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Time evolution of natural orbitals in ab initio molecular dynamics

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One-particle reduced density matrix (1RDM) functional theory is an alternative formalism to both density functional and wavefunction based methods. A pragmatic approach results in approximate functionals of the 1RDM in its diagonal form, that is, the use of natural orbitals and its occupation numbers as the fundamental variables, which define a natural orbital functional (NOF).

In this talk, I will first introduce the recently proposed [1] global NOF (GNOF). The latter has shown a balanced treatment of electron correlation effects in molecular systems with different spins, including complete dissociation curves; as well as an adequate treatment of the strong electronic correlation regime in challenge systems [2,3]. The NOF theory is currently an active research field, which can already be applied to large molecular systems of general chemical interest [4,5] using open-source software like DoNOF [6].

Secondly, I will present a GNOF-based ab initio molecular dynamics (AIMD) within the Born-Oppenheimer approximation. The most prominent feature of GNOF-AIMD is the ability to display the real-time evolution of natural orbitals, providing detailed information on the time-dependent electronic structure of complex systems and processes, including reactive collisions. The quartet ground-state reaction N(4S) + H2(1Σ) ⟶ NH(3Σ) + H(2S) is taken as validation test. Collision energy influences on integral cross sections for different initial ro-vibrational states of H2 and rotational-state distributions of NH product are discussed, showing a good agreement with previous high-quality theoretical results.

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