Simulation and theoretical modeling of L-edge XANES of transition metals

A.L. ANKUDINOV AND J.J. REHR

Dept. of Physics, Univ. of Washington, Seattle, WA 98195, USA

There has been dramatic progress in recent years both in calculations and in the interpretation of x-ray absorption spectra (XAS). Essential in such calculations is a "quasi-particle" treatment that takes into account inelastic losses and lifetime effects and includes a final state potential with a screened core-hole potential.

Moreover, for L-shell spectra "local fields effects," can also be important. Such local fields arise from the dynamic screening of both the external x-ray field and the coupling to the core-hole created in the absorption process. These effects require a theory that goes beyond the independent-particle approximation.

We have developed an efficient approach for treating such effects in solids and molecules based on a generalization of time-dependent density functional theory (TDDFT) together with a local approximation for core-hole screening. This approach has be added to our self-consistent, real-space Green's function code FEFF8. Results are presented for XAS at the $L_{2,3}$ edges of 3d transition metals. This approach accounts for the deviations of the L_3/L_2 intensity branching ratio from the 2:1 value of the independent electron approximation.

Acknowledgements

Supported by DOE grant DE-FG03-98ER45623 and facilitated by the DOE CMSN.

Rigorous theoretical determination of L-edge soft X-ray absorption spectra for transition metal complexes

P.S. BAGUS[1] AND E.S. ILTON[2]

[1]Department of Chemistry, University of North Texas, Denton, TX 76203-5070, USA (bagus@unt.edu)
[2]Pacific Northwest National Laboratory, 902 Battelle Blvd., MSIN: K8-96, Richland, WA 99352, USA (eugene.ilton@pnl.gov)

The structures of spectra generated by L-edge soft x-ray absorption spectroscopy contain a wealth of information on the chemical state of the element of interest. Coupling experiment with theory is a powerful approach to better interpret these spectral featuress. Most theoretical approaches that are used for this purpose are semi-empirical, e.g., de Groot (1994). There are of course both strengths and weaknesses in following the semi-empirical path. By increasing the number of adjustable parameters and scaling exchange integrals, one can usually get good agreement between experiment and theory. In some cases, a minimum number of adjustable parameters may suffice, which can lead to a better understanding of the physics and bonding environment. However, as recently shown by Bagus *et al.* (2004), there is the very real danger of not discovering the correct physics when taking semi-empirical short cuts. We believe that it is the discrepancies between experiment and theory that are most illuminating and have great scientific value because they may indicate that the theoretical model used is incorrect or incomplete. Consequently, we have been developing and applying rigorous *ab initio* models for the description of core-level excitation processes. In our work, we include the response of the orbitals, used to form the final state wavefunctions, to the presence of the core-hole; an effect neglected in semi-empirical treatments. This orbital relaxation may involve changes in the covalent character of oxide valence levels. We will report on our methodology and initial results for clusters that model bulk transition metal oxides, and compare these cluster results with those obtained for isolated atomic cations.

References

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