0.0.1 X-ray Spectroscopy : Recent Advances in Modelling and New Challenges

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CECAM, Psi-k, ESF

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http://www.cecam.org/workshop-537.html

Scope of the workshop

Representatives for many different methods to simulate x-ray spectra have been gathered to present the state-of-the-art in the field and discuss the applicability and limitations of the available theoretical tools. Experimental specialists were also invited to show recently developed techniques, thus suggesting future challenges direction for future development of the theoretical methods.

The presentations of invited speakers and contributing talks were a mixture of method development and applications, which gave opportunities for lively discussions on technical details of the methods, as well as on the kind of physical properties that can be addressed and on general issues concerning the various level of theory and range of reliability. The crucial role of these methods in the interpretation and design of new experiments are obvious from the strong interest from the experimental groups and a continuous interplay between theory and experiment is valid to the field.

Main outcomes

A variety of advanced new computational approaches based on the Bethe-Salpeter equation, multi-configurational wave function methods and time-dependent density functional theory (DFT) have been discussed in depth. Several speakers presented new or renewed program packages a variety of features related to the calculation of x-ray spectra at different level of approximation, which points to a stimulating development in the field. Several cases of successful applications of the simplest transition potential DFT methods to both simple and large complex systems have been illustrated. Among these, there were a few examples of disordered systems like polymers, molecular liquids and solutions, for which there is a need of extensive configurational sampling in extended systems. Applications on more realistic systems have become possible thanks to the implementation of X-ray spectroscopy tools within fast DFT based codes for simulations on condensed matter systems, like GPAW, CP2K, QuantumEspresso, and Wein2k. On the other hand, limitations of DFT methods have been highlighted in comparison to new results obtained from more advanced methods, which however are still strongly limited to small system size. Many contributions presenting new methodology from wave function based methods and response-theory formalism have shown that the field is extending into new areas. Although

multi-configurational post-Hartree-Fock methods are only applicable to small systems, they serve as an important calibration schemes. This helps the evaluation of more approximated, providing a systematic way to improve the description of more and more complex effects, thus bringing new ideas for method development. One of the hot topics in the workshop was transition metal L-edge spectra, and the related issues affecting x-ray absorption, x-ray emission and resonant inelastic x-ray scattering. Presentations of experimental groups showed the rapid development of new techniques and facilities in this direction, pointing to an urgent demand for accurate theoretical tools. Especially, the new achievements in the field of time-resolved measurements pose new challenges for the interpretation of the spectra and the theoretical modeling. The speakers were positively inspired by the scope of the workshop and made reference to different methods in their presentations, which created an open minded atmosphere and stimulated frank discussions. The richness of comparison between experiments and electronic structure calculations seen at the workshop is expected to increase with new insights onto e.g. orbital ordering and x-ray spectro-microscopy. Indeed, the importance and strength of x-ray spectroscopy is that it enables studies of the electronic properties in which the length scales from experiment and theory is meeting.

From the discussion on the modeling of transition metal L-edge spectra, we can extract the following conclusions. The L-edge spectra of transition metals are particularly complicated and the simplified transition potential approach based on DFT does not reproduce the pre-edge features accurately. This is due to the lack of multi-configurational effects, which results in wrong intensity and energy positions of the peaks. It can be argued that TD-DFT has some success but the representation of the interaction between the core-hole and the excited electron is only approximate. But the conclusion seems to be that one has to resort to the Bethe-Salpeter equation methods to have real predictive power. However, more extensive testing in various applications is necessary to clarify this statement. The development of new techniques and sources for acquiring time-resolved x-ray spectra of chemical reactions is beginning to approach the time-scales were it is meaningful to speak about electronic changes during the reaction rather then just differences between the reactants and the products. Applications of time resolved spectroscopy in the field of solution chemistry, surface science, and solid state physics were presented.

Conclusive remarks

The announcement of this workshop was followed by strong interest and we got requests for attendance long after the official dead-line. This resulted in an almost full room for both the invited and contributed presentations. Thanks to the excellent facilities and support at ETH we also enjoyed a highly appreciated video conference with Vancouver, Canada. In the poster session, the foyer was crowded and lively discussions around the 25 poster presentations continued until late in the evening. Our aim to gather representative scientists working on many different branches in the field of x-ray spectrum calculations was achieved and was a key ingredient in the intense and balanced discussion about the performance and limitations of the methods. In some cases, however, the methodologies were not fully explored and it was not possible to reach conclusive and comprehensive statements of the applicability range of the methods. We suggest that a conference on similar topics should be organized in a few years time, when the new methodologies have matured, have a better chance of being successful . Applications to large systems primarily employed transition potential DFT calculations. As a consequence of the only partially conclusive discussion of the limitations of that approach, the issues with simulating large systems and sampling of configurations were not addressed very much.

We would look forward to a future workshop within a few years at a time when the recently developed

methodologies are more mature and on a particular timely topic. That would inspire the participants to really provide prerequisites for a conclusive comparison of methods in particular applications

Program

Day 1 .
Introduction to problems and overview: Chair Michael Odelius

- 08:30 to 08:45 Welcome
- 08:45 to 09:30 Nils Martensson: New Opportunities for Multidimensional Electron Spectroscopy
- 09:30 to 10:15 Frank Neese:A new first principle approach to calculate transition metal L-edge spectra

Methods in core-level spectroscopy I: Chair Frank DeGroot

- 10:45 to 11:30 Benjamin Watts: Scanning Transmission X-ray Spectro-microscopy of Organic Materials
- 11:30 to 12:15 Lars Pettersson: X-ray spectroscopies and scattering applied to water: What can we learn from experiment and simulations?
- 12:15 to 12:45 Moniek Tromp: Development of XAS and XES techniques as a tool in homogeneous catalysis

Methods in core-level spectroscopy II: Chair John Rehr

- 14:00 to 14:45 Mauro Stener: TDDFT and DFT approaches for core electron excitations: molecules, bulk materials and large clusters
- 14:45 to 15:30 Patrick Norman: Response theory calculations of near-edge X-ray absorption and circular dichroism spectra
- 15:45 to 16:30 Nicholas A Besley: Development of Exchange-Correlation Functionals for Time-Dependent Density Functional Theory Calculations of Core Excitations
- 16:30 to 17:15 Delphine Cabaret: Successful and unsuccessful applications of DFT for XANES simulations and how to improve
- 17:15 to 17:45 Weijie Hua: X-ray spectroscopy of DNA

Poster Session wit Apero

Day 2 .
Time-resolved x-ray spectroscopy - experiment and theory: Chair Thomas James Penfold

- 08:30 to 09:15 Shaul Mukamel: Coherent Attosecond Multidimensional X-ray Spectroscopy of Molecules

- 09:15 to 10:00 Wilfried Wurth: Ultrafast dynamics in solids and at surfaces probed with time-resolved x-ray spectroscopy

Time-resolved x-ray spectroscopy - experiment and theory: Chair Wilfried Wurth

- 10:30 to 11:15 Thomas James Penfold: Time-resolved X-ray absorption spectroscopy
- 11:15 to 11:45 Amlie Bordage: Probing the electronic structure of Fe in switchable molecules using time-resolved hard X-rays spectroscopies
- 11:45 to 12:15 Enrique Sanchez Marcos: Coupling Computer Simulations and X-ray Absorption Spectroscopy for Solving the Structure of Metal Ion Solutions
- 12:15 to 12:45 Artur Braun: Application of x-ray and electron spectroscopy to energy materials

Methods in core-level spectroscopy III: Chair Lars Pettersson

- 14:00 to 14:45 John Rehr: Advances in the Theory of X-ray Spectra Beyond the Quasi-particle Approximation
- 14:45 to 15:30 Frank de Groot: Towards an ab-initio description of X-ray absorption spectra of transition metal systems
- 15:30 to 16:00 Sonia Coriani: Coupled Cluster Methods for X-ray absorption spectroscopy

Applications of x-ray spectroscopy: Molecules, Liquids, Materials: Chair Daniele Passerone

- 16:30 to 17:15 Serena DeBeer: Valence to Core X-ray Emission as a Novel Probe of Metal-Ligand Interactions
- 17:15 to 18:00 Peter Blaha: BSE calculations of L23 edges of transition metal compounds
- 18:00 to 19:00 George Sawatzky : The pros,cons and problem related selection of theoretical approaches to x-ray spectroscopies

Social dinner.

Day 3 .

Methods in core-level spectroscopy IV: Chair Mauro Stener

- 09:00 to 09:45 Calogero Natoli: Multiple Scattering Theory: a versatile tool for calculating x-ray spectroscopic response functions as well as ground state properties of a condensed matter system.
- 09:45 to 10:30 Peter Kruger: Multichannel multiple scattering calculations on dichroic L23-edge spectra of titanium oxide nanostructures
- 11:00 to 11:45 Eric Shirley: The NIST Core BSE program (NBSE) and OCEAN, its nearly Turn-key Implementation

- 11:45 to 12:30 Pieter Glatzel: Electronic structure analysis by hard X-ray photon-in/photon-out spectroscopy
- 12:30 to 13:00 Donat Adams: Characterization of conformational changes in small molecules and polymers by means of ab initio MD and X-ray absorption spectroscopy

Applications of x-ray spectroscopy: Catalysis, material science: Chair Marcella Iannuzzi

- 14:00 to 14:45 Jeroen Anton van Bokhoven: Application of X-ray absorption in catalysis
- 14:45 to 15:30 John Tse: X-rays at high pressures
- 15:30 to 16:00 Grigory Smolentsev: X-ray absorption and emission spectroscopy to study the local structure in coordination complexes

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