Single reference wavefunctions as first-order approximations for efficient variational and orthogonal description of multistate reaction pathways

Lee M. Thompson
University of Louisville

Computational simulation is vital to understand and corroborate mechanistic and spectroscopic experiments of excited states processes. However, methodologies for simulating excited states are limited, either due to inability to describe important effects away from the vertical excitation region (e.g. response based approaches), or due to poor computational scaling (e.g. configuration-interaction based approaches). In this talk we discuss our developments towards a hierarchy of efficient computational approaches that can simulate excited state reaction paths, potentially without limitation as to the nature of electronic states involved. We discuss our first steps in constructing models that behave variationally with regard to any electronic state and yield orthogonal solutions consisting of nonlinearly optimized basis solutions which form the set of first-order approximations to different electronic states. In addition, we discuss our developments for obtaining sets of nonlinearly optimized solutions that approximate different electronic states for use as initial basis states in the models.