



Guillaume Radtke (IMPMC, CNRS/UPMC, Paris, France)

Standard approaches for core level spectroscopies. From single particle to multielectronic methods

In this talk, I will give a basic and non-exhaustive presentation of the standard methods currently employed to model core-level spectroscopies such as X-ray Absorption (XAS), X-ray Raman (XRS) or Electron energy loss (EELS) spectroscopies. The main features of ab initio methods based on the mean-field approximation such as Density Functional Theory (DFT) and of parametrized local many-body techniques such as Ligand Field Multiplet (LFM) theory will be discussed on a qualitative basis and illustrated through simple examples. In particular, the applicability and limitations of each approach will be emphasized.

Francesco Sottile (LSI, CNRS/Ecole Polytechnique, Palaiseau, France)

Introduction to standard methods for valence spectroscopies

This is a schematic and brief introduction to the Green's functions approaches typically used in valence electron excitations. One- and two-particle Green's functions will be used to describe photoemission, optical absorption and scattering experiments, like Inelastic X-ray Scattering (IXS) and electron energy loss (EELS). A second part of the discussion will be devoted to the specificities of valence electrons and their difference with core electrons excitations, in order to stimulate comments, corrections, and suggestions of meeting points.

Jianqiang Zhou (LSI, CNRS/Ecole Polytechnique, Palaiseau, France)

Photoemission spectroscopy from first principles

Photoemission spectroscopy has become increasingly used to elucidate the electronic properties of materials, since it provides both quasi-particle band structures, with information of one-particle-like excitations, and satellite structures that reflect the coupling to bosonic excitations such as phonons, plasmons, magnons, etc.. Accurate descriptions of photoemission spectra from first principles have been a challenge for ages. Currently, the most widely used approach for moderately correlated materials is the GW approximation (GWA) proposed by L. Hedin in 1965 [L. Hedin Phys. Rev. 139, A796 (1965)]. However, one of its notable shortcomings is the poor description of the satellite structures in photoemission spectra. Alternatively, the cumulant expansion approximation (CEA) has been quite promising for giving a better description the full photoemission spectra in a number of systems [see e.g., J. S. Zhou et al, arXiv:1708.04313v1 (2017) and references there].

In the first part of my talk, I will explain why the GWA fails and how the CEA improves the satellite spectra, using exactly solvable electron-boson coupling models. Moreover, the challenges of the CEA will be discussed, especially in the valence photoemission of metals.

The second part of my talk will focus on the comparison between calculated and measured photoemission spectra, in particular the photoemission spectra of simple metals (bulk sodium and aluminum). In order to fully explain the measured spectrum, a straightforward intrinsic calculation is not enough due to the so-called extrinsic and interference effects in a three-step model [C.N. Berglund and W.E. Spicer, Phys. Rev. 136:A1030 (1964)], as well as the presence of surface. Our recent studies show how one can model the entire photoemission process beyond the sudden approximation and obtain a good agreement with photoemission experiment.

Pierluigi Cudazzo, Lucia Reining (LSI, CNRS/Ecole Polytechnique, France)

Cumulant expansion of the electronic polarizability: beyond the static Bethe-Salpeter equation

One of the big challenges of theoretical condensed matter physics is the description, understanding, and prediction of the effects of the electronic correlations induced by the mutual interaction between particles on materials properties. In both electronic and optical spectra the Coulomb interaction causes a renormalization of the energies and change of spectral weight. Most importantly, it induces a finite lifetime on the quasi-particle (QP) excitations and can lead to new structures, often called satellites. The latter are pure many body effects and can be linked to the coupling of excitations, also termed dynamical effects. Standard methods developed in the framework of many body perturbation theory namely *GW* and the Bethe-Salpeter equation (BSE) are often not able to capture this complex physics. Instead, approaches based on a picture of electron-boson coupling such as the cumulant expansion are promising for the description of plasmon satellites.

Motivated by the recent success of the cumulant expansion of the one particle Green's function in the description of photoemission spectra[1,2,3], we generalized the cumulant approach to the evaluation of the electronic polarizability. In this way we provide a new full *ab-initio* tool to include dynamical effects beyond the standard BSE in the description of neutral excitations as measured in optical absorption, electron energy loss and inelastic X-rays scattering spectroscopies.

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Yves Joly, Oana Bunau (Institut Néel, CNRS, Grenoble, France)

From DFT to time-dependent DFT: focus on the hole-electron interaction

Though DFT is a ground state theory, it is often used to calculate core spectroscopies. We shall see in what cases it is anyway roughly valid to reproduce the data thanks to some ad hoc procedure. A typical way to calculate x-ray absorption and resonant-x-ray diffraction spectra will be shown. The time dependent DFT is in principal able to calculate spectroscopies. Although, many level of approximations can be used in this theory and we shall see what can be obtained when using one of its simplest local approximation. We will see the resulting improvement one reaches, and its limitations. Some connections with optics will also be given.

Maurits Haverkort (University of Heidelberg, Germany)

When and why do we need multi-configurational methods in spectroscopy whereas mean-field approaches work for the ground state of the same material?

The *ab initio* calculation of material specific properties including various forms of spectra is hard due to the exponential scaling of the Hilbert space of quantum many body problems. Mean-field approximations, including Hartree-Fock and Density Functional Theory reduce the complexity of the problem enormously making the calculations tractable. For the ground-state of interest these methods often give sufficient descriptions. For excited states and thus spectroscopy or dynamics mean-field descriptions are often not sufficient. Within this talk I will show by some examples where the problem originates and introduce methods that allow the description of correlated local states including their multiplets as well as the excitation into delocalized continuum states.

Christian Broder (IMPIC, CNRS/UPMC, Paris, France)

The challenge of optical spectra calculations: the unsolved problem of the colour of materials

The colour of most coloured materials (pigments, plants, gemstones) cannot be precisely calculated *ab initio*. Some examples of failed calculations will be presented. The reason why optical spectroscopy is more difficult to calculate than, for example, x-ray absorption or infrared spectroscopies will be discussed. The challenging road to a better modelling of colours will be sketched.

Calculating x-ray emission and fluorescence yield

de Groot, Frank

Debye Institute, Utrecht University, Netherlands
Email: f.m.f.degroot@uu.nl, Web site: <http://www.anorg.chem.uu.nl>

I will discuss the procedures to calculate resonant and non-resonant x-ray emission spectra. The calculation of resonant x-ray emission (or RIXS) spectra is equivalent to x-ray absorption, where the Kramers-Heisenberg equation is used for the XAS and XES matrix elements. Non-resonant XES is more complex and several levels of approximation exists. In principle all (incomplete) screening effects in the core hole creation should be included and complemented with their x-ray emission spectral shape [1].

The calculation of x-ray emission has also consequences for the use of fluorescence yield detection in XAS. For soft x-rays FY does not measure the XAS spectral shape [2]. For hard x-rays there can be differences between HERFD and XAS. Some recent examples are given where FY and HERFD can not be used to measure the XAS spectral shape.

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Finite lifetime broadening of calculated x-ray absorption spectra: possible artefacts close to the edge

Šípr, Ondřej^{1,2}

¹Institute of Physics, Czech Academy of Sciences, Prague, Cukrovarnická 10, CZECH REPUBLIC
Email: sipr@fzu.cz, Web site: <http://www.fzu.cz/~sipr>

²New Technologies Research Center, University of West Bohemia, Pilsen, Univerzitní 8, CZECH REPUBLIC

X-ray absorption spectra calculated within an effective one-electron approach have to be broadened to account for the finite lifetime of the core hole. For Green's function based methods this can be achieved either by adding a small imaginary part to the energy or by convoluting the spectra on the real axis with a Lorentzian [1]. We demonstrate on the case of Fe K and $L_{2,3}$ edge spectra that these procedures lead to identical results only for energies higher than few core level widths above the absorption edge. For energies close to the edge, spurious spectral features may appear if too much weight is put on broadening via the imaginary energy component. Special care should be taken for dichroic spectra at edges which comprise several exchange-split core levels, such as the L_3 edge of $3d$ transition metals (see Fig. 1).

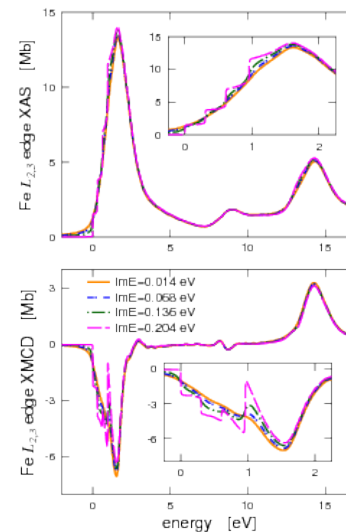


Fig.1: Fe $L_{2,3}$ edge XAS and XMCD calculated for different imaginary energies and convoluted subsequently with Lorentzians chosen so that the total spectral broadening $2 \text{Im}E + \Gamma$ remains constant. The insets show detailed views on the L_3 edge region.

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Electronic structure of greigite (Fe_3S_4) derived from the XMCD spectra

Fernandez-Rodriguez, Javier¹; van der Laan, Gerrit¹

¹Magnetic Spectroscopy Group, Diamond Light Source, Didcot OX11 0DE, United Kingdom

Email: Javier.fernandez-rodriguez@diamond.ac.uk

Greigite (Fe_3S_4) is a mineral that crystallizes in the same inverse spinel crystallographic structure as its counterpart oxide magnetite (Fe_3O_4). Although greigite and magnetite have similar structural and magnetic properties, the results of spectroscopy for greigite evidence important differences in magnetic and electronic structure. In particular, the measured shape of the XMCD spectra for greigite [1,2] changes significantly from the case of magnetite. We discuss a ligand-field model including charge-transfer for the XAS and XMCD spectra in greigite. Our model can attain a good agreement with the experimental XAS and XMCD spectral shape, extract information on the sublattice magnetizations and identify the differences in the electronic structure from the case of magnetite.

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All-electron Many-body Approach to Core Excitations in Solids

Vorwerk, Christian¹; Cocchi, Caterina¹, and Draxl, Claudia¹

¹Institut für Physik and IRIS Adlershof, Humboldt Universität zu Berlin, Berlin, Zum Großen Windkanal 6, Germany
Email: vorwerk@physik.hu-berlin.de, Web site: <http://www.sol.physik.hu-berlin.de>

We present an all-electron, many-body approach to describe core excitations in solid-state materials [1]. Highly accurate Kohn-Sham single-particle energies and wavefunctions [2] are obtained from all-electron full-potential DFT calculations using the linearized augmented plane-wave (LAPW) basis set. Core states are obtained from solutions of the Dirac equation, and, as such, include the spin-orbit splitting of core states with nonzero angular momentum. We obtain the density-density response matrix through the solution of the Bethe-Salpeter equation, which includes the full non-local, screened interaction between electron and core hole. From the density-density response matrix, we can reproduce various experimental spectra, such as x-ray absorption near-edge spectroscopy (XANES), electron energy-loss near-edge spectroscopy (ELNES), and (non)-resonant inelastic x-ray scattering (N)RIXS. Our approach to XANES is already available to the community in the open-source, all-electron full-potential code **exciting** [3]. Exemplary, we discuss core spectra of several materials, from simple oxides, e.g. CaO, to complex materials, such as hybrid organic-inorganic perovskites and provide an in-depth analysis of the excitations, revealing their character in terms of electronic distribution and real-space localization. Our results are in good agreement with available experimental data.

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Optical properties of vanadates: an accurate theoretical description

Reshetnyak, Igor; Wiktor, Julia; Ambrosio, Francesco; Pasquarello, Alfredo

Chaire de Simulation à l'Echelle Atomique (CSEA), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, SWITZERLAND

Email: igor.reshetnyak@epfl.ch, Web site: <https://people.epfl.ch/igor.reshetnyak>

Several complex metal oxides have been extensively investigated recently due to their potential applications for solar-to-fuel conversion. Bismuth vanadate (BiVO_4) and copper vanadate ($\text{Cu}_2\text{V}_2\text{O}_7$) are representative examples of this class of materials. We present *ab-initio* calculations of their absorption spectra within the framework of the Bethe-Salpeter Equation based on the GW approximation to the self-energy. Good agreement between theory and experiment is obtained after including the effects of spin-orbit coupling, nuclear quantum motion and thermal vibrations. Furthermore, we are able to give an interpretation to the various structures in the absorption spectra.

Exciton interference in hexagonal boron nitride

Sponza, Lorenzo¹; Amara, Hakim¹; Attacalite, Claudio²; Ducastelle, François¹; Loiseau, Annick¹

¹LEM UMR 104, ONERA – CNRS, 92322 Châtillon, 29 av. de la Division Leclerc, FRANCE
Email: lorenzo.sponza@onera.fr

²CINaM UMR 7325, Aix Marseille University, 13288 Marseille, campus de Luminy, FRANCE

Among 2D materials, hexagonal boron nitride (hBN) stands out owing to its wide band gap (~6 eV in the bulk) and the possibility to tune it by nanostructuring. In this context, several investigations have been carried out on hBN thin films, most of them focusing on the mono-layer. However fundamental aspects of exciton formation and relaxation in hBN are still unclear at the bulk level. For instance, the usual theory of light emission in indirect-gap semiconductors, recently invoked [1,2], contrasts with its very high intensity [3,4,5].

In this work [6] we report a thorough analysis of the exciton dispersion in bulk hexagonal boron nitride. We solve the ab initio GW Bethe-Salpeter equation at finite q // ΓK , which is relevant for spectroscopic measurements. Simulations reproduce the dispersion and the intensity of recent high-accuracy electron energy loss data (see Fig.1). We demonstrate that the excitonic peak comes from the interference of two groups of transitions involving the points K and K' of the Brillouin zone. The number and the amplitude of these transitions determine variations in the peak intensity. Our results contribute to the understanding of electronic excitations in this system, unveiling a non-trivial relation between valley physics and excitonic properties. Furthermore, the methodology introduced in this study is completely general and can be applied successfully to the investigation of excitonic properties in any system.

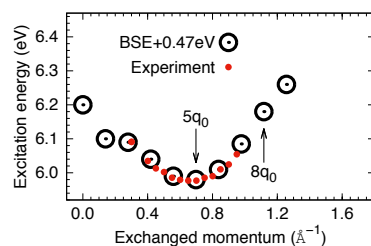


Fig. 1: Theoretical and experimental dispersion of the loss function along ΓK .

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Lattice mismatch drives spatial modulation of corannulene tilt on Ag(111)

Baby, Anu¹; Lin, He¹; Floreano, Luca²; Ravikumar, Abhilash¹; Bittencourt, Carla³; Wegner, Hermann A.⁴; Goldoni, Andrea⁵ and Fratesi, Guido⁶

¹ Università degli Studi di Milano-Bicocca, Dipartimento di Scienza dei Materiali, via Cozzi 55, I-20125, Milano, Italy

Email: a.baby@campus.unimib.it

²CNR-IOM, Laboratorio TASC, Basovizza SS-14, Km 163.5, I-34149 Trieste, Italy

³Chimie des Interactions Plasma-Surface, University of Mons, 20 Place du Parc, 7000 Mons, Belgium

⁴Institute of Organic Chemistry, Justus Liebig University Giessen, Heinrich-Buff-Ring 17, 35392 Giessen, Germany

⁵Elettra Sincrotrone Trieste, and INSTM - Elettra, Lab. Micro & Nano-Carbon, s.s. 14 km 163.5 in Area Science Park, 34169 Trieste, Italy

⁶Dipartimento di Fisica, Università degli Studi di Milano, via Celoria 16, I-20133, Milano, Italy

The adsorption of a monolayer of corannulene ($C_{20}H_{10}$) molecules on the Ag(111) surface is investigated by simulated and experimental core-level electron spectroscopic techniques (both photoemission and absorption) and scanning tunneling microscopy (STM). Structural optimizations of the adsorbed molecules were performed by density functional theory (DFT) using Quantum Espresso platform. Corannulene is physisorbed in a bowl-up orientation displaying a very high mobility (diffusion) and dynamics (tilting and spinning) at room temperature. Molecules order into a close compact albeit incommensurate phase at the monolayer saturation coverage. They line up with a periodic intermolecular spacing of $\sim 10.5 \pm 0.5 \text{ \AA}$ which is intermediate between a three-fold and a four-fold phase. The molecular rows display a very small angular orientational mismatch with respect to the substrate high symmetry direction, thus yielding a long wavelength structural modulation. Near edge X-ray absorption fine structure spectroscopy (NEXAFS) with polarized light is used to distinguish the unoccupied molecular orbitals with σ and π symmetries from which an effective molecular tilt angle of $28 \pm 2^\circ$ was determined. The same was simulated using the XSPECTRA code in Quantum Espresso within the transition potential (TP) approach to work out the initial and final state effects. The experimental effective tilt is larger than calculated for a planar geometry where the molecule adsorbs on its pentagon (which would yield an equilibrium four-fold phase) and smaller than calculated for a tilted geometry where it adsorbs on one of its hexagons (yielding an equilibrium three-fold phase). The X-ray photoemission spectroscopy (XPS) data instead shows an interesting trend for the three-fold phase tilted molecules where with increasing distance of C atom from the surface, its binding energy also increases due to a less effective substrate screening. We show that both the structural properties and the spectroscopic ones are intermediate between those predicted for a three-fold on-hexagon geometry and a four-fold on-pentagon one. We suggest that molecules smoothly change their configuration between these two structural phases along the observed long wavelength modulation of the molecular rows due to small variations of the molecular tilt and azimuth.

Theoretical modeling of experimental EELS data for free-standing and supported graphene

Radović, Ivan¹; Despoja, Vito²; Mišković, Zoran L.^{3,4}

¹Vinča Institute of Nuclear Sciences, University of Belgrade, Belgrade, P.O. Box 522, SERBIA
E-mail: iradovic@vin.bg.ac.rs, Web site: http://www.vin.bg.ac.rs/040/members/mem_ira.htm

²Department of Physics, Faculty of Science, University of Zagreb, Zagreb, Bijenička c. 32, CROATIA

³Department of Applied Mathematics, University of Waterloo, Waterloo, Ontario N2L 3G1, CANADA

⁴Waterloo Institute for Nanotechnology, University of Waterloo, Waterloo, Ontario N2L 3G1, CANADA

Firstly, we present a theoretical modeling of the experimental electron energy loss (EEL) spectra of free-standing films consisting of N graphene layers in a scanning transmission electron microscope (STEM) [1]. We treat the multi-layer graphene (MLG) as layered electron gas with in-plane polarizability modeled by a two-dimensional (2D), two-fluid hydrodynamic (HD) model [2] for the inter-band transitions of π and σ electrons of single-layer graphene (SLG), and find good agreement (as shown in Fig. 1) with the experimental EEL spectra [3] for $N < 10$ graphene layers.

Secondly, we present a theoretical modeling of the experimental EEL spectroscopy (EELS) data for monolayer graphene supported by Pt(111), Ru(0001), and Ni(111) substrates [4], as well as for high-quality graphene grown on peeled-off epitaxial Cu(111) foils [5]. To reproduce the experimental loss function, we use the same version of the HD model for graphene's π and σ electrons in conjunction with an empirical Drude-Lorentz model for metal substrate.

Finally, we present an analytical modeling of the experimental EELS data for free-standing graphene obtained by STEM using an *ab initio* method and the 2D, two-fluid extended HD (eHD) model [6]. We use an optical approximation based on the conductivity of graphene given in the local, i.e., frequency-dependent form derived by these two methods and find very good agreement with the EEL spectra from three independent experiments [3,7,8], especially in the case of the eHD model.

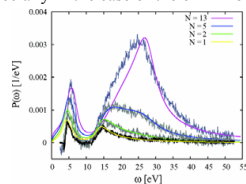


Fig. 1: Probability density $P_{\omega}(\omega)$ (in $1/eV$) versus energy loss ω (in eV), evaluated for $N=1, 2, 5,$ and 13 graphene layers [1] [smooth solid (yellow, green, blue, and pink) curves], along with the corresponding experimental EEL spectra [3] [noisy (gray) curves].

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Resonant inelastic x-ray scattering probes the electron-phonon coupling in the spin-liquid $\mu\kappa$ -(BEDT-TTF)₂Cu₂(CN)₃

Illakovac, Vita^{1,2}; Carniato, Stéphane¹; Foury-Leylekan, Pascale³; Tomic, Silvia⁴; Pouget, Jean-Paul³; Lazic, Predrag⁵; Joly, Yves⁶; Miyagava, Kazuya⁷; Kanoda, Kazushi⁷; Nicolaou, Alessandro⁸

¹Sorbonne Universités, UPMC, Univ. Paris 6, CNRS UMR 7614
Laboratoire de Chimie Physique-Matière et Rayonnement, Paris, France
Email: vita.illakovac-casses@upmc.fr

²Université de Cergy-Pontoise, F-95031 Cergy-Pontoise, France

³Laboratoire de Physique de Solides, CNRS UMR 8502, Univ. Paris Sud, Université Paris Saclay, Orsay, France

⁴Institut za Fiziku, P.O.Box 304, HR-10001 Zagreb, Croatia

⁵Ruder Bošković Institute, Bijenička cesta 54, HR-10000 Zagreb, Croatia

⁶Institut Néel, 25 Avenue des Martyrs, Grenoble, France

⁷Department of Applied Physics, University of Tokyo, Tokyo 113-8656, Japan

⁸Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, B.P. 48, F-91192 Gif-sur-Yvette, France

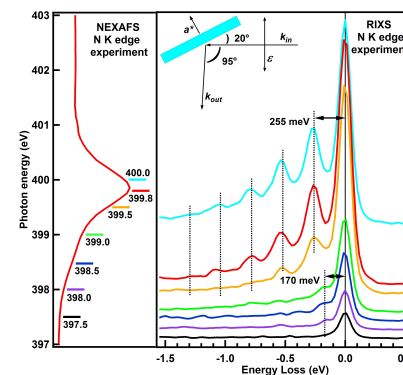


Figure: N K edge NEXAFS and RIXS spectra of κ -(BEDT-TTF)₂Cu₂(CN)₃

Resonant inelastic x-ray scattering at the N K edge reveals clearly resolved harmonics of the anion plane vibrations in the bi-dimensional organic charge-transfer salt κ -(BEDT-TTF)₂Cu₂(CN)₃, known as a spin-liquid insulator [1] and superconductor under pressure [2,3]. Tuning the incoming light energy at the K edge of two distinct N sites permits to excite different sets of phonon modes. Cyanide CN stretching mode is selected at the edge of the ordered N sites which are more strongly connected to the BEDT-TTF molecules, while positionally disordered N sites show multi-mode excitation. Combining measurements with calculations on an anion-plane cluster permits to estimate the site-dependent electron-phonon coupling of the modes related to nitrogen excitation [4].

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Direct extraction of exact individual excited-state energies from (time-independent) ensemble density-functional theory

Killian Deur and Emmanuel Fromager*

Laboratoire de Chimie Quantique, Institut de Chimie, Université de Strasbourg, 4 rue Blaise Pascal, 67000 Strasbourg, France

*Email address: fromager@unistra.fr

Ensemble density-functional theory (eDFT) [1] is in principle exact alternative to time-dependent DFT for the calculation of electronic excitation energies. The ensemble energy, which is a weighted sum of ground- and excited-state energies, is expressed in eDFT as a functional of the ensemble density (weighted sum of ground- and excited-state densities). In the standard formulation, normalized ensemble weights are used (*i.e.*, they sum up to 1) so that the ensemble density integrates to the number of electrons, like in regular DFT. Consequently, differentiating the ensemble energy with respect to the ensemble weights only gives access to excitation energies [1-6] (*i.e.* energy differences) and *not* to individual state energies. In this talk I will explain how non-normalized weights can be used, thus providing an exact energy expression for each state in the ensemble [7]. It will be shown that, in this context, the weight dependence of the exchange-correlation functional plays a crucial role. Such a formalism could be used, for example, for computing excited-state molecular gradients. The use of individual state densities for computing approximate excited-state energies in eDFT will also be discussed. Finally, if time permits, I will show how a similar approach can be applied to grand canonical ensembles, thus leading to exact density-functional expressions for both the ionization potential and the electron affinity [8].

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Theoretical soft X-ray spectroscopy of transition metal compounds: A multi-reference wave function approach

Bokarev, Sergej¹

¹*Institute of Physics, Rostock University, Albert-Einstein-Str. 23-24, 18059 Rostock, GERMANY*
Email: sergej.bokarev@uni-rostock.de, Web site: <https://molscience.wordpress.com/>

To date, 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. Here, we aim at the development of 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 electronic structure theory combined with a perturbative LS-coupling scheme for spin-orbit coupling [1]. A special focus is put on the L-edge photon-in/photon-out and photon-in/electron-out processes, *i.e.* X-ray absorption, resonant inelastic scattering, partial fluorescence yield, photoelectron and Auger spectroscopy treated on the same theoretical footing [2-4]. We address the application of the X-ray metal L-edge and ligand K-edge as well as XUV spectroscopy to unraveling electronic structure and nature of chemical bonds [5-7], oxidation and spin-states [4], the interplay of radiative and non-radiative decay channels [3], fingerprints of nuclear dynamics [8,9] and non-adiabatic transitions [10-12] as well as ultrafast electron dynamics triggered by X-ray light [13,14]. The investigated systems range from the small prototypical coordination compounds [1--12] and catalysts [5,10] to the aggregates of biomolecules [15].

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Modelling of X-ray Raman Spectroscopy: The core-hole and core-wave function issue in the single-particle approximation

Emmanuelle de Clermont Gallerande¹; Guillaume Radtke¹; Gérald Lelong¹; Christophe Sahle,² Delphine Cabaret¹

¹IMPMC, Sorbonne Universités, UPMC-CNRS, Paris, France

¹ESRF, Grenoble, France

Email: emmanuelle.de_clermont_gallerande@upmc.fr

X-ray Raman Spectroscopy (XRS), is a powerful technique to study the electronic structure of compounds containing low-Z elements such as Li, B, C and O. Based on a non-resonant inelastic scattering process, it is an alternative technique for X-ray Absorption Spectroscopy (XAS) in the soft X-ray range. In addition, depending on the magnitude of the photon momentum transfer (q), non-dipole transitions can be easily induced. We have implemented the calculation of the XRS dynamic structure factor within the module XSpectra [1] of the suite of codes Quantum ESPRESSO [2]. XSpectra is based on density functional theory in a plane-wave pseudopotential reciprocal space formalism, reconstructs the all-electron wave function of the final state using the PAW method [3], and builds Lanczos basis set to compute the spectrum as a continued fraction.

In this presentation, we will show recent XRS spectra obtained for lithium model compounds (LiF, Li₂O, LiBO₂, Li₂CO₃) at the K edge of all the elements. The q -dependence of monopole versus dipole transitions will be pointed out. In particular, the fact that the monopole transitions are supposed to vanish when q tends to zero reveals a problem of orthogonality between the initial and final state mono-electronic wave functions that will be discussed. Calculations are performed on supercells in the presence of an absorbing atom obtained by removing one $1s$ core electron from its electronic configuration. K edges of low-Z element, and especially Li, are highly sensitive to the core-hole screening, which can be modeled in various ways in the one-electron framework [4,5]: Full Core-Hole (FCH), the eXcited Core-Hole (XCH) and the Half Core-Hole (HCH) approaches. In the FCH approach, the excited electron is modeled as a uniform background whereas in the XCH approach, the excited electron is put in the lowest available unoccupied band, and the HCH approach is similar to the FCH with considering the lacking charge on the absorbing atom and the background charge as half of an electron charge. By comparison between experimental and calculated spectra, the appropriate approach is determined and trends can be identified.

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Ab-Initio Modelling of Scandium K-edge XANES Spectra

Chassé, Mathieu¹; Delhommaye, Steven¹; Cabaret, Delphine¹; Juhin, Amélie¹; Vantelon, Delphine²; Cotte, Marine³; Calas, Georges¹

¹ IMPMC – Sorbonne Universités – UPMC Univ Paris 06 – 4 Place Jussieu, 75005 Paris, France.
Email: mathieu.chasse@normalesup.org, website: www-ext.impmc.upmc.fr/~chasse/index.html

²SOLEIL synchrotron, L'Orme des Merisiers, Saint-Aubin, BP 48, F-91100 Gif-sur-Yvette, France

³European Synchrotron Radiation Facility (ESRF), F-38000 Grenoble, France

The economic demand for scandium (Sc) is growing due to its use in high-performance alloys and solid oxide fuel cells. However, future supply will depend on our ability to determine Sc speciation in geological contexts, essential to understand the processes of formation of Sc deposits. Despite the Sc concentrations of natural samples, rarely exceeding a few parts per millions, pioneering results have been obtained on natural samples thanks to the combined chemical selectivity and high sensitivity of X-ray absorption near-edge structure (XANES) spectroscopy [1]. However, the absence of an extensive series of Sc K-edge XANES reference spectra [2] and the scarcity of direct structural data on Sc limited the interpretations. In addition, the development of innovative Sc-based applications rely on our knowledge of Sc inorganic chemistry, but the coordination chemistry of Sc remains a challenging topic due to the same issues [3]. These limitations demonstrated the need for improved theoretical knowledge on the influence of crystallographic environment on Sc spectral signature. In order to explain the origin of the different structures observed in Sc K-edge XANES spectra in terms of coordination number, local symmetry, orbital hybridisation and short and medium-range structure, we recorded high-resolution Sc K-edge XANES spectra of model compounds: Sc_2O_3 , $\text{Ca}_3\text{Sc}_2(\text{SiO}_4)_3$ and $\text{ScPO}_4 \cdot 2\text{H}_2\text{O}$, in which the crystallographic environment around Sc is known, and tried to interpret these spectra using density functional theory (DFT) calculations.

Preliminary calculations of XANES spectra in the DFT framework are consistent with the experimental spectrum of Sc_2O_3 (Fig. 1). In the pre-edge region, the lowest energy structure, (i), probes the empty 3d orbitals of the absorbing atom and is divided in two due to the splitting of 3d orbitals expected from the octahedral environment of Sc. The second structure, (ii), also split, probes the empty 3d orbitals of Sc second neighbour by hybridisation with the p orbitals of the Sc absorber via the p orbitals of the first O neighbours. However, the underestimation of the core-hole effect in our calculations in a limitation in the modelling of experimental spectra: the (i) structure is shifted at higher energy in the calculated spectrum, compared to the experimental data.

In the light of these results and of future calculations on reference model compounds mentioned above, we expect to get original information on Sc speciation in geological contexts by modelling Sc K-edge XANES spectra of natural samples.

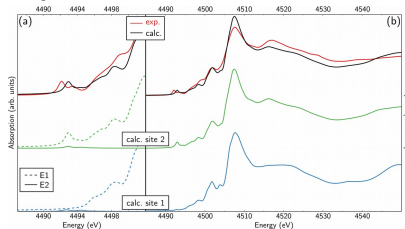


Figure 1: Comparison between experimental and calculated Sc K-edge XANES spectra of Sc_2O_3 : (a) pre-edge; (b) XANES (electric dipole and quadrupole contributions are noted E1 and E2)

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Direct extraction of individual state energy from the ensemble energies : Application in the non-symmetric Hubbard dimer

Killian Deur ; Emmanuel Fromager

Laboratoire de Chimie Quantique, Institut de Chimie, CNRS / Université de Strasbourg, Strasbourg, France, email: deur@unistra.fr, Web site: quantique.u-strasbg.fr

Abstract

Ensemble density functional theory (eDFT) [1] is in principle an exact alternative to time dependent density functional theory (TD-DFT) for the calculation of excitation energy [2]. Indeed one shortcoming of the standard adiabatic approximation in TD-DFT is the absence of multiple excitations in the spectrum. Moreover, TD-DFT cannot describe multiconfigurational situation adequately. An exchange-correlation energy depending on the weight as been derived in the case of the Hubbard dimer [6]. However in eDFT a calculation for an individual state is usually not possible due to the normalization constraint on weight (i.e they sum up to 1). To overcome this constraint we propose a formalism with non-normalized weight [3]. In this poster, an analysis is presented with two states applied on the non-symmetric Hubbard dimer [4, 5, 6].

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Keywords: ensemble density-functional theory for excited states, generalized adiabatic connection for ensembles, Hubbard dimer, strong correlation.

Multiplet calculations with the XCLAIM code

Fernandez-Rodriguez, Javier¹; Brian Toby²; Michel van Veenendaal^{2,3}

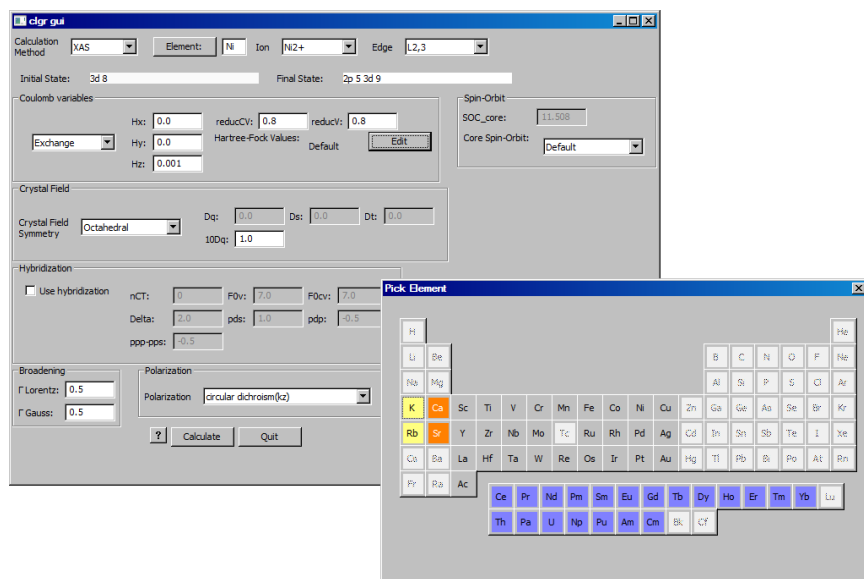
¹Magnetic Spectroscopy Group, Diamond Light Source, Didcot OX11 0DE, United Kingdom

²Department of Physics, Northern Illinois University, DeKalb, Illinois 60115, USA

³Advanced Photon Source, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439, USA

Email: Javier.fernandez-rodriguez@diamond.ac.uk

Xclaim, is a multi-platform code (Linux, Windows and MacOS) based on a ligand-field multiplet model in an arbitrary point group symmetry for calculating core-hole spectroscopy (XAS, XPS, RIXS) and obtaining information on ground and excited states. We present examples of the application of the code and discuss the use of Python scripting together with the Numpy and Scipy libraries to obtain more flexibility beyond the use of the graphical user interface.



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Electronic Structure Studies of Thorium Systems

Galanzew, Jurij^{1,2}; Kvashnina, Kristina^{1,2}

¹Institut of Resource Ecology, Helmholtz Zentrum Dresden-Rossendorf, Dresden, Bautzner Landstrasse 400, GERMANY

²Rossendorf Beamline, ESRF, Grenoble, 71 Avenue des Martyrs, FRANCE

Email: jurij.galanzew@esrf.fr; website: <http://www.hzdr.de/db/Cms?pNid=247>

The content of thorium (Th) on the earth's crust is three to four times higher than the uranium, so the idea of using thorium as the main component of nuclear fuel is currently developing^[1]. But our understanding of actinide chemistry lags behind that of the rest of the periodic table. There are some knowledge gaps in fields controlling the chemical reactivity and bonding mechanisms between Th and ligands in complex actinide systems. In recent years **High Energy Resolution Fluorescence Detected (HERFD)** and **Resonant Inelastic X-ray Scattering (RIXS)** were shown to be a highly valuable tool for investigation of the electronic structure of actinides^[2-4]. Also methods for theoretical *ab initio* calculations underwent drastical improvement, especially for the *f*-element systems^[5]. We report here, the HERFD and RIXS experiment at the Th L₃ edge for the number of the Th systems, performed at Rossendorf Beamline (BM20) of ESRF^[6]. We aim to probe the electronic structure of thorium systems, in terms of possible electron-electron interactions, role of valence *f*- electrons in bonding and ligation and effects of hybridization between molecular orbitals.

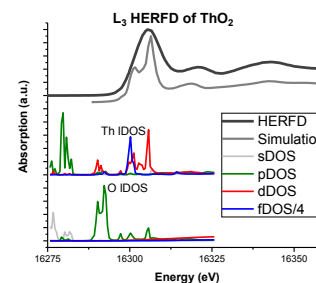


Fig. 3: Experimental and simulated Th L₃ HERFD spectrum of ThO₂

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Combining Density-functional Theory And Wave-function Methods: The RS λ H + MP2 Scheme

Cairedine Kalai

Université Pierre & Marie Curie and CNRS, (Chemistry department), Paris, France, cairedine.kalai@upmc.fr

Julien Toulouse

Université Pierre & Marie Curie and CNRS, (Chemistry department), Paris, France, julien.toulouse@upmc.fr

Abstract

Over the past two decades, Kohn-Sham [1] DFT (KS-DFT) has been a method of choice to study ground state properties of large system. KS-DFT is formally exact, but it involves a functional called the exchange-correlation functional. Nevertheless, the exact form of the exchange-correlation functional is still unknown, hence density functional approximations (DFAs) has been developed in order to improve the accuracy of KS-DFT. DFAs are able to describe properties that depend on short range exchange-correlation effects, molecular geometries and bond enthalpies for instance. However, there are still some problems to address to the current approximations:

The issue of self-interaction error (SIE): in one electron systems, the Hartree and exchange functional do not cancel each other exactly. Another problem associated to the current DFAs is related to the fact correlation functional does not take into account the dispersion interactions. Perhaps, the most appealing approach to deal with the problem mentioned above consist in developing range separated double hybrid functionals, which mix exact exchange and non local correlation effects. These methods are able to deal with the SIE and to take into account the dispersion interactions.

In standard range separated hybrid methods[2], the short range part of the Coulomb interaction is usually handled by a functional of the density while the long range electron interaction is treated by wave-function theory. Herein, we propose to include a fraction wave-function theory in the short range part in order to improve the accuracy of short range properties.

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Keywords: range separated, double hybrid, KS-DFT multi-determinantal extension

Green functions in site-occupation embedding theory

Laurent Mazouin¹ and Emmanuel Fromager¹

Laboratoire de Chimie quantique, Institut de Chimie, CNRS/Université de Strasbourg,
4 rue Blaise Pascal, Strasbourg, France

Email: lmazouin@unistra.fr. Web site: <https://quantique.u-strasbg.fr/>

In exact density-functional theory (DFT), the physical electronic density is recovered by using a fictitious non-interacting reference system known as the Kohn-Sham system. In practice, this approach is insufficient because the single-determinantal KS wave function generated by an approximate density-functional potential turn out to be a poor starting point, especially for strongly correlated systems. In order to improve on DFT, one could start from another fictitious reference system, namely a partially interacting one such as an embedded impurity-interacting system, like in site-occupation embedding theory (SOET)^{1,2,3}.

In SOET, the embedded impurity system can be treated exactly with a high level method. In practice, an impurity solver would be used whereas the non-interacting bath is treated by a local and static density-functional. By means of second-order perturbation theory and the GW approximation^{4,5,6}, we derive several approximate self-energies in the case of the analytically solvable asymmetric two-site Hubbard model. Thanks to the simplicity of this toy model, we gain more insight into the Green's function SOET formalism and obtain analytical self-energies that explicitly depend on the site-occupation. These self-energies are used to calculate a Green's function for the impurity. We also investigate a different approach where the density functional and embedding potential are derived from the Green's function formalism. The correlation energy functional for the bath is derived by means of Sham's equation⁷ via the adiabatic connection and the trace of the product between the non-interacting Green's function and the approximate self-energy. The embedding potential ensures that both the density of the impurity-interacting and the fully interacting system are the same and is obtained from the Sham-Schlüter equation⁸, in analogy to the optimized effective potential method (OEP)⁹.

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Time-Dependent Quantum Description of Molecular Double Core Hole States: Vibrationally Resolved Photoelectron Spectra of CO

Oberli, Solène; Sisoura, Nicolas; Selles, Patricia, Carniato, Stéphane
LPCMR, Université Pierre et Marie Curie, Paris, France
Email: solene.oberli@upmc.fr

The unprecedented radiation intensity of x-ray free electron lasers (XFELs) offers the opportunity to create double core hole (DCH) states via sequential absorption of two x-ray photons within a single pulse [1]. This x-ray two-photon process opens the way to a highly sensitive spectroscopy known as x-ray two-photon photoelectron spectroscopy (XTPPS). The theoretical description of XTTPPS is challenging owing to the competition between photon absorption and electronic relaxation by Auger decay which occur at similar femtosecond timescales. In case of molecular targets, nuclear dynamics, which takes place in this timescale, complicates further the analysis. Previous studies are limited to classical rate-equation models for describing the time evolution in the different ionization channels [1,2]. In this work, we present for the first time a full quantum model to investigate DCH states formation through sequential one x-ray photon absorption. Our model includes explicitly the interaction with the pulse, the Auger decay and the nuclear dynamics. Absolute double core hole cross sections are provided using a time-dependent scheme within the local approximation [3]. The influence of the nuclear dynamics is assessed for the prototype CO molecule. Signature in double core hole photoelectron spectra of the competition between photon absorption and Auger decay is discussed. We show that DCH states formation can be actively triggered by varying the laser pulse characteristics.

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Relativistic range-separated density-functional theory

Paquier Julien, Toulouse Julien

Laboratoire de Chimie Théorique, Université Pierre et Marie Curie, Paris, France
Email: julien.paquier@etu.upmc.fr

Range-separated density-functional theory allows one to rigorously combine a (semi)local density-functional approximation for the short-range part of the electron-electron interaction with explicit many-body methods for the long-range part of the electron-electron interaction (see, e.g., Ref. [1]).

This theory has been designed first with non-relativistic formalism, but may be extended so as to encompass relativistic effects as it was recently done by Kullie & Saue [2] through the use of the Dirac-Coulomb Hamiltonian, using a non-relativistic short-range functional. The goal of this work is to study short-range relativistic effects in order to design such a relativistic short-range exchange-correlation functional. It would be the first step toward a range-separated four-component relativistic density functional theory, offering new possibilities in the study of core properties of heavy atoms.

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Electronic and magnetic properties of core-excited organic molecules on hybrid graphene interfaces

A. Ravikumar¹, G. Kladnik², M. Muller³, A. Cossaro⁴, G. Bavdek⁵, L. Patera⁶, D. Sánchez Portal³, L. Venkataraman⁷, A. Morgante^{4,6}, G. P. Brivio¹, D. Cvetko^{2,4}, G. Fratesi⁸

¹Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, Italy

²Faculty of Mathematics and Physics, University of Ljubljana, Slovenia

³Centro de Física de Materiales, San Sebastian, Spain

⁴CNR-IOM, Laboratorio TASC, Trieste Italy

⁵Faculty of Education, University of Ljubljana, Slovenia

⁶Dipartimento di Fisica, Università di Trieste

⁷Department of Chemistry, Columbia University, NY

⁸Dipartimento di Fisica, Università degli Studi di Milano, Italy

E-mail: a.ravikumar@campus.unimib.it

The electronic and magnetic properties of 2-D heterostructure interfaces are actively pursued topics of research. In this regard we explore the magnetism induced due to core level excitation of organic molecule adsorbed on graphene. We predict the induction/ suppression of magnetism in the valence shell of physisorbed and chemisorbed organic molecules on graphene occurring on the femtosecond time scale as a result of core level excitations and electron transfer at the interface [1]. For a weakly interacting physisorbed molecule, the system is non-magnetic in the ground state but numerical simulations based on density functional theory show that the valence electrons relax towards a spin polarized configuration upon molecular core-level excitation. The system is magnetic until the core electron de-excites via one of the several electronic decay channels [2]. The magnetism depends on efficient electron transfer from graphene and the corehole lifetime is in the femtosecond (fs) time scale. On the other hand, when graphene is covalently functionalized, the system is magnetic in the ground state showing two spin dependent mid gap states localized around the adsorption site. At variance with the physisorbed case, upon core-level excitation, the valence shell relaxes to a non-magnetic configuration until the core-electron de-excites.

The influence of a substrate is then considered for charge transfer between molecules and supported graphene. Here we focus on the case of graphene functionalized by organic molecules and grown on Ni(111) substrate. This is investigated by X-ray resonant photoemission spectroscopy, that is able to measure electron transfer rates occurring within few femtoseconds and by a theoretical framework based on density-functional theory [3,4]. We use 4,4'-bipyridine as the prototypical molecule for these explorations as the energy level alignment of core-excited molecular orbitals allows ultrafast injection ($\tau=4$ fs) of electrons from the substrate to the molecule adsorbed on epitaxial graphene/Ni(111) [2], which is characterized by a strong hybridization between C and metal states. We demonstrate that this interface can be decoupled by the addition of a second layer of graphene, where the one in contact with the metal acts as a buffer layer and the one in contact with the molecule is less hybridized with Ni underneath. This decreases the charge transfer rates by about one order of magnitude and is seen in both theory and experiments.

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Site occupation embedding theory

Bruno, Senjean¹; Naoki, Nakatani²; Masahisa, Tsuchiizu³; Emmanuel Fromager¹

¹Laboratoire de Chimie Quantique, Institut de Chimie, CNRS / Université de Strasbourg, 1 rue Blaise Pascal, F-67000 Strasbourg, France. Email : senjean@unistra.fr

²Department of Chemistry, Graduate School of Science and Engineering, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan

³Department of Physics, Nara Women's University, Nara 630-8506, Japan

Conventional density-functional theory (DFT) relies on the mapping of interacting electrons onto non-interacting ones. It has been widely used to study real materials, however, it often fails in reproducing experimental findings when electron correlation is strong. In this communication, I will present an improved formulation of DFT for the Hubbard model based instead on an impurity-interacting system, thus leading to an in-principle-exact site-occupation embedding theory (SOET)^{1,2} (Fig. (1)). This novel extension of DFT sheds a new light on conventional embedding techniques and paves the way towards the development and application of versatile frequency-independent theories for strongly correlated electrons in both extended and molecular systems.

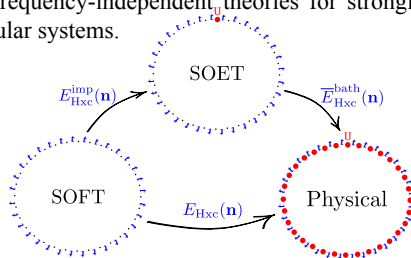


Fig.1: Fully-interacting (Physical) system mapped onto a non-interacting (SOFT) and partially-interacting (SOET).

The mapping is made possible by the use of a bath Hartree-exchange-correlation (Hxc) energy, functional of the density as shown in Fig. (1). We have recently constructed different density-functional approximations, based on the Bethe ansatz solutions to both Hubbard and Anderson models³, leading to promising results when combined with the explicit treatment of the interacting impurity. At the end of the talk, a more practical way of resolving the self-consistent SOET equation will be described using a SIAM solver⁴, and a grand canonical formulation of SOET will be proposed in comparison to the density matrix embedding theory⁵.

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Fano-CI method for decay widths of metastable excited states of atomic and molecular systems

Kolorenč, Přemysl¹; Votavová, Petra¹

¹Institute of Theoretical Physics, Charles University, Prague, V Holešovičkách 2, Czech Republic
Email: afar@email.cz Web site: <http://utf.mff.cuni.cz/en/index.html>

Electron correlation is an essential driver of a variety of relaxation processes in metastable excited atomic and molecular systems. These are phenomena which often lead to autoionization involving two-electron transitions, such as Auger effect or inter-atomic Coulombic decay (ICD). Recently, even higher-order multi-electron decay processes has come into focus since their significance increases in multiply excited systems produced, e.g., after irradiation by high-intensity free electron lasers [1]. Among fundamental characteristics of a metastable state belongs decay width, directly related to its lifetime. This quantity can be computed using complex absorbing potential (CAP) in combination with various tools of excited-state quantum chemistry, such as configuration interaction (CI), algebraic diagrammatic construction (ADC) or equation-of-motion coupled-cluster methods. The CAP-based methods can build on the highly developed foundations of computational quantum chemistry if standard square-integrable (L^2) basis sets are used. The approach is rather demanding with respect to the quality of the basis set necessary for reliable representation of the CAP since it has to be localized in a region sufficiently distant from the system.

Another class of L^2 methods is based on the Fano theory of resonances, again in combination with CI or ADC expansions for the description of the many-electron wave functions. These methods were established as very accurate and possibly the most efficient tools for computation of intra- and inter-atomic decay widths and have been utilized in several important studies of ICD [2]. Fano-ADC was applied successfully also to study collective decay processes involving more than two electrons [3]. In contrast to CAP, this class of methods can be used to calculate also the partial decay widths, even though the use of square integrable still prohibit rigorous definition of the decay channels and the partial widths are therefore only approximate. Furthermore, since only the coupling matrix elements between the discretized continuum and a compact discrete state wave functions are needed, less diffuse basis sets are usually sufficient to obtain converged results.

At the heart of the Fano theory is separation of the Hilbert space into background continuum subspace \mathcal{P} and complementary subspace \mathcal{Q} containing the discrete states representing the resonances. Since the natural distinction between the continuum and L^2 wave functions associated with the discrete states is lost when standard Gaussian or other L^2 one-particle basis set is employed, other criteria for the separation have to be devised. Recently, universal procedure for the classification of individual many-electron configurations appearing in the CI or ADC expansions has been developed [4]. However, it is restricted to configurations characterized by only a single electron occupying virtual orbital and cannot be used, in the case of ADC for ionized systems, beyond the second-order. The task becomes significantly more complicated when configurations with two or more electrons in virtual orbitals are involved. Such configurations are found in higher-order ADC or CI expansions or already in the second-order ADC scheme for polarization propagator needed to study decay of excited states of electronically neutral systems. Therefore, universal Fano-ADC method for the latter is missing.

We will present generic Fano-CI method for electronically neutral systems in which the projectors on the \mathcal{P} and \mathcal{Q} subspaces are constructed using separate CI calculation for singly-ionized decay channels. Unfortunately, such a straightforward approach cannot be applied to the more accurate ADC schemes. However, the method can be utilized in the future for testing different classification procedures generalizing the approach of Ref. [4]. The work was funded by the Czech Science Foundation under the project GAČR 17-10866S.

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Name	First name	Institution	e-mail address
Ablett	James	SOLEIL, France	james.ablett@synchrotron-soleil.fr
Amara	Hakim	ONERA, France	hakim.amara@onera.fr
Baby	Anu	Universita' Milano Bicocca, Italy	a.baby@campus.unimib.it
Beauvois	Anthony	SOLEIL, France	anthony.beauvois@synchrotron-soleil.fr
Bokarev	Sergey	Universität Rostock, Germany	sergey.bokarev@uni-rostock.de
Bordage	Amelie	Université Paris Sud, France	amelie.bordage@u-psud.fr
Bouildi	Nadejda	IMPMC, Paris, France	nadejda.bouildi@upmc.fr
Brouder	Christian	IMPMC, Paris, France	christian.brouder@upmc.fr
Bugnet	Mathieu	INSA-Lyon, France	mathieu.bugnet@insa-lyon.fr
Cabaret	Delphine	IMPMC, Paris, France	delphine.cabaret@upmc.fr
Carniato	Stéphane	LCPMR, Paris, France	stephane.carniato@upmc.fr
Chassé	Mathieu	IMPMC, Paris, France	mathieu.chasse@normalesup.org
Chassé	Mathieu	IMPMC, Paris, France	mathieu.chasse@normalesup.org
Cudazzo	Pierluigi	Ecole Polytechnique, France	pier-luigi.cudazzo@polytechnique.fr
Dai	Zongbei	INSP, Paris, France	benix1916@gmail.com
de Clermont Gallerande	Emmanuelle	IMPMC, Paris, France	emmanuelle.de_clermont_gallerande@upmc.fr
de Groot	Frank	Utrecht University, Netherlands	f.m.f.degroot@uu.nl
Deur	Killian	Univ Strasbourg, France	deur@unistra.fr
Ducastelle	François	Onera, France	francois.ducastelle@onera.fr
Fernandez Rodriguez	Javier	Diamond, United Kingdom	javier.fernandez-rodriguez@diamond.ac.uk
Ferradas	Ruben	LCPQ Toulouse, France	rubenferradas@gmail.com
Fronsager	Emmanuel	Univ Strasbourg, France	fromager@unistra.fr
Galanzew	Jurij	ESRF, Grenoble, France	jurij.galanzew@esrf.fr
Gatti	Matteo	Ecole Polytechnique, France	matteo.gatti@polytechnique.fr
Haverkort	Maurits	Univ Heidelberg, Germany	m.w.haverkort@thphys.uni-heidelberg.de
Ilakovac	Vita	LCPMR, Paris, France	vita.ilakovac-casses@upmc.fr
Joly	Yves	Institut Néel, Grenoble, France	yves.joly@neel.cnrs.fr
Jourdain	Noémie	Univ Bordeaux, France	noemie.jourdain@u-bordeaux.fr
Juhin	Amélie	IMPMC, Paris, France	amelie.juhin@upmc.fr
Kalai	Cairédine	LCT, Paris, France	cairedine.kalai@upmc.fr
Koskelo	Jaakko	Ecole Polytechnique, France	jaakko.koskelo@polytechnique.edu
Latil	Sylvain	CEA, France	sylvain.latil@cea.fr
Lee	Min-I	Université Paris Sud, France	min-i.lee@u-psud.fr
Liu	Jiawen	INSP, Paris, France	jiawen.liu.kira@gmail.com
Mazouin	Laurent	Univ Strasbourg, France	laurent.mazouin@gmail.com
Miteva	Tsveta	LCPMR, Paris, France	miteva.tsveta@gmail.com
Oberli	Solène	LCPMR, Paris, France	solene.oberli@upmc.fr
Paquier	Julien	LCT, Paris, France	paquier112@yahoo.fr
Radovic	Ivan	University of Belgrade, Serbia	iradovic@vin.bg.ac.rs
Radtke	Guillaume	Univ Strasbourg, France	guillaume.radtke@upmc.fr
Ravikumar	Abhilash	Universita' Milano Bicocca, Italy	a.ravikumar@campus.unimib.it
Recoules	Vanina	CEA, France	vanina.recoules@cea.fr
Rehr	John	University of Washington, USA	jir@uw.edu
Reining	Luca	Ecole Polytechnique, France	luca.reining@polytechnique.edu
Reshetnyak	Igor	EPFL, Lausanne, Switzerland	igor.reshetnyak@epfl.ch
Retagan	Marius	ESRF, Grenoble, France	marius.retagan@esrf.fr
Sainctavit	Philippe	IMPMC, Paris, France	philippe.sainctavit@impmc.jussieu.fr
Senjean	Bruno	Univ Strasbourg, France	bsenjean@gmail.com
Sipr	Andrej	Czech Academy of Sciences	sipr@fzu.cz
Sisourat	Nicolas	LCPMR, Paris, France	nicolas.sisourat@upmc.fr
Sottile	Francesco	Ecole Polytechnique, France	francesco.sottile@polytechnique.fr
Sponza	Lorenzo	Onera, France	lorenzo.sponza@onera.fr
Toulouse	Julien	LCT, Paris, France	julien.toulouse@upmc.fr
Tsetseris	Leonidas	National Technical University of Athens, Greece	leont@mail.ntua.gr
Tzavala	Mariena	Ecole Polytechnique, France	mariena.tzavala@polytechnique.edu
Vantelon	Delphine	SOLEIL, France	delphine.vantelon@synchrotron-soleil.fr
Vonwerk	Christian	Humboldt Universität zu Berlin, Germany	vorwerk@physik.hu-berlin.de
Votavová	Petra	Charles University Praha, Czech Republic	afar@email.cz
Yuki	Utsumi	SOLEIL, France	yuki.utsumi@synchrotron-soleil.fr
Zhou	Jianqiang (Sky)	Ecole Polytechnique, France	zhou@theory.polytechnique.fr