History of the development of the Half-Projected Hartree-Fock method. Application to the calculation of excited states of the same symmetry as the ground state

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Abstract

Spin projected wave functions are known as generalizations of the Hartree-Fock wave function. Among them, the Half-Projected Hartree-Fock (HPHF) model represents a good compromise between the restricted (RHF) and unrestricted (UHF) Hartree-Fock methods. The HPHF wave function is a nearly pure wave function of spin and recovers a small part of the spin correlation energy. This paper reviews the history of the HPHF theory, not only from the conceptual point of view but also providing a compilation of the publications of this method over the years until now. In addition, the extension of the HPHF method to the calculation of non-orthogonal excited states to the ground state will be treated. The variational collapse during the calculation of singlet excited states with the same symmetry as the ground state is avoided by orthogonalizing the excited orbital to the corresponding occupied orbital. As an example, the potential energy surface of the S0 ground and 1S1(n, π*) first excited state of the formic acid HCOOH are calculated. Formic acid exhibits complex energy surfaces with respect two large amplitude motions, the torsional rotation of the O-H group and the waving out-of-plane angle of the H atom. In the excited state, the molecule adopts a pyramidal structure. The obtained energy results are fitted to curves that can be used for the calculation of the theoretical spectrum.

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