

Using local molecular orbitals in diagonalization-free Hartree-Fock calculations.

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We have shown an alternative way to obtain the Slater determinant ground state solution within an independent-particle approximation using the exponential ansatz for the wave function (Thouless theorem)[1] and exact treatment in terms of variational coupled cluster singles[2, 3]. The non-terminating expansions of the wave function within the VCCS can be exactly treated by summing up the one-particle density matrix elements in the occupied block using simple recurrence relation. At the same time, this leads 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.

We apply this approach with a starting determinant using localized orbitals, i.e. we present a 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 incomplete Cholesky decomposition of density matrix. Next, we were running VCCS iterations in local molecular orbitals. Convergence behavior and number of nonzero elements of T1 amplitudes and density matrix were examined for series of medium sized molecules.

[1] D. J. Thouless, Nucl. Phys., **21** (1960), 225-232.

[2] J. Noga, J. Šimunek, J. Chem. Theory Comput., **6** (2010), 2706-2713.

[3] J. Šimunek, J. Noga, AIP Conf. Proc., **1504** (2012), 143-151.