Multicomponent Quantum Chemistry: Integrating Electronic and Nuclear Quantum Effects

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Nuclear quantum effects such as zero point energy, nuclear delocalization, and tunneling play an important role in a wide range of chemical processes. Typically quantum chemistry calculations invoke the Born-Oppenheimer approximation and include nuclear quantum effects as corrections following geometry optimizations. The nuclear-electronic orbital (NEO) approach treats select nuclei, typically protons, quantum mechanically on the same level as the electrons with multicomponent density functional theory (DFT) or wavefunction methods [1]. Recently electron-proton correlation functionals have been developed to address the significant challenge within NEO-DFT of producing accurate proton densities and energies [2]. Moreover, time-dependent DFT and related methods within the NEO framework have been developed for the calculation of electronic, proton vibrational, and electron-proton vibronic excitations [3]. An effective strategy for calculating the vibrational frequencies of the entire molecule within the NEO framework has also been devised and has been shown to incorporate the most significant anharmonic effects [4]. Furthermore, multicomponent wavefunction methods based on coupled cluster and configuration interaction approaches, as well as multicomponent equation-of-motion coupled cluster methods for computing excited electronic and proton vibrational states, have been developed within the NEO framework [5]. These combined NEO methods enable the inclusion of nuclear quantum effects and non-Born-Oppenheimer effects in calculations of proton affinities, pK_a's, optimized geometries, vibrational frequencies, isotope effects, minimum energy paths, reaction dynamics, excitation energies, tunneling splittings, and vibronic couplings for a wide range of chemical applications.

References

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