Multireference algebraic diagrammatic construction theory for simulating X-ray photoelectron spectroscopy

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X-ray spectroscopic techniques have been widely developed and applied to investigate electronic structure and dynamics in molecules and materials. However, new ab initio methods to simulate core-level excited states are essential to understanding the core electron phenomena in chemical systems with various strengths of electron correlation. In this presentation, I will present the algebraic diagrammatic construction (ADC) in the multireference (MR) framework for calculating core ionization energies and X-ray photoelectron spectra. The MR-ADC method uses a multiconfigurational wavefunction as a reference (e.g., CASCI or CASSCF), from which the excited states are calculated. In contrast to conventional multireference methods, MR-ADC can simulate excitations from all molecular orbitals, including inner-shell and core, and does not require the inclusion of these orbitals in the active space. To access the high-energy core ionized states, we implemented the Core-Valence Separation (CVS) approximation to the IP-MR-ADC framework, which enables direct access to the inner-shell excitations by decoupling them from the valence configurations. The resulting CVS-IP-MR-ADC method enables the investigation of core ionized states in multireference electronic problems. I will demonstrate the accuracy of the CVS-IP-MR-ADC approach by showing its applications for bond-breaking processes and open-shell systems, such as biradicals and coordination complexes.