Performance of the NOF Theory in the Description of the Four-Electron Harmonium Atom in the Singlet State

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Abstract: In recent years, the natural orbital functional (NOF) theory has emerged as an alternative approach to both density functional theory (DFT) and wave-function (WFN) methods for electronic structure investigations. Several NOFs have been proposed, for which validation is necessary. A well-known tool for calibration, testing, and benchmarking of an approximate electronic structure method is the harmonium atom. In this model system, the electron-nucleus potential is replaced by a harmonic confinement, but the electron-electron Coulomb interaction remains. By varying the strength of the harmonic potential, the correlation regime can be tuned, making possible the transition from the weakly to the strongly correlated regime. Accordingly, the harmonium stands as an adequate system for studying the behavior of approximate NOFs, since it is possible to contrast them with their exact counterparts obtained from the analytic solution. In this presentation, the comparison between the quasi-exact and approximate electron-electron repulsion energy provided by eight known NOFs, in the singlet state of the four-electron harmonium atom with varying confinements, is analyzed in some detail. The present approach, which will appear soon in the Journal of Chemical Physics 143 (arXiv:1511.06564 [physics.chem-ph]), not only reveals the failures of the functionals but also pinpoints the causes. In general, the functional PNOF6 shows the most consistent behavior, with decent accuracy, along all confinement regimes studied.

Keywords: 4e⁻ Harmonium atom; Electron Correlation; Natural Orbital Functional Theory; PNOF6; 1-Matrix Functionals, Reduced Density Matrices.

1. Introduction

The improvements in computer hardware and software have recently allowed the simulation of molecules with an increasing number of atoms. Unfortunately, the most accurate electronic structure methods based on N-particle wave functions (WFN) remain computationally too expensive to be applied to large systems. On the other hand, the most efficient method is the density functional theory (DFT). However, current implementations of DFT suffer from several problems, as for instance in the description of multireference systems.

An alternative to both DFT and WFN methods lies in the development of a functional theory based on the first-order reduced density matrix (1-RDM) [1] in its spectral expansion, known as natural orbital functional (NOF) theory [2]. Like the density, the 1-RDM is a much simpler object than the WFN. The ensemble N-representability conditions that have to be imposed on variations of the 1-RDM are well known [3]. The existence and properties of the 1-RDM energy functional are also well established [4]. 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. Several correlation functionals of this type have been proposed, for which validation is necessary.

A well-known tool for calibration, testing, and benchmarking of an approximate electronic

structure method is the harmonium atom [5]. In this model, the replacement of the Coulombic central confining electron-nucleus potential occurring in real systems by a harmonic potential makes the problem separable in terms of center-of-mass and relative coordinates. Accordingly, the harmonium stands as an adequate system for studying the behavior of approximate NOFs, since it is possible to contrast them with their exact counterparts obtained from the analytic solution. Moreover, by varying the strength of the harmonic potential, ω, the correlation regime can be tuned, making possible the transition from the weakly to the strongly correlated regime.

The energies of several electronic states of the four-electron harmonium atom are presently known within ca. 1 µhartree for arbitrary values of ω [6]. The respective 1-RDMs and individual energy components are also available from such calculations. Finally, exact asymptotics of these electronic properties are available at both the weak- and strong-correlation limits. Recently [7], the comparison between the exact and approximate electron-electron repulsion energy (U) obtained with several approximate NOFs, for several states of few-electron harmonium atoms, has been reported. The aim of this presentation is to analyze in some detail the performance of eight well-known NOFs in the singlet state of the four-electron harmonium atom with confinements that range from ω=0.001 to ω=1000.

2. Results and Discussion

The NOFs assessed in [7] fall into two broad categories. The first of them encompasses expressions for U that involve only the exchange integrals (K). This category includes:

1. The NOF introduced by Müller [8].
2. The NOF of Goedecker and Umrigar (GU) [9].
3. The NOF of Csányi and Arias (CA) [10].
4. The NOF of Csányi, Goedecker and Arias (CGA) [11].
5. The BBC2 NOF [12].

6. The NOF of Marques-Lathiotakis (ML) [13].
7. The NOF of Marques and Lathiotakis corrected for self-interaction (ML-SIC) [13].

The last NOF included in this report is PNOF6 [14], which corresponds to a JKL functional, that is, involves only the Coulomb (J), exchange (K) and time-inversion-exchange (L) integrals. This NOF is the last member of the family of functionals [15,16] obtained from the reconstruction of the two-particle cumulant in order to satisfy known necessary N-representability conditions for the second-order reduced density matrix.

In Figure 1, the electron-electron repulsion energy $U = V_{ee} - V_{ee}(HF)$ is depicted for the four-electron harmonium atom in the $^1D_+$ state. These values are taken from Tables VI and X of Ref. [7]. Due to its multireference character, this singlet state is challenging for K-only functionals 1-7. A rough agreement with the exact data is observed only for the GU, ML, and ML-SIC when the confinements are weak.

Among the functionals included, only PNOF6 goes parallel and above the exact solution for all confinements considered. Moreover, it is the only one capable of describing the $\omega \to \infty$ limit of this state with decent accuracy, however its perfor-mance deteriorates upon weakening of the confi-nement since the error represents a higher percentage of the total repulsion energy U. It is worth to note that the PNOF family understi-mates the electron correlation effects in high-spin states [7] of the four-electron harmonium atom. These results provide clear clues for the future work.
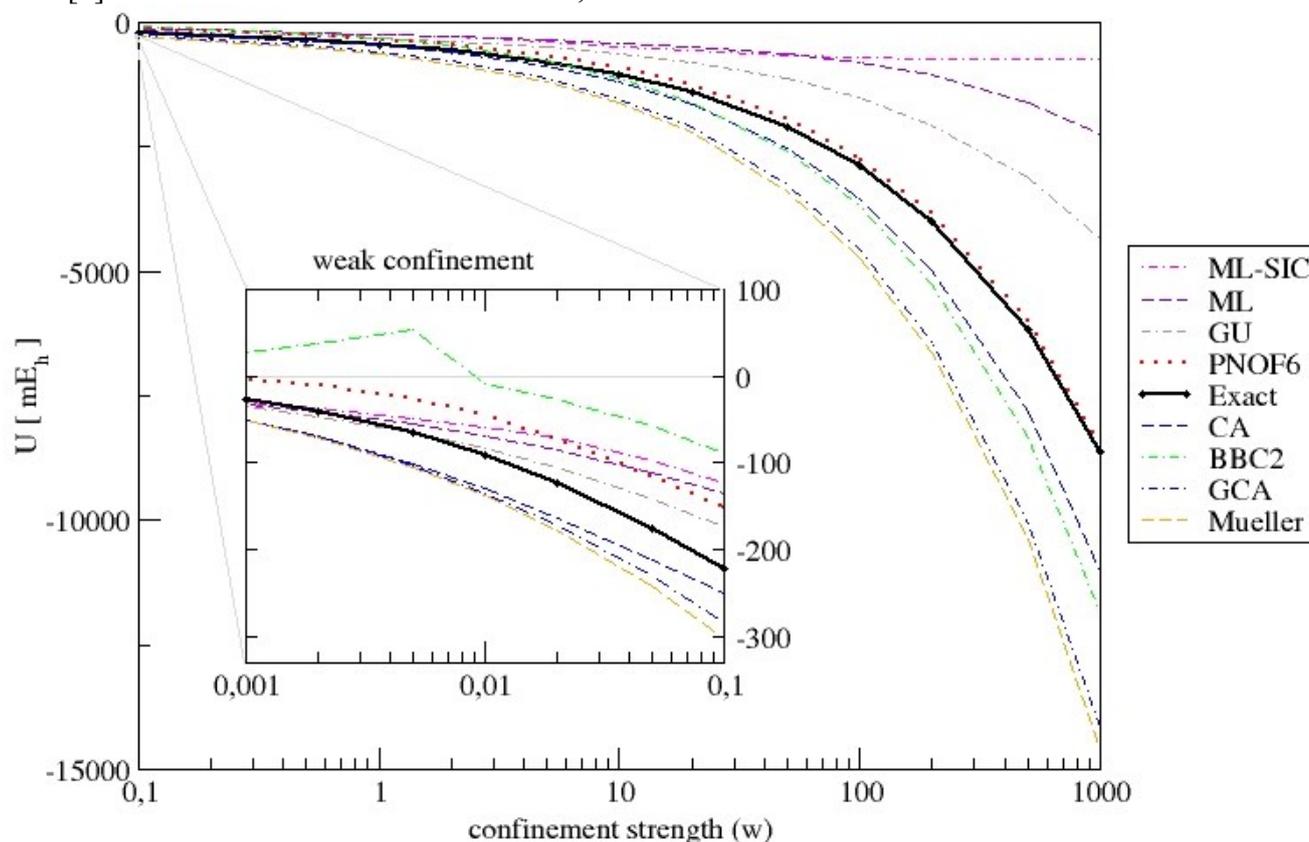

Figure 1. The electron-electron repulsion energy $U = V_{ee} - V_{ee}(HF)$ of the four-electron harmonium atom in the $^1D_+$ state (values taken from Tables VI and X of reference [7])

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Conflicts of Interest. The author declares no conflict of interest.

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