University of Louisville
Department of Chemistry

Hoang Gia An Tran
Literature Seminar
When: March 7, 2024
Time: 1:30 p.m.
Location: CBLL-16

Partitioning chemical systems to capture static correlation

Abstract:

Static correlation plays an important role in determining the electronic structure of systems with orbital near-degeneracies. Static correlation is ubiquitous in bond dissociation and formation processes, bi- or multi-radical systems, and transition metals where its inclusion is a requirement to achieve qualitatively correct behavior. Capturing static correlation in electronic structure calculations requires the inclusion of multiple Slater determinants into the total wavefunction (1). However, due to the factorial scaling that results from describing strong correlation with such an approach (2), there has been significant interest in development of alternative computationally efficient schemes (3).

In this presentation, I will outline the use of computational models that partition strongly correlated systems to reduce the number of interactions that must be accounted for with factorial scaling (4). In particular, I will introduce three methods that have been developed in recent years based on the premise that strong correlation can be partitioned between more weakly interacting regions that can then be recoupled with polynomial cost. In particular I will discuss the cluster mean-field approach (4), where interactions between partitions are treated as tensor product states. Subsequently, I will outline how a protocol for how selecting the most important determinants can be incorporated into the cluster mean-field framework to further reduce the polynomial scaling (1). Finally, I will describe the localized active space state-interaction approach, where partitioning of the molecular framework based on spatially localized correlated regions is used (5).

References:

(1) Mayhall et al. J. Chem. Theory Comput. 2020, 16, 6098−6113

(2) Li et al. J. Chem. Theory Comput. 2021, 17, 5482−5491

(3) Gill et al. J. Chem. Phys. 134, 114111 (2011)

(4) Scuseria et al. Phys. Rev. B 92, 085101

(5) Gagliardi et al. J. Chem. Theory Comput. 2022, 18, 6557−6566