A Comparative Study of Core-Valence Separation Approximation Schemes for Simulating Core-Level Ionization

Abdelrahman Ahmed[†], Alexander Yu. Sokolov
Department of Chemistry and Biochemistry,
The Ohio State University, Columbus, OH, 43210
[†]E-mail: ahmed.796@osu.edu

X-ray spectroscopy is a powerful tool for studying the electronic structure and dynamics of matter. Accurate simulations of experimental X-ray spectra is critical for their reliable interpretation and assignment. However, simulation of core-level excited states can be challenging. One of the primary challenges is that core-level excited states are embedded in a continuum of valence-level excited states, making convergence onto the states of interest difficult. One widely used solution to this problem is to invoke the Core-valence Separation (CVS) approximation. Despite its widespread use, many different CVS schemes exist. For example, the CVS approximation can include different classes of excitations, and may or may not introduce the frozen-core approximation. Furthermore, while CVS has been widely used and studied for K-edges (i.e. ionizations from 1s orbitals), its performance for L-edges (2s and 2p ionizations) is less understood. In this work, we analyze the performance of various CVS schemes for simulating K- and L-edge core-level ionization energies and spectra within the framework of single-reference Algebraic Diagrammatic Construction theory. We demonstrate that the choice of CVS scheme can yield appreciably different ionization energies, and discuss the role of various approximations.