GNOF: Balanced treatment of electron correlation

Mario Piris

Kimika Fakultatea, Euskal Herriko Unibertsitatea (UPV/EHU);
Donostia International Physics Center (DIPC), 20018 Donostia;
IKERBASQUE, Basque Foundation for Science, 48013 Bilbao, Spain

mario.piris@ehu.eus

Appropriate representations of the electronic structure of atoms, molecules and solids without explicit recourse to the N-particle density matrix or wavefunction can alternatively be obtained by the one-particle reduced density matrix (1RDM) functional theory. In practical applications, we employ the exact energy functional but using an approximate two-particle RDM (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). In this talk, I will 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 [2–5]. 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 program [6] 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. Besides, it is now possible to perform realistic simulations of electronic systems using GNOF-based ab initio molecular dynamics. Different examples will be analyzed where weak and strong electronic correlations are revealed. Our results will be compared with those obtained by accurate theoretical methods and experimental data.

(1) Piris, M. *Phys. Rev. Lett.* **2021**, *127*, 233001.

(2) Mitxelena, I.; Piris, M. *J. Chem. Phys.* **2022**, *156*, 214102.

(3) Lew-Yee, J. F. H.; del Campo, J. M.; Piris, M. *J. Chem. Theory Comput.* **2023**, *19*, 211–220.

(4) Lew-Yee, J. F. H.; Piris, M.; Campo, J. M. *J. Chem. Phys.* **2023**, *158*, 084110.

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

(6) Piris, M.; Mitxelena, I. *Comput. Phys. Commun.* **2021**, *259*, 107651.