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Recent advances in modelling core-electron spectroscopy

 John J. Rehr, ^a David Prendergast ^b and Johannes Lischner ^c

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With the proliferation of next-generation synchrotron radiation X-ray facilities world-wide, core level X-ray spectroscopies have become some of the most important and widely used probes of materials and molecular systems. They include, for example, X-ray absorption (XAS), X-ray emission (XES), X-ray photoemission (XPS), and resonant inelastic X-ray scattering (RIXS). Their applications range throughout the chemical and physical sciences. These spectra encode a variety of site- and element-specific information over a broad range of energy and time-scales. This information characterizes the local atomic, chemical and excited-state electronic structure and dynamics of a given system. Theoretical modelling is essential to interpret the data quantitatively, and hence to exploit the full potential of these powerful experimental techniques. However, the theory of core-level spectra differs significantly from that for valence spectra and cannot be captured by conventional electronic structure or quantum-chemistry methods. The reason

is that core spectra derive from high energy excitations and many-body effects due to the creation of a core-hole by photo-absorption. Temperature-dependent effects due, for example, to vibrational motion can also be important. Consequently, specialized theory and analysis methods are needed to cover the broad range of experimental results. Fortunately, there has been significant progress in recent years, driven in part by advances both in fundamental theory, software, and computational resources. This themed collection provides a broad overview of recent theoretical developments in the theory and modelling of these core-level spectroscopies.

The present issue consists of more than 20 articles including three perspectives, which are representative of the state of the art in theoretical simulations of core-level X-ray spectra. They highlight the progress made during the past decade. For comparison, see the Themed Issue on **Recent developments in X-ray absorption spectroscopy** (*Phys. Chem. Chem. Phys.*, 2010, 21, 5489–5724).

Broadly, they represent advances in three categories: (i) the fundamental theory of X-ray spectra; (ii) first principles codes and simulation software; and (iii) advanced analysis tools for interpreting the spectra and extracting physical information.

(i) Advances in fundamental theory continue to be developed. They have been driven in part by the parallel development of 3rd and 4th generation X-ray sources

such as XFELs which call for novel theories of ever-increasing precision to interpret the results. For example, accurate real-time methods are needed to understand time-resolved X-ray spectra, *e.g.*, in pump-probe spectroscopies for non-equilibrium systems. Relativistic theories and all-electron methods are often important. Notably, hybrid density functional theories and coupled-cluster methods have been developed for accurate calculations of core binding energies.

(ii) Codes and simulation software – although formally, the basic theory of X-ray spectra has been understood for decades, quantitative treatments of many-body effects have posed formidable challenges. These include lifetime broadening due to self energy effects and inelastic losses, as well as dynamic relaxation processes due to the creation of the core hole. During the past decade, advanced codes have been developed for practical simulations that can capture these effects. For example, the Perspective on *ab initio* calculations (<https://doi.org/10.1039/D2CP01167K>) describes advances in the widely used real-space Green's function approaches. Novel is the use of a computational workflow tool CORVUS, which links the X-ray spectroscopy code FEFF to auxiliary codes to facilitate automated calculations of a broad range of core-level spectroscopies. Another important development is the development of linear-response TDDFT for accurate calculations of near-edge XAS and RIXS.

^a Department of Physics, University of Washington, Seattle, WA 98195-1560, USA. E-mail: jjr@uw.edu; Fax: +1-206-685-0635; Tel: +1-206-543-2770

^b The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA. E-mail: dgprendergast@lbl.gov; Fax: +1-510-486-7424; Tel: +1-510-486-4948

^c The Thomas Young Centre for Theory and Simulation of Materials, Department of Materials, Imperial College London, London SW7 2AZ, UK. E-mail: j.lischner@imperial.ac.uk; Tel: +44 (0)20 7594 9949

(iii) Since the information content in experimental signals is limited, specialized analysis techniques are generally needed to interpret the spectra. This limitation has spurred the development of a host of advanced analysis methods.

Among those discussed in this issue are Reverse Monte Carlo and Neural Network methods.

As Guest Editors, we wish to thank all the authors for their contributions to this Themed Issue and to the editorial staff of

PCCP for their support. We hope that the topics in this issue will inspire many more developments in this field in the years to come.