Multiconfigurational Pair-Density Functional Theory is More Complex Than You May Think

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Among different methods that have been proposed for combining DFT with MCSCF, the multiconfigurational pair-density functional theory (MC-PDFT) [1] approach is one of the most popular. In MC-PDFT, instead of taking spin-densities as our functional arguments as in standard spin-density DFT (SDFT), we define it in terms of the total density ρ and the on-top pair density Π. This idea is a generalization of KS-DFT and it was already suggested in 1995 by Becke, Savin and Stoll [2], upon realizing that SDFT can lead to unphysical results, *e.g.* failing to describe the degeneracy of the three triplet components.

The standard SDFT functionals can be translated to PDFT functionals so that they give identical results for a single determinant by using the relations between ρ, Π and the usual spin-densities: $\rho(r) = \rho_\alpha(r) + \rho_\beta(r)$ and $\Pi(r) = 2\rho_\alpha(r)\rho_\beta(r)$, resulting in a pair of solutions that correspond to α and β densities:

$$\rho_{\alpha/\beta} = \frac{\rho \pm \sqrt{\rho^2 - 2\Pi}}{2} \tag{1}$$

Observing Eq. 1, the value in square root can be negative in some conditions, making our densities complex with non-zero imaginary component. This problem was already noticed in the 1995 article where the authors showed that this would happen in a spin-adapted open-shell singlet. Despite the fact that this configuration is relatively common, the wide popular implementation of Li Manni [3] neglected theses cases by setting the square root to zero (absence of spin-polarization) or resorting to an *ad-hoc* modification of the translation formula to smooth its behavior around 0.

In this work we present a new implementation of MC-PDFT that is not only variationally optimized, but considers the complex nature of Eq. 1 and extends the translation to cases where $\phi^2 - 2\Pi$ is negative. The implementation was done in the very efficient massively parallel MultiPsi code and it is noteworthy that the resulting algorithm is more efficient than standard MCSCF, at roughly the cost of regular DFT for small to medium active spaces.

Finally, we showcase both the performance of variational MC-PDFT and the importance of the new translation by benchmarking on several examples, including a number of singlet-triplet gaps and open-shell singlets from low-lying excited states. Our results show that our new translated formulas improved the accuracy of MC-PDFT for PDFT versions of SLDA and PBE, and it is the way to go when translating spin-density functionals to on-top pair density ones.

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