

Born-Oppenheimer molecular dynamics in NOF theory

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Appropriate representations of the electronic structure of atoms, molecules and solids without explicit recourse to the N-particle density matrix can alternatively be obtained by the one-particle reduced density matrix (1RDM) functional theory¹. Regrettably, computational schemes based on the exact constrained search formulation are too expensive, so the 1RDM functional requires a practical approach. In practical applications, we employ the exact energy functional but using an approximate 2RDM that is built from the 1RDM. The 2RDM reconstruction is conveniently done in the natural orbital representation where the 1RDM is diagonal. In this spectral representation of the 1RDM, the energy is clearly called natural orbital functional (NOF).

So far, several approximate functionals have been proposed², but solely PNOFs³ are based on the reconstruction of the 2RDM subject to necessary N-representability conditions. In this talk, I will firstly present the latest member of this family of functionals, named global NOF (GNOF)⁴. The latter has shown⁴ a balanced treatment of electron correlation effects in molecular systems with different spins, including full dissociation curves, and ionization potentials of transition metal atoms; as well as an adequate treatment of the strong electron correlation regime in challenge systems of one, two and three dimensions⁵. Note that the adjective "global" is used instead of "universal" to differentiate our approximate multipurpose NOF from the exact functional. The concept of the dynamic part of the occupation numbers will be introduced. It will be shown that GNOF describes the complete intra-pair electron correlation and the correlation between orbitals that make up both the pairs and the individual electrons. The inter-orbital correlation is composed of static and dynamic terms. Different examples will be analyzed where the weak and strong electron correlations are revealed. Our results will be compared with those obtained by established accurate theoretical methods and the experimental data.

Nowadays, an open-source implementation of NOF-based methods is available to the scientific community (<https://github.com/DoNOF>, <https://donof.readthedocs.io/>):

The associated computer program⁶ DoNOF (Donostia Natural Orbital Functional) is designed to solve the energy minimization problem of an approximate NOF, describing the ground state of an N-electron system in terms of the natural orbitals and their occupation numbers.

One of the main features of the DoNOF code is its ability to efficiently compute the analytic derivatives of the NOF energy with respect to nuclear coordinates in singlet and spin multiplet states⁷. This allowed us to increase efficiency by a factor proportional to the number of cores and greatly improve numerical accuracy in molecular structure studies such as geometry optimizations. Furthermore, it is now possible to perform realistic simulations of the electronic systems and complex processes that occur using the *ab initio* molecular dynamics. In the second part of the talk, I will focus on the development of Born-Oppenheimer molecular dynamics within NOF theory.

Index Terms: Electron Correlation, Reduced Density Matrix (RDM), Natural Orbital Functional (NOF), Analytical Gradients, Born-Oppenheimer Molecular Dynamics

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