/GOVIND5%20Zhang%20JCTC%202015.pdf) [6] [Mortenson PRB 96, 125136 (2017)](FXS/GOVIND6%20Mortensen%20PRB%202017.pdf)

**MONDAY 13.00 – 14.30: L edges (part 1) Maurits Haverkort**

***Maurits Haverkort, Heidelberg, Germany***

**Quanty and first-principle multiplet calculations**

Within this talk I will review different types of core level excitations, related to the amount of correlations needed to describe these states. I will discuss band transitions, excitons and resonances, why in some materials (La2CuO4 for example) the O-K edge is well described by a band transition, whereas the Cu-L edge is a strong exciton and what this means for the level of theory needed.

[1] [Haverkort PRB 85, 165113 (2012)](FXS/HAVERKORT1%20PRB%202012.pdf)

***Robert Green, Vancouver, Canada*  
2p3d spectroscopy in high valence 3d oxides –beyond conventional multiplet ligand field theory**

In this talk, I will discuss the challenge of 3d transition metal oxides with unusually high formal oxidation states. Such materials can exhibit a small or even negative charge transfer energy, and subsequent “self-doping” of oxygen 2p holes. Examples include the formally trivalent perovskite nickelates (RNiO3, with R a rare earth) and the formally tetravalent perovskite ferrates (CaFeO3, for example). These materials pose a significant difficulty for conventional multiplet ligand field theory, and even single impurity Anderson model calculations do not seem to capture the XAS spectral shape. I will discuss our recent implementation of a double cluster ligand field theory for the interpretation of 2p3d XAS and resonant magnetic diffraction in these materials. The model can account for effects such as bond disproportionation, and yields excellent agreement with both XAS and resonant diffraction lineshapes. I will give some examples of other systems where it might be applied and go over some shortcomings that could be improved in future work.

[1] [Green PRB 94, 195127 (2016)](FXS/GREEN1%20PRB%202016.pdf)

***Atsushi Hariki, Vienna, Austria***

**Nonlocal charge-transfer effect on L-edges of 3d transition metal oxides.**

We present a systematic study of L-edge X-ray photoemission spectroscopy (XPS) of transition-metal monoxides MO (M=Ni,Co,Mn) and sesquioxides M2O3 (M=V, Cr, Fe), paying attention to the nonlocal charge-transfer screening effect on fine spectral features [1]. We employ the local-density approximation (LDA) + dynamical mean-field theory (DMFT), where the impurity Anderson model including the core states of the studied atom is constructed using the continuous LDA+DMFT hybridization function, which reflects the correlated dynamics of the valence electrons in the realistic crystal. This allows us to obtain the fine structure of the spectra missing in the conventional cluster-model calculations, which capture only the metal-ligand hybridization.

We find overall a good agreement with recent HAXPES experiments. We show how the fine structures in the XPS are related to specific microscopic processes. We will also present selected examples of application of the present approach to the L-edge X-ray absorption spectra and L-edge resonant inelastic X-ray scattering.

[1] [Hariki PRB 96. 045111 (2017).](FXS/HARIKI1%20PRB%202017.pdf)

***Yaroslav Khvashnin, Uppsala, Sweden***

**DMFT based interface to multiplet calculations**

In my talk I will present our implementation of the method for *L*-edge x-ray spectroscopy (XAS), which combines the density-functional theory with multiplet ligand field theory.  We adopted the idproposed few years ago [1] and reformulated it in the language of dynamical mean field theory (DMFT) [2]. As an example, I will show the recent results for CoFe2O4 spinel. We found a distinct differences in the simulated *L*-edge spectra of Co and Fe atom depending on the symmetry of the occupied (tetragonal or octahedral) site. A comparison with high-resolution experimental data allowed us to identify the degree of disorder in the actual sample.

The main part of the talk will be dedicated to the existing challenges of the approach, such as the role of the projection, i.e. the choice of the localised orbitals, explicit account of the core-hole and its impact on the valence electrons and estimation of the screening of the Slater integrals.

[1] [Haverkort PRB 85, 165113 (2012)](FXS/HAVERKORT1%20PRB%202012.pdf);   
[2] [Lüder arXiv:1706.08168](FXS/KVASHNIN2%20Luder%202017.pdf)

**MONDAY 15.00 – 17.40: L edges (part 2) Michael Odelius**

***Tom Regier, CLS Saskatoon, Canada***

**Designing XAS experiments to optimize model constraints**

Experimental design for XAS has traditionally focused on the approach that the measurement should probe the true x-ray absorption coefficient of the sample which can then be compared to the modeled absorption cross section. An alternative approach is to design the experiment to generate a set of observations that can provide the best achievable set of constraints on theoretical models of the core excitation and decay processes. A physical model of the sample and detector system is used to account for distortions, sample inhomogeneity and optical effects. Results can then be compared with the full theoretical treatment of the core excitation and x-ray emission processes to determine the validity of the model used. In this approach, a deviation free measurement of the absorption coefficient is no longer the goal of the experiment as the deviations have become part of the model. The soft XAS endstation at the CLS was designed to measure x-ray emission and scattering from a sample over a wide energy range at the extreme geometries with respect to the polarization of the incident beam. This instrumental configuration is able to provide a set of observations that offer a unique picture of the core excitation process that is well suited for comparison with theory. Initial measurements suggest potential tight constraints on the theoretical modelling of the core excitation process.

***Michael Odelius, Stockholm, Sweden***

**Quantum chemical calculations of excited state molecular dynamics and ground state vibrations with RIXS**

Through multi-configurational quantum chemical (RASPT2) calculations we can simulate L-edge resonant inelastic X-ray scattering (RIXS) spectra for possible reaction intermediates, including both electronically excited and structurally distorted species. In the presentation, I show how this allows us both to guide the interpretation  of time-resolved L-edge RIXS spectra of transition metal complexes and to determine dynamical effects in ultra-high resolution RIXS. In both applications, the theoretical simulations allows us to extract  experimental information on extended region of the potential energy surfaces  of the states involved. Thereby, we can fully utilize this powerful probe of the local electronic structure.

***Oliver Kuhn, Rostock, Germany*  
First principles approach of L-edge spectra**

X-ray spectroscopy has become a routine tool that can reveal highly local and element-specific information on the electronic structure of atoms in complex environments. Theoretical predictions for L-edge spectra of transition metal compounds are rather challenging due to the often pronounced multiconfigurational character of the electronic wave function as well as strong spin-orbit coupling. Recently, we have developed an efficient and versatile theoretical methodology for the treatment of soft X-ray spectra of transition metal compounds mainly based on the multi-configurational self-consistent field (RASSCF) electronic structure theory combined with a perturbative LS-coupling scheme for spin-orbit coupling [1-7]. In this contribution, the developed protocol will be illustrated for the case of Fe(CO)5 [4], which will also serve to demonstrate the shortcomings of standard density functional theory (ROCIS). Further, a wave function based approach adapted from exciton theory will be introduced as a means to quantify aggregation effects on X-ray absorption and scattering (RIXS) spectra [7].

[1] [Bokarev PRL 111, 083002 (2013).](KUHN1%20Bokarev%20PRL%202011.pdf) [2] [Golnak Sci. Rep. 6, 24659 (2016).](FXS/KUHN2%20Golnak%20SR%202016.pdf) [3] [Bokarev JPCC 119, 19192 (2015).](FXS/KUHN3%20Bokarev%20JPCC%202015.pdf) [4] [Suljoti AC 52, 9841 (2013).](FXS/KUHN4%20Suljoti%20AC%202013.pdf) [5] [Engel JPCB 118, 1555 (2014).](FXS/KUHN5%20Engel%20JPCB%202014.pdf) [6] [Atak JPCB 117, 12613 (2013).](FXS/KUHN6%20Atak%20JPCB%202013.pdf) [7] [Preuße SD 3 062601 (2016).](FXS/KUHN7%20Preusse%20SD%202016.pdf)

***Hidekazu Ikeno, Kyoto, Japan***

**DFT-CI Calculations for *L*2,3-edge RIXS-MCD**

In this presentation, the *ab-initio* configuration interaction method using the four-component molecular orbitals obtained by relativistic density functional calculations (DFT-CI) is introduced. The method has quantitatively reproduced and predict the multiplet structures at the transition metal *L*2,3-edge x-ray absorption spectra (XAS) and its magnetic circular dichroism (XMCD) of many compounds with different *d*-electron numbers and atomic coordination. The resonant inelastic x-ray scattering (RIXS) and RIXS-MCD at *L*2,3-edge, which is a photon-in/photon-out spectroscopy and allows us to access the d-d electronic excitations, can also be calculated following the Kramers-Heisenberg formula using the many-electron wavefunctions obtained by the DFT-CI method. The soft x-ray RIXS-MCD can potentially be applied to reveal the magnetic structures which cannot be reached by XMCD. The results of the Fe-*L*2,3 RIXS-MCD for weak ferromagnetic α-Fe2O3 will be discussed. [Ikeno microscopy 1, (2017)](file:///C:\Users\groot113a\Downloads\FXS\IKENO%20micr%202017.pdf)

***Harry Ramanantoanina, PSI, Suisse***

**LFDFT - A non-empirical ligand-field method that calculates 2*p* core-electron excitations in 3*d* compounds using DFT**

We present progress in the development of the Ligand-Field Density Functional Theory (LFDFT) program, [1-4] which has been recently implemented in ADF. [5] Methodological concepts are reported for the (1) calculation, without empirical parameters, of multiplet energy levels and ligand-field effects associated with two-open-shell 2*p*53*d*n+1 electron configurations; and (2) modeling of X-ray absorption spectra in relation to the intra-atomic 3*d*n → 2*p*53*d*n+1 electron transitions. A Density Functional Theory method is used for the determination of the electronic structure using an average of configuration type calculation. [6,7] An effective ligand-field Hamiltonian is also used to incorporate many body effects and corrections *via* configuration interaction algorithm within the active space of Kohn-Sham orbitals with dominant 2*p* and 3*d* characters. The theoretical method insures a parameter-free ligand-field model, which is illustrated with examples for applications. [3] Comparison with available experimental data is realized, revealing in fine the advantages and limitations of the LFDFT program in terms of predictive power and performance.   
[1] [PCCP 15, 13902 (2013](FXS/RAMANA1%20PCCP%202013.pdf)); [2] [PCCP 16, 14625 (2014](FXS/RAMANA2%20PCCP%202014.pdf)); [3] [PCCP 17, 18547 (2015](FXS/RAMANA3%20PCCP%202015.pdf)); [4] [PCCP 18, 19020 (2016](FXS/RAMANA4%20PCCP%202016.pdf)) [5] <http://www.scm.com> [6] [JMM 23, 243 (2017);](FXS/RAMANA6%207%20JMM%202016.pdf) [7] [PCCP 19, 20919 (2017](FXS/RAMANA7%20PCCP%202017.pdf))

**TUESDAY 9.00 – 10.40: Non-dipole Hao Tjeng**

**Hao Tjeng, MPG Dresden, Germany**

**4f crystal field ground state of the strongly correlated topological insulator SmB6**

It was recently proposed that the intermediate valent Kondo insulator SmB6 [1,2] could be a topological insulator. The proposal is appealing since rare earth Kondo insulators have the necessary ingredients for strong spin-orbit coupling and electrons of opposite parity, namely the 4f and 5d. The concept of strongly correlated topological insulators is also exciting because their surfaces may host novel phenomena not present in the surfaces of semiconductor-based topological insulators. Information of the surface topology can be unambiguously inferred from the symmetries and parities of the bulk states involved. Knowledge about the crystal electric field (CEF) ground state symmetry of SmB6 therefore plays an essential role. For example, theoretical predictions for the spin texture of the sought-after topological surface states depend very much whether the ground state of the 4f5 J5/2 configuration is the Γ8 quartet or the Γ 7 doublet CEF state. The resulting type or direction of the winding of the spin with wave vector is opposite [3-6]. We performed bulk-sensitive NIXS measurements that target specifically the ground state symmetry of SmB6. Here we make use of highly excitonic character of the higher multipole transitions made possible by the large momentum transfer q in our experiment and of the strong directional dependence of the scattering function S(q,ω) [7-9], giving the symmetry information of the ground state wave function, even for cubic compounds. We found from our spectra that the Γ8 quartet governs the ground state symmetry and hence the topological properties of SmB6 [10].

[1] [Dzero PRL 104, 106408 (2010).](FXS/TJENG1%20Dzero%20PRL%202010.pdf) [2] Takimoto J. Phys. Soc. Jpn. 80, 123710 (2011). [3] [Baruselli PRL 115, 156404 (2015).](FXS/TJENG3%20Baruselli%20PRL%202015.pdf) [4[] Legner PRL 115, 156405 (2015).](FXS/TJENG4%20Legner%20PRL%202015.pdf) [5] [Baruselli PRB 93, 195117 (2016).](FXS/TJENG5%20Baruselli%20PRL%202014.pdf) [6] [Xu NC 5, 4566 (2014).](FXS/TJENG6%20Xu%20NC%202010.pdf) [7[], Willers PRL 109, 046401 (2012)](FXS/TJENG7%20Willers%20PRL%202012.pdf) [8[] Sundermann SR 5, 17937 (2015)](FXS/TJENG8%20Sundermann%20SR%202015.pdf) [9] [Sundermann NAS 113, 13989 (2016)](FXS/TJENG9%20Sundermann%20PNAS%202016.pdf) [10] [Sundermann arXiv: 1706.08072](FXS/TJENG10.pdf)

**Simo Huotari, Helsinki University, Finland**

**X-ray Raman Spectroscopy**

We investigate non-correlated metal L edges using x-ray Raman spectroscopy (notably Mg and Al) in systems relevant for catalysis and energy storage. Owing to the low excitation energy (below 100 eV), at low momentum transfers, where dipole transitions dominate, the Compton line overlaps with the L edges, and hence from experimental aspects the data is easier to extract if using high momentum transfers (~10 inverse Angstroms). In this case the non-dipolar transitions can dominate the spectra, and their interpretation is done, e.g., using FEFF's routines for non-resonant inelastic x-ray scattering. The work shows how to unify the information given by the L edges with the one from corresponding metal's K edges.

***Steve Collins, Diamond, UK***

**Borrmann spectroscopy**

We introduce Borrmann Spectroscopy as an example of x-ray absorption of a wave field composed of multiple (two in this case) coherent plane waves. We show that the spectroscopic selection rules are modified to give a huge relative enhancement of quadrupole absorption over dipole [1,2]. The dipole and quadrupole contributions can be identified by their unique temperature dependence [3,4]. Generalization to other non-trivial wave fields is discussed.  
[1] [Pettifer Nature 454 196(2008)](FXS/COLLINS1%20Pettifer%20N%202008.pdf); [2] [JP Conf. 190 012045 (2009)](FXS/COLLINS2%20JPCS%202012.pdf); [3] [Tolkiehn PRB  84  241101 (2011)](FXS/COLLINS3%20Tolkiehn%20PRB%202011.pdf) [4] [EPJ 208, 75 (2012)](FXS/COLLINS4%20EJP%202012.pdf)

***Christoph Jacob, Braunschweig, Germany***

**Origin-Independent Quadrupole Intensities in XAS**

Theory has become an important tool for the interpretation of X-ray spectra, for instance, of catalytically active transition metal complexes. For X-ray spectroscopy at the metal K-edge, the calculation of the intensity faces conceptual difficulties. Often, the dipole approximation is not sufficient and higher-order (quadrupole) contributions have to be included. These electric-quadrupole and magnetic-dipole contributions are both origin-dependent [1]. Here we derive and implement a methodology that makes the total oscillator strength origin-independent by consistently including all terms that belong to the same order in the wave vector as the electric-quadrupole and magneticdipole contributions. These are the electric-dipole–electric-octupole and electric-dipole–magneticquadrupole interference terms [2]. The generalization of this methodology to octupole (and higherorder) transitions as well as circular dichroism is also discussed.

[1] [DeBeer ICA 361, 965 (2008).](FXS/JACOB1%20Debeer%20ICA%202008.pdf)

[2[] Bernadotte JCP 137, 204106 (2012).](FXS/JACOB2%20Bernadotte%20JCP%202012.pdf)

**Elisa Costantini, SRON, Netherlands**

**interstellar dust in space and in the laboratory**

Interstellar dust takes part in every important process in the Universe, from distant galaxies down to planet formation. Recently it has been realized that X-rays are a powerful tool to study the chemical and physical characteristics of interstellar dust grains. Dust can be indeed observed through extinction features in the X-ray spectrum (in the range 0.5-10 keV) of bright background sources [1]. It is crucial to compare the astronomical data with laboratory measurements of interstellar dust analogues. In the past years we carried on an extensive measurement campaign using several facilities in Europe. The goal is to characterize all the main components of cosmic dust in the X-ray band via the XAFS measurements around the edges of O, Fe, Mg and Si [2,3] and also trace elements, like Al and S. The synergy between laboratory measurements and the high-energy resolution provided by modern X-ray telescopes allows us to investigate important open issues, such as the iron inclusion in silicates, crystallinity of dust, and map abundances and depletions of the most abundant elements in our Galaxy.

[1] [AA 539, 32 (2012)](FXS/COSTANTINI1%20AA%202012.pdf)

[2] [Zeegers AA 599, 117 (2017)](FXS/COSTANTINI%20zeegers%20AA%202016.pdf)

[3] [Rogantini AA (2017) arXiv:1709.05359](FXS/COSTANTINI4%20Rogantini%20AA%202017.pdf)

**TUESDAY 11.00 – 12.40: RIXS Pieter Glatzel**

***Pieter Glatzel, ESRF, France***

**Challenges for theoretical spectroscopy**

I will present data that to the best of my knowledge pose a challenge to theoretical spectroscopy:  
(1) 1s2p and 1s3p RIXS at the K pre-edge of 3d transition metals: The pre-edges in absorption spectroscopy are broad and show too little structure to rigorously probe a theoretical model. RIXS planes provide considerably more information but the calculations are even more challenging because the p-hole in the final states gives rise to a rich multiplet structure. Crystal field multiplet calculations give satisfactory results for ionic systems with the transition metal in Oh or Td symmetry. Reliable calculations of 1snp RIXS for a larger family of systems are indispensable in order to render this technique useful to a large community.  
(2) Some multi-electron excitations can be understood within the Anderson impurity model. In this case, the ground state is described by a linear combination of configurations that consider charge transfer. Core hole potential induced charge transfer excitations can nicely be made visible in RIXS. This is often interpreted as “covalence” because it adds metal-ligand orbital mixing to a crystal field picture. This is different from orbital mixing and thus covalence found in a DFT description. DFT struggles to model the multi-electron excitations. Can the definitions of covalence be reconciled? How can I understand multi-electron excitations in a DFT picture? Does a multi-determinant description of the ground state as it becomes necessary to model the multi-electron excitations have important consequences for the macroscopic properties of the system?

***Myrtille Hunault, Soleil, France***

**Non-local states in XAS and RIXS: the example of FeTiO3**

“Non-local” features at the onset of the K-edge have been reported for several transition metal oxides, among which the well-known cases of titanium oxides. These features are assigned to states from the neighboring cations. In the case of ilmenite (FeTiO3), the non-local peaks at the Fe K-edge are assigned to the mixing with Ti 3d states. [1] The element selectivity of RIXS reveal the contrast between the localized Fe 3d states and the delocalized Ti 3d states. The resonant character of the emission spectra obtained at the non-local features will be discussed in the perspective of probing metal-metal charge transfer excited states. [1] [IC 56, 10882(2017)](file:///C:\Users\groot113a\Downloads\FXS\HUNAULT1%20IC%202017.pdf)

***Philippe Wernet, BESSY, Berlin***

**Why new tools for x-ray spectroscopy enable new science**

Based on some of our recent studies [1-3] and with ongoing investigations I will try to illustrate how readdressing the fundamentals of x-ray spectroscopy may give access to hitherto inaccessible correlations between experimental observables and theoretical concepts. We combine new experimental tools at synchrotron radiation sources and at x-ray free-electron lasers with ab initio quantum-chemical calculations. We test fundamental concepts of chemical interactions, probe the excited-state dynamics of 3d metal complexes and wonder why the L-edge absorption energy of 3d transition-metal complexes shifts with oxidation state.   
[1] [Nature 520, 78 (2015),](FXS/WERNET1%20N%202015.pdf) [2] [JCP 146, 211103 (2017)](FXS/WERNET2%20JCP%202017.pdf) [3] [Kubin SD 4, 054307 (2017).](FXS/WERNET3%20Kubin%20SD%202017.pdf)

***Kurt Kummer, ESRF, France***

**Excitations of the 4f shell in lanthanides using soft X-rays**   
  
New instrumentation in resonant inelastic X-ray scattering in the soft X-ray range has made this technique applicable for studies of the 4f shell in the lanthanides. It is now possible to study excitations at the strong M\_4,5 resonances with a resolution of a few tens of eV, as a function of momentum transfer and with polarisation analysis. This makes RIXS an ideal tool for determining, for instance, the crystal field   
scheme of the 4f levels with very high accuracy and we will show some examples for that. But pushing the resolution we also find signatures in the excitation spectra that suggest significant damping and coupling to non-local excitations. What M\_4,5 RIXS really measures in rare earth compounds is still an open question.

***Jeroen van den Brink, Dresden, Germany***

**Electron-phonon interaction in antiferromagnetic and superconducting cuprates probed by 2p3d RIXS**

The electron-phonon (e-ph) interaction underpins many phenomena in solids, including instabilities towards superconducting states [1-3]. Whereas all essential physical properties of conventional superconductors depend on the e-ph interaction, its precise role in the high-Tc superconducting cuprates remains unresolved. An analysis of the Cu L-edge RIXS intensities enables the direct extraction of the momentum dependent e-ph coupling strength in high-Tc cuprates. We establish that in NdBa2Cu3O6+δ (NBCO) and CaCuO2 (CCO) a set of buckling modes couples more strongly than the stretching modes by about a factor of two. We further observe a significant doping dependence, where doping enhances the coupling to the buckling modes by up to 50-60%. This gives a new experimental basis to the study of synergy between phonons and spin excitations in high Tc superconductivity.

[1] [Johnston NC 7, 10653 (2016)](FXS/GILMORE2%20Johnston%20NC%202016.pdf)  
[2] [Lee PRL 110, 265502 (2013)](FXS/VANDENBRINK2%20Lee%20PRL%202013.pdf)  
[3] [Ament EPL 95, 27008 (2011)](FXS/VANDENBRINK3%20Ament%20EPL%202012.pdf)

***Di-Jing Huang, NSRRC, Taiwan***

**XAS and RIXS of polar magnet Fe2Mo3O8**

Multiferroic materials which possess more than one ferroic order have attracted many interests, due to the spontaneous coexistence of electricity and (anti)magnetism. The magnetoelectric effect (ME) is a key in designing novel electronic devices. The polar magnet Fe2Mo3O8 shows not only strong ME coupling but also chemical-doping controllability of the distinct ME phases [1, 2]. We will present XAS and RIXS studies on Fe2Mo3O8 to reveal its electronic structure properties. We carried out multiplet calculations using Quanty to disentangle the contributions of the octahedral and tetrahedral Fe2+ sites and to understand the effect of trigonal distortion.

[1] [Kurumaji SR 5, 12268 (2015)](FXS/HUANG1%20Kurumaji%20PRX%202015.pdf)

[2] [Wang PRX 5, 031034 (2015)](FXS/HUANG2%20Wang%20SR%202015.pdf)

**TUESDAY 14.00 – 15.30: Angles & Dichroism Amelie Juhin**

***Amelie Juhin, Paris, France*  
Quantifying th*e* Gd *5d* crystal field splitting and *5d-6p* mixing in GGG using X-ray Natural Linear Dichroism**

The electronic structure of Gadolinium Gallium Garnet Gd3Ga5O12 (GGG) has been studied by X-ray Absorption Spectroscopy performed at the Gd *L1-*edge, with high-resolution fluorescence detection using the *5p2s* emission channel. By performing XAS and X-ray Natural Linear Dichroism measurements on a GGG single crystal, which were compared to single particle calculations with FDMNES, we have identified the nature and quantified the different terms contributing to the absorption cross-section. In addition to the intense electric dipole transitions (*E1-E1*, *2s6p*) that build the main absorption edge, two peaks of electric quadrupole origin (*E2-E2, 2s5d*) are identified in the pre-edge, providing an estimated of the crystal field splitting on the *5d* orbitals. Another interesting result is that at ~20 eV below the main edge, the *4f* empty states of the Gd ion are probed due to the interference between electric dipole and electric octupole terms (*E1-E3*). The XNLD signal measured at this energy therefore quantifies the admixture between the Gd *4f* and *6p* states. Finally, a new sum rule providing access to this “cross hexadecapole moment” will be presented.

***Hebatalla Elnaggar, Utrecht, Netherlands***

**Unravelling Fe orbital moments in magnetite**

Fe3O4 is an archetype correlated material that displays competing ordering effects. Although intensively studied, the ground state of Fe in Fe3O4 is under debate. In particular, the magnitude of the spin and orbital moments of Fe, quantities of unique interest to spintronic applications, remain controversial. Orbital moments as small as 0.01μB [1] and as large as 0.65μB [2] in addition to fully compensated large orbital moment contributions [3] were reported. In order to shed light on this long lasting dispute, we performed a detailed angular study of Fe 1s2p resonant inelastic x-ray scattering magnetic linear dichroism (RIXS-MLD) and Fe K-edge  x-ray magnetic circular dichroism (XMCD) on a (110) Fe3O4 single crystal. We identified spectral features arising from formal Fe2+ sites employing the strong restrictions on the accessible excited and final states imposed by the crystal symmetry and scattering geometry. Comparing our results to multiplet ligand-field calculations, we showed that formal Fe2+ sites in Fe3O4 have large un-quenched orbital moments. The methodology that we developed opens up new avenues for site-selective, bulk-sensitive studies of the ground state properties in strongly correlated systems.  
[1] [Goering EPL, 73, (2005)](FXS/ELNAGGAR%20Goering%20EPL%202005.pdf)  
[2] [Huang PRL, 96, 096401 (20046)](FXS/ELNAGGAR%20Huang%20PRL%202006.pdf)  
[3] [Goering, PSS, 248, 2345 (2011](FXS/ELNAGGAR%20Goering%20PSS%202011.pdf))  
[4] [Haverkort PRB 85 165113 (2012)](FXS/HAVERKORT1%20PRB%202012.pdf)

***Gerrit van der Laan, Diamond, UK***

***Theoretical concepts of angular dependent core-level spectroscopy***

I will discuss some of the fundamental theoretical concepts arising across different core-level spectroscopies that include dichroism and angular dependence. While the angular dependence of x-ray magnetic circular dichroism (XMCD) is rather simple, increasing complexity is present in the angular dependence of (resonant) photoemission spectroscopy (PES) [1].

[[1] JES 200, 143 (2015).](FXS/VANDERLAAN%20JES%202015.pdf)

***Philippe Sainctavit, Paris, France*  
X-ray optical activity of a tricobalt metal atom chain**

A simple procedure based on anion exchange was employed for the enantiomeric resolution of the extended metal atom chain (EMAC) [Co3(dpa)4(MeCN)2]2+. Use of the chiral anion [As2(tartrate)2](NBu4)2, (L-**1** or D-**1**), resulted in the selective crystallization of the EMAC enantiomers as diastereomeric (D-**2**) and (L-**2**), respectively, in the P4212 space group, whereas a racemic mixture of **1** yielded (rac-**3**), which crystallized in the C2/c space group. The local electronic and magnetic structure of the EMAC enantiomers was studied, exploiting a variety of dichroisms in single crystals [1]. A strong linear dichroism at the Co K-edge was observed in the orthoaxial configuration, whereas it vanished in the axial orientation, thus spectroscopically confirming the D4 crystal symmetry. Compounds D-**2** and L-**2** are shown to be enantiopure materials as evidenced by mirror-image natural circular dichroism spectra in the UV/vis in solution and in the X-ray range at the Co K-edge in single crystals. The surprising absence of detectable X-ray magnetic circular dichroism or X- ray magnetochiral dichroism signals at the Co K-edge, even at low temperature (3 K) and a high magnetic field (17 Tesla), is ascribed to a strongly delocalized spin density on the cobalt ions

[1] [Rogalev ZhETF (JETP) 124, 445 (2003)](FXS/SAINCTAVIT%20Rogalev%20JETP%202003.pdf)

**TUESDAY 16.00 – 18.00: Time Michel van Veenendaal**

***Michel van Veenendaal, APS & de Kalb, USA***

**Nonequilibrium X-ray spectroscopy**

Nonequilibrium X-ray spectroscopy is studied for a model spin crossover compound. The ultrafast spin crossover is calculated for Fe-Co Prussian blue analogues using a dissipative quantum-mechanical model of a cobalt ion coupled to a breathing mode [1]. All electronic interactions are treated on an equal footing. The divalent cobalt ion reaches 90% of the *S*=3/2 value within 20 fs after photoexciting a low-spin Co3+ ion by an iron-to-cobalt charge transfer. The doublet-to-quartet spin crossover is significantly faster than the oscillation period of the breathing mode. The system relaxes to the lowest manifold of divalent cobalt (4*T*1) in 150–200 fs. X-ray absorption is calculated from the time-dependent nonequilibrium wavefunction. The resulting spectra cannot be decomposed into incoherent superpositions of transient states. Oscillations in the spin-orbit coupling gives rise to strong variations in the isotropic branching ratio. [1] [SR 7, 6672 (2017)](FXS/VANVEENENDAAL%20SR%202017.pdf)

***Tom Penfold, Newcastle, UK***

**Femtosecond x-ray spectroscopy with quantum dynamics**

Advances in experimental methodology aligned with technological developments, such as X-FELs and HHG, has led to a paradigm shift in the capability of X-ray Spectroscopy to deliver simultaneously high temporal and spectral resolution. Importantly, the complex nature and high information content of this class of techniques means that detailed theoretical studies are often essential to provide a firm link between the spectroscopic observables and the underlying molecular structure and dynamics. For molecules in electronically excited states, these simulations must often go beyond the single nuclear configuration regime and the Born-Oppenheimer approximation. Herein I will present some recent work on simulating and understanding ultrafast X-ray spectra using excited state simulations based upon quantum nuclear dynamics. This will include predictions of ultrafast time-resolved experimental signals of a Cu transition metal complex and new avenues, which exploit *on-the-fly* quantum dynamics simulations to reduce the computational expense of these calculations.

***Sonia Coriani, Lyngby, Denmark***

**Local & ultrafast spectroscopies by coupled cluster methods**

Recent advances in synchrotron and free-electron laser sources have led to a renaissance in spectroscopic techniques in the x-ray region. New types of experiments are done and/or are envisaged. Theoretical calculations play an important role in the analysis and interpretation of experimental spectra. Advances in theory and data analysis that parallel the advances in experiment are required to retrieve quantitative chemical information. Coupled cluster (response) approaches are undoubtedly among the most accurate ab initio techniques currently available for molecular properties and spectra, but their application to spectroscopies of core electrons is still somewhat limited. Selected results from our work on the extension of Coupled Cluster Response Theory to compute XAS spectra and photoelectron spectroscopy descriptors of both ground and excited states will be presented [1-7], including the results of a combined experimental and theoretical investigation of the transient NEXAFS spectroscopy at the oxygen edge of thymine. [1] [JCP 143, 181103 (2015)](FXS/CORIANI1%20JCP%202015.pdf) [2] [Myhre JCTC 12, 2633 (2016)](FXS/CORIANI2%20Myhre%20JCTC%202016.pdf) [3] [PRA 85, 022507 (2012](FXS/CORIANI3%20PRA%202012.pdf)) [4] [JCTC 8, 1616 (2012)](FXS/CORIANI4%20JCTC%202012.pdf) [5] [Kauczor JCP 139 211102 (2013)](FXS/CORIANI5%20Kauczor%20JCP%202013.pdf) [6] [List JCP 141, 244107 (2014)](FXS/CORIANI6%20List%20JCP%202014.pdf) [7] [Fransson JCP 138 124311 (2013)](FXS/CORIANI7%20Fransson%20JCP%202013.pdf)

***Piter Miedema, Hamburg, Germany***

**FEL experiments: coherence and excited-state RIXS**

At x-ray FELs like FLASH, besides enhanced x-ray brilliance compared to synchrotrons, there is an intrinsically high degree of coherence. Here I will show preliminary results applying FLASH's coherence and beam splitting unit [1] in measuring simultaneously the absorption (Imaginary part relative permittivity εr) as well as the associated phase shift due to absorption (Real part of relative permittivity εr) and discuss some open questions remaining on these preliminary results. Secondly I would like to discuss a FEL experiment preparation for excited-state RIXS [2] studies and will question my simulations approach in planning a possible FEL experiment. [1] [Schlotter RSI 81 (2010) 43107.](FXS/MIEDEMA1%20Schlotter%20RSI%202010.pdf)

[2] [Kunnus NJP 18 (2016) 103011.](FXS/MIEDEMA2%20Kunnus%20NJP%202016.pdf)

***Yu Zhang, Stanford, USA***

**Nonlinear X-ray Spectroscopy of Molecules**

The recently developed intense X-ray laser sources offer new opportunities to detect molecular structure and dynamics at an unprecedented level, thanks to the element selectivity and localized nature of core excitations generated by ultrashort X-ray pulses. Nonlinear infrared or optical spectroscopy techniques which have been proven successful are now extended to the X-ray regime. Here we briefly survey the quantum chemistry methods of nonlinear X-ray spectroscopy simulation of molecules, introduce the possible applications of nonlinear X-ray spectroscopy signals, and discuss the existing challenges in theoretical development.

***Thomas Kroll, Stanford, USA***

**Stimulated Hard XES in Manganese Solutions**  
  
The emission signal of conventional XES is emitted into the full 4π solid angle, but only a fraction of it can be detected with state-of-the-art X-ray analyzer optics for both hard and soft X-rays. A fundamentally new approach of stimulated, non-linear X-ray spectroscopy is discussed. Here, all emitted photons are directed exclusively in the forward direction, leading to an altered and narrower spectral shape. This approach has the potential to not only overcome the limitations of 4π signal collection, it can also lead to several orders of magnitude larger signal yields and information not obtainable with conventional methods. The strong gains in signal strength and an exponential spectral sensitivity can be used to selectively probe subsets of emission lines. In addition, emission signals with a spectral width way beyond the natural life-time broadening have been observed. A finding that is unique to the non-linear processes in stimulated emission. In this presentation, the whole intensity region leading to gain narrowing and final state broadening will be discussed with a focus on chemical information and results unique to non-linear, stimulated X-ray emission spectroscopy.

AA = Astronomy & Astrophysics

AC = Angewandte Chemie

IC = Inorganic Chemistry

JPCB = Journal of Physical Chemistry B

JPCC = Journal of Physical Chemistry C

JCTC = Journal of Chemical Theory and Computation

NJP = New Journal of Physics

PCCP = Physical Chemistry Chemical Physics

PRB = Physical Review B

PRL = Physical Review Letters

RSI = Review of Scientific Instruments