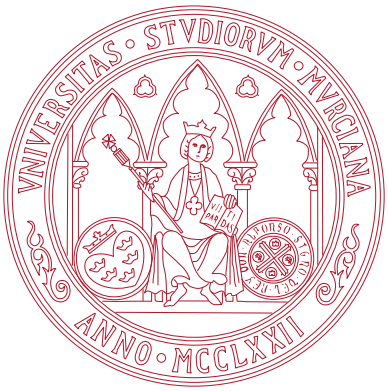

Máster Erasmus Mundus en Química Teórica y Modelización Computacional

Universitat de Valencia

Trabajo Fin de Máster

New parametrization of the Second-order Reduced Density Matrix (2-RDDM)

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Julio - Agosto de 2022

1 Introduction

Functionals of one-electron reduced density matrix (1-RDDM), γ, defined for an N-electron wavefunction, Ψ, as

$$\gamma\left(\mathbf{x},\mathbf{x}'\right)=N\int\cdots\int\Psi\left(\mathbf{x},\mathbf{x_2},\ldots,\mathbf{x}_N\right)\Psi^*\left(\mathbf{x}',\mathbf{x_2},\ldots,\mathbf{x}_N\right)\mathrm{d}\mathbf{x}_2\cdots\mathrm{d}\mathbf{x}_N\,, \tag{1}$$

where $\mathbf{x}=(\mathbf{r},s)$ is a combined spatial and spin coordinate.

As inmidiate advantage of using 1-RDDM instead of the electron density, ρ, is that the kinetic energy is an explicit functional of γ but not of ρ. Then, there is no need to introduce a ficticious noninteracting system. Moreover, orbitals present in RDMFT are fractionally occupied, so functionals of γ seem to be better suited to account for static correlation.

Self-adjointness of γ, as defined in eq. (1), allows for its spectral representation [1]

$$\gamma\left(\mathbf{x},\mathbf{x}'\right)=\sum_p n_p\varphi_p\left(\mathbf{x}\right)\varphi_p^*\left(\mathbf{x}'\right). \tag{2}$$

The eigenvalues of 1-RDM are called natural occupation numbers, $\{n_p\}$, and the eigenfunctions are known as natural spinorbitals, $\{\varphi_p\}$. For convention, the indices p,q,r,s are referred to natural spinorbitals and a,b,c,d to arbitrary one-eletron functions.

References

1. Löwdin, PO Quantum Theory of Many-Particle Systems. I. Physical Interpretations by Means of Density Matrices, Natural Spin-Orbitals, and Convergence Problems in the Method of Configurational Interaction. *Physical Review* **1955**, *97*, 1474–1489.