

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 $\text{N}(4\text{S}) + \text{H}_2(1\Sigma) \rightarrow \text{NH}(3\Sigma) + \text{H}(2\text{S})$ is taken as validation test. Collision energy influences on integral cross sections for different initial ro-vibrational states of H_2 and rotational-state distributions of NH product are discussed, showing a good agreement with previous high-quality theoretical results.

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[2] I. Mitxelena, M. Piris, J. Chem. Phys. 2022, 156, 214102.

[3] J.F.H. Lew-Yee, M. Piris, J.M. del Campo, J. Chem. Phys. 2023, 158, 084110.

[4] J.F.H. Lew-Yee, J.M. del Campo, M. Piris, J. Chem. Theory Comput. 2023, 19, 211.

[5] J. M. Mercero, R. Grande-Aztatzi, J. M. Ugalde, M. Piris, M. Adv. Quantum Chem. 2023, 88, DOI: 10.1016/BS.AIQ.2023.02.006

[6] M. Piris, I. Mitxelena, Comput. Phys. Commun. 2021, 259, 107651; available at <https://github.com/DoNOF/>, documentation at <https://donof.readthedocs.io/>

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