

# Theoretical computation of X-ray absorption spectroscopy with multi-reference driven similarity renormalization group theory

Meng Huang, Francesco Evangelista

Emory University

The development of high-resolution, time-resolved X-ray spectroscopy has raised the demand for developing new electronic structure theories for computing core-excited states. In this study, we extended our multireference driven similarity renormalization (MR-DSRG) method to the core-excited states by combining it with a generalized-active-space self-consistent-field (GASSCF) treatment which accounts for static correlation. We have applied three different levels of MR-DSRG treatments, including perturbative theories (DSRG-MRPT2/3) and iterative theory [MR-LDSRG(2)]. These methods are benchmarked on the C, N, and O K-edge transitions of more than 40 molecules in the gas phase, as large as nucleobases and naphthalene. The GASSCF-MR-DSRG theories show good agreement with the experimental X-ray absorption spectroscopy in both transition energy and intensities. A comparison of the computed vibrational structure for five diatomic molecules with experimental results shows that our method can accurately predict the potential energy curve of core-excited states even far from the equilibrium geometry. Dynamical correlation corrections beyond the second-order level in perturbation theory improve the accuracy of core-excited states, especially in the bond-dissociation region.