

“NOF Theory of the molecular electronic structure”

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The idea of a one-particle reduced density matrix (1-RDM) functional appeared few decades ago [1]. The major advantage of a 1-RDM formulation is that the kinetic energy is explicitly defined and it does not require the construction of a functional. The unknown functional only needs to incorporate electron correlation. The ensemble N-representability conditions that have to be imposed on variations of the 1-RDM are well-known. Here, the obstacle is the construction of the functional capable of describing a quantum-mechanical N-electron system, which is related to the N-representability problem of the two-particle RDM (2-RDM).

The 1-RDM functional is called natural orbital functional (NOF) when it is based upon the spectral expansion of the 1-RDM [2]. An approximate NOF requires an expression of the 2-RDM in terms of the 1-RDM. Such reconstruction of the 2-RDM has been achieved using the cumulant expansion leading to the PNOF [3]. The PNOF is based on an explicit ansatz of the two-particle cumulant $\lambda(\Delta, \Pi)$ satisfying the D-, Q- and G-necessary positivity conditions for the 2-RDM. Appropriate forms of matrices Δ and Π lead to different implementations of the PNOF [4].

In this presentation, the theory behind the PNOF is outlined. Special emphasis will be put on the recent proposed algorithm [5] which yields the natural orbitals by an iterative diagonalization of a generalized pseudo-Fockian matrix. Some examples are presented to illustrate the potentiality of the NOF theory. The calculations were carried out with our implementation, the PNOFID code (<http://www.ehu.es/mario.piris/#Software>). Our results are accurate values as compared to high level wave function methods and available experimental data.

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