Stochastic-CASSCF and Multi-Configuration Pair-Density Functional Theory: A new era for strongly correlated molecular systems

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Mimicking nature's biochemical conversions by theoretical means requires solving at molecular scale the complex electronic structures involved for ground and excited states. Advanced standard ab initio theoretical methods currently available are not able to meet this challenge and density functional theory (DFT) has been for a long time the only computational tool to support and complement experimental findings. High-level many-body methods for the strongly correlated systems are urged.

In the past decade several approaches have come to life to offer scientists the opportunity to tackle by computer simulations challenging topics in bio-mimicry, activation of small molecules, oxygen transport, organic electronics, spin inversion in metallo-porphyrins and more.

In this talk, I will give an overview on the multi-configurational methods I have been developing in the recent years:

- The Stochastic-CASSCF approach uses the stochastic Full-CI Quantum Monte-Carlo approach (FCIQMC) to solve the CI secular problem while the Super-CI scheme is employed to variationally optimizing the molecular orbitals.
- The Multi-Configuration Pair-Density Functional Theory (MC-PDFT) method is a post-SCF method that combines the advantages of multiconfigurational wave function theory based methods and DFT to recover both static and dynamic correlation energy.

The application of these methods to systems of practical interest will be presented, including the Fe(II) porphyrin and a set of polyacenes. By these approaches (a) much larger active spaces, easily up to 60 electrons and 70 orbitals, (b) basis set expansions of up to several thousands contracted functions and (c) molecular systems of a few hundreds atoms are accessible and both non-dynamic and dynamic correlation effects can be tackled. These methods are completely general and can be applied to systems of great interest.