

The Combined Effects of Electron Correlation and Relativity on Core Excitation Spectra

Ria Broer, Rob Klooster

Theoretical Chemistry, Zernike Institute for Advanced Materials,
University of Groningen, Nijenborgh 4, 9747AG Groningen, The Netherlands

E-mail address: r.broer@rug.nl

Core spectroscopies can give accurate information on the electronic structure of matter, but the interpretation of the spectra is often rather complicated, especially in materials that contain open shell ions. The consequences of electron-electron interaction and in many cases also relativity influence the spectroscopic properties. For example, the relative intensities of spin-orbit split peaks in X-ray absorption spectra (XAS) can only in special cases be estimated from the statistical weights of the final states. In most cases the angular momentum couplings of the open shell valence electrons, the external crystal field and covalent effects strongly affect these branching ratios [1, 2]. Accurate first principles calculations can provide important information about these influences. It seems natural to use the 4-component relativistic formalism based on the Dirac-Fock equations to accurately calculate the spectra. This scheme is however complicated and computationally demanding. An alternative is to employ a 2-component method based on the use of the normalized elimination of the small component, combined with the restricted active space state interaction approach [3].

In this contribution we show benchmark calculations of the 4f X-ray Photo-electron Spectrum (XPS) of U^{5+} and of the 2p XPS of MnO, which show that the approach is capable of reproducing the results of the full 4-component relativistic calculations with good accuracy. Next we focus on the 2p XAS of small positively charged titanium clusters. The X-ray absorption spectra at the $L_{2,3}$ edge of size-selected clusters have been investigated experimentally by Lau and coworkers [4]. The spectrum of bulk Ti shows two broad lines, attributed to excitations from the $2p_{3/2}$ and the $2p_{1/2}$ shells. Spectra of Ti_3^+ and larger clusters have the same characteristics. The spectra of the Ti^+ and Ti_2^+ ions have however a much richer structure and the assignment of peaks nor the explanation of the branching ratios are straightforward. We have calculated the 2p XAS of these ions and, for comparison, also of a Ti atom. The computed spectra, which agree well with the experimental ones, enable us to interpret the experimental spectra in terms of many-electron and relativistic effects.

- [1] Bagus, P.S., Freund, H., Kuhlbeck, H., Ilton, E.S., Chem. Phys. Lett. 455:331-334, 2008.
- [2] R. Broer, in: *Relativistic Methods for Chemists*, M. Barysz, Y. Ishikawa (Eds.), *Challenges and Advances in Computational Chemistry and Physics*, vol.10, Springer:pp351-371, 2010.
- [3] R. Klooster, R. Broer, M. Filatov, *Chemical Physics* 395:122–127, 2012.
- [4] J. T. Lau, J. Rittmann, V. Zamudio-Bayer, M. Vogel, K. Hirsch, P. Klar, F. Lofink, and T. Möller, *Phys. Rev. Lett.*, 101:153401, 2008.