NOF theory approach to strong electron correlation in chemistry

M. Piris^{1,2}, J.M. Matxain², F. Ruipérez¹, X. Lopez¹, J. M. Ugalde¹

¹Faculty of Chemistry, University of the Basque Country UPV/EHU, and Donostia International Physics Center (DIPC), P.K. 1072, Donostia, 20080, Spain ²IKERBASQUE, Basque Foundation for Sciece, Bilbao, 48011, Spain

e-mail: mario.piris@ehu.es

To describe the challenging regime of strong correlation, several attemps have been made in the development of approaches beyond wave-function (WFN) based methods and density funcional theory (DFT). One of them is the development of a functional theory based upon the one-particle reduced density matrix (1-RDM) [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. This functional N-representability is related to the N-representability problem of the 2-RDM.

The 1-RDM functional is called natural orbital functional (NOF) [2] when it is based upon the spectral expansion of the 1-RDM. An approximate NOF requires an expression of the two-particle reduced density matrix (2-RDM) in terms of the 1-RDM. Such reconstruction of the 2-RDM has been achieved using the cumulant expansion leading to the Piris NOF (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 [4]. Appropriate forms of matrices $\Delta(\{n_p\})$ and $\Pi(\{n_p\})$ lead to different implementations of the PNOF [5]. In this presentation, the theory behind the PNOF is outlined. Special emphasis will be put on the spin conserving NOF theory [6]. Some examples of strongly correlated systems, where density functionals yield pathological failures, are presented to illustrate the potentiality of the NOF theory. The calculations carried out by our implementation, the PNOFID code [7], have produced very accurate values as compared to high level wave function methods and available experimental data.

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