

Global Natural Orbital Functional

Wednesday, 5 October 2022 10:00 (30 minutes)

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 theory [1]. Regrettably, computational schemes based on the exact constrained search formulation are too expensive; so the 1RDM functional requires a practical approach. For a Hamiltonian involving no more than two-body interactions, the ground-state energy can be cast as an exact functional of the two-particle reduced density matrix (2RDM). In practical applications, we employ this exact energy functional but using an approximate 2RDM that is built from the 1RDM.

Approximating the energy functional has an important consequence: the functional N-representability problem arises. In this presentation, the role of the N-representability in approximate functionals [2] will be analyzed. The 1RDM functional is called Natural Orbital Functional (NOF) when it is based upon the spectral expansion of the 1RDM. So far, several approximate functionals have been proposed [3], but solely PNOFs [4,5] are based on the reconstruction of the 2RDM subject to necessary N-representability conditions. For the latter, an open source software is available [6] for quantum chemistry calculations. These functionals are capable of producing a correct description of systems with a multiconfigurational nature, however, they also suffer from an important lack of dynamic correlation. To recover this correlation, second-order perturbative corrections have been implemented with significant results [5,7]. Nevertheless, our goal is to recover the missing dynamic correlation only within the NOF theory framework.

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In this talk, a new accurate NOF will be presented for all electronic structure problems, that is, a global NOF [8,9]. Note that the adjective “global” is used instead of “universal” to differentiate our approximate multi-purpose NOF from the exact functional. The concept of the dynamic part of the occupation numbers will be introduced. The emergent functional describes the complete intrapair electron correlation and the correlation between orbitals that make up both the pairs and the individual electrons. The interorbital 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 experimental data.

1. T. L. Gilbert, Phys. Rev. B 12, 2111 (1975); M. Levy, Proc. Natl. Acad. Sci. USA 76, 6062 (1979); S. M. Valone, J. Chem. Phys. 73, 1344 (1980).
2. M. Piris, in Many-body approaches at different scales: a tribute to N. H. March on the occasion of his 90th birthday, Chap. 22, pp. 231-247. New York: Springer (2018).
3. K. Pernal and K. J. H. Giesbertz, Top Curr Chem 368, 125-184 (2016); I. Mitxelena, M. Piris, J. M. Ugalde, Adv. Quantum Chem. 79, 155-177 (2019).
4. M. Piris, J. M. Ugalde, Int. J. Quantum Chem. 114, 1169-1175 (2014).
5. M. Piris, Phys. Rev. Lett. 119, 063002 (2017); Phys. Rev. A 98, 022504 (2018); Phys. Rev. A 100, 032508 (2019).

6. M. Piris, I. Mitxelena, *Comp. Phys. Comm.* 259, 107651 (2021).
7. M. Piris, X. Lopez, M. Piris, *Theor. Chem. Acc.* 138, 89 (2019).
8. M. Piris, "Global Natural Orbital Functional: Towards the Complete Description of the Electron Correlation", *Phys. Rev. Lett.* 127, 233001 (2021).
9. I. Mitxelena, M. Piris, "Benchmarking GNOF against FCI in challenging systems in one, two and three dimensions", *J. Chem. Phys.* 156, 214102 (2022).

Keywords:

Electron Correlation, Reduced Density Matrix Functional Theory (RDMFT), Natural Orbital Functional Theory (NOFT)

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