Coupled cluster theory in Hartree-Fock calculations with localized orbitals

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More than a decade ago, we have suggested an alternative way to obtain the Slater determinant ground state Hartree-Fock (HF) solution using Thouless theorem, i. e. an exponential ansatz for the wave function [1]. Exact treatment was accomplished in the framework of variational coupled cluster singles (VCCS) [2,3]. The non-terminating Hausdorff expansion of the transformed Hamiltonian within the VCCS can be exactly treated after summing up the one-particle density matrix elements in the occupied-occupied block using a simple recurrence relation. Such an approach gave rise to an extremely simple diagonalization-free algorithm for the solution of the Hartree-Fock equations. This treatment corresponds to a non-unitary transformation of orbitals, however, preserving the idempotency of the density matrix.

Here, we apply this approach with a starting determinant using localized orbitals, i.e. we present an *a priori* localized Hartree-Fock method. The initial guess was obtained from diagonalising the Fock matrix constructed from the superposition of atomic densities. Starting molecular orbitals were localized using Pipek-Mezey procedure or an incomplete Cholesky decomposition of density matrix. Next, we were running VCCS iterations in local molecular orbitals. Convergence behavior and number of nonzero elements of T_1 amplitudes and/or non zero elements of the density matrix were examined for a series of medium sized molecules.

[1] D. J. Thouless, *Nucl. Phys.* **21**, 225-232 (1960).
[2] J. Noga and J. Šimunek, *J. Chem. Theory Comput.* **6**, 2706-2713 (2010).
[3] Šimunek and J. Noga, *AIP Conf. Proc.* **15O4**, 143-151 (2012).