

Multicomponent coupled cluster methods for combining electronic and nuclear quantum effects

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An accurate description of multicomponent systems, in which more than one type of particle is described quantum mechanically, is an important yet challenging task for quantum chemistry. The most essential example of a multicomponent system is a molecule where both electrons and nuclei are treated quantum mechanically beyond the Born-Oppenheimer approximation. Among different approaches for achieving that goal, the nuclear-electronic orbital (NEO) method¹ provides a framework for the accurate and efficient description of multicomponent systems. In the NEO approach, select nuclei, in addition to all electrons, are treated quantum mechanically with molecular orbital techniques, including nuclear quantum effects such as proton delocalization, anharmonicity, and zero-point energy directly into energy calculations and geometry optimizations. The simplest method that can be formulated in the NEO framework is Hartree-Fock (NEO-HF).¹ However, due to the lack of inclusion of correlation effects between quantum particles (i.e., electron-electron, proton-proton and electron-proton), NEO-HF delivers a poor performance for the calculation of properties such as energies and proton densities.

This talk will present the development and efficient implementation of various coupled cluster based methods within the NEO framework for the calculation of nuclear quantum effects of molecules. We will start by discussing an efficient implementation of the coupled cluster singles and doubles method within the NEO framework (NEO-CCSD).² Because inclusion of single excitations in the NEO-CCSD method is shown to play a crucial role in the level of accuracy, the two different multicomponent orbital optimized NEO-CCD approaches will also be discussed. These are denoted as the Brueckner coupled cluster with doubles (NEO-BCCD) method in which orbitals are optimized with projective technique,³ and the orbital optimized coupled cluster with doubles (NEO-OOCCD) method in which orbitals are optimized variationally. The NEO-OOCCD method can be approximated to give orbital optimized second-order Møller-Plesset NEO-OOMP2 method or scaled-opposite-spin version of the NEO-OOMP2. The implemented methods were then employed to calculate proton affinities that were benchmarked against both experimentally determined values, as well as to calculate other molecular properties such as proton densities.^{2,3} To allow calculation of the excited electronic and proton vibrational states, as well as excited mixed electron-proton vibronic states, the multicomponent equation-of-motion coupled cluster with singles and doubles (NEO-EOM-CCSD) method is presented.⁴

¹ S. P. Webb, T. Iordanov, and S. Hammes-Schiffer, *J. Chem. Phys.* **117**, 4106 (2002).

² F. Pavošević, T. Culpitt, and S. Hammes-Schiffer, *J. Chem. Theory Comput.* **15**, 338 (2018).

³ F. Pavošević, and S. Hammes-Schiffer, *J. Chem. Phys.* **151**, 074104 (2019).

⁴ F. Pavošević, and S. Hammes-Schiffer, *J. Chem. Phys.* **150**, 161102 (2019).