A transformed framework for multireference dynamic correlation

Alexander Yu. Sokolov,[†] Garnet K.-L. Chan
Department of Chemistry
Princeton University, Princeton, NJ, 08540
[†]E-mail: alexsokolov@princeton.edu

Multireference correlation remains a driving force for the development of new quantum chemical methods. There are now many methods to describe the correlation in the active spaces with up to 50 orbitals that produce a multireference wavefunction that is formally the sum of many determinants. The remaining challenge is to efficiently describe dynamic correlation outside of the active space. Dynamic correlation from a *single* reference can be captured by low-order perturbation theory, configuration interaction or coupled cluster methods. While analogs of these methods for multireference problems have also been formulated, these multireference theories are algebraically more opaque and computationally much more expensive than their single-reference counterparts.

In this talk I will describe a new framework[1] that allows to formulate multireference dynamic correlation theories as single-reference correlation theories in a canonically transformed frame. Such canonically transformed correlation theories are very simple and involve identical expressions to their single-reference counterparts. The corresponding excitations involve quasiparticles rather than the bare particles of the system. High-order density matrices (or their approximations) and the numerical metric instabilities common to multireference correlation theories do not appear. As an example, we will consider the Bogoliubov canonically transformed version of second-order Møller-Plesset perturbation theory and discuss its performance for bond dissociation.

References:
[1] A.Yu. Sokolov and G.K.-L. Chan, "A transformed framework for dynamic correlation in multireference problems", e-print arXiv:1411.0067 (2014).