Theory for Surface Processes and Spectroscopies Focus Topic
Room B116 - Session TH2+AS+SS-TuM

Core-Level Spectroscopies II

Moderators: Ria Broer, University of Groningen, **Bianca Schacherl**, Karlsruhe Institute of Technology

11:00am **TH2+AS+SS-TuM-10 Cumulant Green's Function Approaches for Satellites and Multiplets in X-Ray Spectra***, John J. Rehr,* Dept of Physics, University of Washington*; J. Kas,* Department of Physics, University of Washington **INVITED**

The treatment of electronic correlations in open-shell systems is one of the most challenging problems in atomic, molecular, and condensed matter physics. Their importance is particularly evident in x-ray spectra, where the single particle theory breaks down and many-body effects such as satellites and atomic multiplet effects are observed. Conventional approximations are only partly successful. Ligand-field multiplet theory and dynamical mean field theory can describe intra-atomic correlation effects well but typically ignore long range correlation effects. The real-time cumulant Green's function method can describe shake-up effects well [1] but ignores multiplets. We have found, however, that separating the dynamic Coulomb interactions into local and longer-range parts with *ab initio* parameters yields a combined multiplet-plus-cumulant approach that can account for both local atomic multiplets and satellite excitations [2]. The approach is illustrated for transition metal oxides and explains the multiplet peaks, charge-transfer satellites, and distributed background features observed in XPS experiment. In an alternative approach for molecular systems, we have found that a real-time equation of motion coupled-cluster (RT-EOM-CC) cumulant approach can also describe both correlation effects at the CCSD level and intrinsic losses in x-ray spectra, including orthogonality corrections that enhance XAS at the edge [3]. Comparisons with other approaches [4] are also discussed.

[1] Strengths of plasmon satellites in XPS: Real-time cumulant approach: J. J. Rehr and J. J. Kas, J. Vac. Sci. Technol. A **39,** 060401 (2021).

[2] Ab Initio Multiplet-Plus-Cumulant Approach for Correlation Effects in X-Ray Photoelectron Spectroscopy, J. J. Kas, J. J. Rehr, and T. P. Devereaux, Phys. Rev. Lett. **128**, 216401 (2022).

[3] Equation of motion coupled-cluster cumulant approach for intrinsic losses in x-ray spectra, J. Chem. Phys. J.J. Rehr, F.D. Vila, J.J. Kas, N.Y. Hirshberg, K. Kowalski, and B. Peng**152**, 174113 (2020).

[4] Analysis of the Fe 2p XPS for hematite Fe_2O_3: Consequences of covalent bondinand orbital splittings on multiplet splittings, P.S. Bagus, C. J. Nelin, C. R. Brundle, N. Lahiri, E. S. Ilton, and K. M. Rosso, J. Chem. Phys. **152**, 014704 (2020).

11:40am **TH2+AS+SS-TuM-12 Understanding Multiplets in the XPS of Transition Metal Oxides: Experiment and Theory and the Effects on Quantitation Procedures***, Christopher Richard Brundle,* C. R. Brundle and Associates*; B. Christ,* XPS library*; P. Bagus,* Center for Advanced Scientific Computing and Modeling (CASCAM) Department of Chemistry University of North Texas **INVITED**

Atoms with open valence shells suffer splitting to their XPS core-levels owing to the different spin-spin coupling possibility between the remaining unpaired core electron and the electrons in the open shell (1). This results in a spectrum with two components of unequal intensity, separated by an ev or two. Gupta and Sen (2) expanded the multiplet splitting theory to include spin-orbit coupling (angular momentum coupling), providing highly cited predictions for the 2p spectra of TM cations (eg Ni^{2+}). Bagus, et al (3), and others, using rigorous ab initio MO calculations on clusters, have expanded theory further to allow XPS predictions for solid TM compounds (eg Ni^{2+} in NiO, Fe^{3+} in Fe_2O_3) which include both ligand field and bonding effects. Finally, they included shake-up effects (excitation of valence electrons in addition to core level ionization), which can substantially alter the distribution of intensities across the complete core-level spectrum, for example Ni 2p for NiO (4). This progression in the understanding of the origin of the features of TM core-level spectra is discussed, as is also the effects on requirements for providing quantitation of TM compounds using core level intensity ratios or peak fitting. Comparison is then made to alternative theory approaches to modeling the spectra, such as the freely available semi-empirical charge transfer method, CTM4XAS, (5), and the many-body cumulative theory of Rehr and Kass (6). We examine how these agree/differ in the interpretation/understanding of the XPS features, usefulness in ascribing chemical states, and quantitation aspects.

1. C. S. Fadley, D. A. Shirley, A. J. Freeman, P. S. Bagus, and J. V. Mallow, Phys. Rev. Lett., 1969, **23**, 1397-1401.
2. R. P. Gupta and S. K. Sen, Phys. Rev. B, 1974, **10**, 71-77; P. Gupta and S. K. Sen, Phys. Rev. B, 1975, **12**, 15-19.
3. P. S. Bagus, C. J. Nelin, C. R. Brundle, B. V. Crist, N. Lahiri, and K. M. Rosso, Phys. Chem. Chem. Phys., 2022, **24**, 4562-4575.
4. P. S. Bagus, C. J. Nelin, C. R. Brundle, B. V. Crist, E. S. Ilton, N. Lahiri, and K. M. Rosso, Inorganic Chemistry, 2022, **61**, 18077
5. F. De Groot and A. Kotani, *Core level spectroscopy of solids. CRC Press, Boca Raton*, 2008.
6. J. J. Kas, J. J. Rehr and T. P. Devereaux, Phys. Rev. Lett. 2022, **128**, 216401

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