Computing L-edge Resonant Inelastic X-ray Scattering (RIXS) Spectra with Dynamical Density Matrix Renormalization Group Algorithm (DDMRG^{++})

Seunghoon Lee, Huanchen Zhai, and Garnet Kin-Lic Chan

Division of Chemistry and Chemical Engineering, Caltech
Pasadena, CA, USA, 91125

We are investigating a new theoretical approach which computes the cross section of the L-edge resonant inelastic X-ray scattering (RIXS) spectroscopy using a dynamical density matrix renormalization group (DDMRG^{++}) algorithm. In this new approach, we directly compute the RIXS spectra without any detailed wave-function information of the intermediate and the final states. Therefore, the new approach would have a great advantage in computing RIXS spectra for strongly correlated systems, e.g. iron-sulfur metal clusters, which have huge amounts of the intermediate and the final states. We present good agreement between experiment and the new theoretical approach, considering the scalar relativistic and spin-orbit mean-field (SOMF) effects on top of the ab-initio Hamiltonian based on the matrix product states (MPS) ansatz.

The L-edge RIXS spectroscopy is a key technique to probe the element-specific electronic structure. In contrast to X-ray absorption, emission, and photoemission spectroscopies (XAS, XES, and XPS), the resolution of RIXS spectra is not limited by the core-hole lifetime broadening. For transition metal complexes, the electric-dipole allowed transitions between 2p and valence d orbitals make the intensity of the spectra large. Although the spectra contains invaluable information of bond covalency and exchange coupling, the interpretation of the experimental spectra is extremely challenging.

Recently, various ab-initio methods have been used to simulate and to interpret the L-edge spectra, including restricted open-shell configuration interaction (ROCIS) [1], restricted active space self-consistent field (RASSCF) [2], and multi reference CI (MRCI) [3]. All these approaches computed RIXS spectra based on sum over states (SOS) representation of the cross section. Although these approaches have been successful in many molecular systems, these have clear limitations to compute the spectra of metal clusters. ROCIS would underestimate the number of final states and intermediate states, which cannot describe spectra for the dense low-lying excited states of metal clusters. [4] On the other hand, the multi reference methods (RASSCF and MRCI) cannot use the large size of the active spaces (c.a. larger than 20 orbitals), which is commonly required for the metal clusters. In addition, many intermediate and final states make these approaches inefficient.

The new method we propose can address these shortcomings by using MPS ansatz and avoiding SOS representation. The attractive features of the new method open a new possibility to unveil the electronic structure of the iron-sulfur metal clusters.

References

[1] D. Maganas, S. DeBeer, and F. Neese, *Inorg. Chem.*, **56**, 11819 (2017)

[2] I. Josefsson, K. Kunnus, S. Schreck, A. Fohlisch, F. de Groot, P. Wernet, and M. Odelius, *J. Phys. Chem. Lett.*, **3**, 3565 (2012)

[3] D. Maganas, P. Kristiansen, L-C. Duda, A. Knop-Gericke, S. DeBeer, R. Schlögl, F. Neese, *J. Phys. Chem. C*, **118**, 20163 (2014)

[4] B. E. V. Kuiken, A. W. Hahn, B. Nayyar, C. E. Schiewer, S. C. Lee, F. Meyer, T. Weyhermüller, A. Nicolaou, Y-T Cui, J. Miyawaki, Y. Harada, S. DeBeer, *Inorg. Chem.*, **57**, 7355 (2018)