

Hartree-Fock (Self-Consistent Field, SCF) method

Method for determination of the spatial orbitals ψ_i of the many-electron determinantal wave-function (see Slater determinant) based on reducing coupled non-linear differential equations for the optimum forms of the molecular orbitals by use of the variational method (see variational principle). The Hartree-Fock hamiltonian operator is defined in terms of these orbitals through the operators of coulomb and exchange repulsion. The general procedure for solving the Hartree-Fock equations is to make the orbitals self-consistent with the potential field they generate. It is achieved through an iterative trial-and-error computational process, for which reason the entire procedure is called the self-consistent field method. In the case of open-shell systems one should distinguish between the spin-restricted Hartree-Fock (RHF) method and spin-unrestricted Hartree-Fock (UHF) method. In the former approach a single set of molecular orbitals is preset, some being doubly occupied and some being singly occupied with an electron of spin. In the UHF approach different spatial orbitals are assigned to electrons with α and β spins and the orbitals ψ_i doubly occupied in the RHF method are replaced by two distinct orbitals $\psi_i(\alpha)$ and $\psi_i(\beta)$.

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