Different Orbitals for Different Configurations: Compact Wavefunction Descriptions for Modeling Excited State Processes

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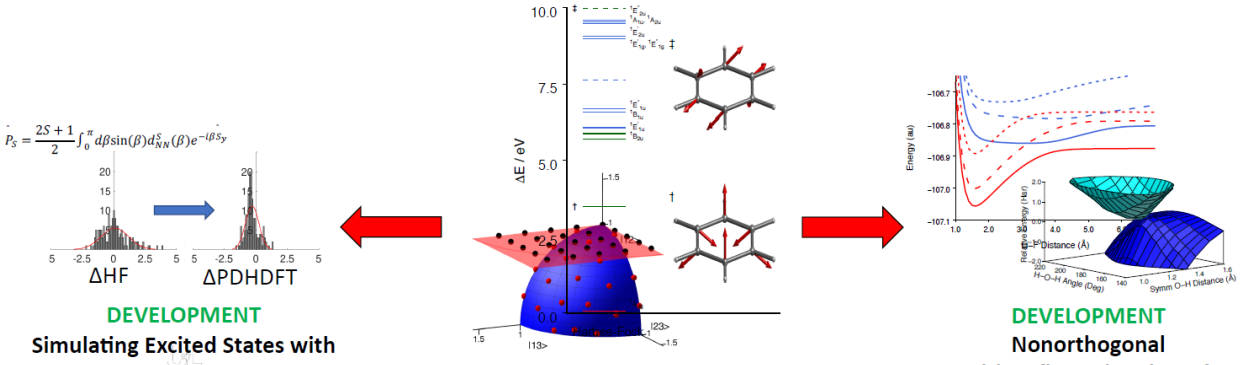
Computational simulation is vital to understand and corroborate mechanistic and spectroscopic experiments of excited states processes. However, methodologies for simulating excited states are limited, either due to inability to describe important effects, including charge transfer, multielectron excitations, and nonadiabatic effects (e.g. response-based approaches), or due to poor computational scaling (e.g. configuration-interaction-based approaches). In this talk, I will describe our groups work to overcome the bottlenecks inherent to computing properties of molecular excited electronic states. We have developed the different orbitals for different configurations (DODC) approach, in which important electron configurations in the wavefunction, for example the set that describe resonance in a molecule, are described by different sets of orbitals. In this talk, I will illustrate how DODC models provide a compact description of the wavefunction to overcome the computational bottlenecks of standard electronic structure methods. The applicability of the presented DODC models will be demonstrated with example applications of importance to simulation of excited state processes, including calculation of vertical excitation energies, intersystem crossings and conical intersections.



DEVELOPMENT

Simulating Excited States with Difference Projected DFT For Excited States

CONCEPT

Different Orbitals For Different Electron Configurations to Develop New Methods of Computational Simulation

DEVELOPMENT

Nonorthogonal Multiconfigurational SCF for Nonadiabatic Processes