Canonical form of the Hartree-Fock orbitals in the open-shell systems

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This work compares two new approaches to deriving Hartree-Fock (HF) orbitals and orbital energies for the open-shell systems. The first approach is the *constrained* UHF (CUHF) method [1], and the second one is the *canonical* ROHF method [2-4]. In both methods, the wave function of a system under study is an eigenfunction of the operator $\hat{S}^2$, and the orbital energies ε_i^σ ($\sigma = \alpha$ or β, $\varepsilon_i^\alpha \neq \varepsilon_i^\beta$) obey Koopmans' theorem (KT).

The specific deficiency of the CUHF method which does not arise in the canonical ROHF method is that the wave functions of both ionized and excited states treated in the "frozen" orbital approximation are not generally eigenfunctions of $\hat{S}^2$. The latter contradicts the fundamentals of KT and also leads to spin contamination in post-HF (post-CUHF) approaches.

In the present work we combine the approaches underlying two discussed methods and develop the new ROHF method based on the use of different orbitals for different spins (DODS). The new ROHF-DODS method is free of the deficiencies inherent to the CUHF method. The main result of this work is that the orbitals and orbital energies derived with the new method appear identical to those derived with the canonical ROHF method.

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