Elevia Manual

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1 The Hartree-Fock-Roothaan Method (SCF LCAO MO)

1.1 The Self-Consistent Field Method

The SCF procedure is carried out as follows:

1. Specify a system (a set of nuclear coordinates $\{\mathbf{R}_a\}$, atomic numbers $\{Z_a\}$, and the total number of electrons N) and a basis set $\{\chi_s\}$.
2. Calculate all required molecular integrals S_{rs}, h_{rs}, and $(rp|sq)$, $(rp|qs)$.
3. Diagonalize the overlap matrix $\mathbf{S}$ and obtain a transformation matrix $\mathbf{X} = \mathbf{U}\mathbf{s}^{-1/2}$.
4. Assume an initial bond-order matrix $\mathbf{P}$ (often in the first iteration, we put $\mathbf{P} = \mathbf{0}$, as if there were no electron repulsion).
5. Find the $\mathcal{F}$ matrix using matrix $\mathbf{P}$.
6. Calculate the transformed Fock matrix $\mathcal{F}' = \mathbf{X}^\dagger \mathcal{F} \mathbf{X}$.
7. Diagonalize $\mathcal{F}'$ to obtain $\mathbf{C}'$ and $\boldsymbol{\epsilon}$.
8. Calculate $\mathbf{C} = \mathbf{X}\mathbf{C}'$.
9. Form a new $\mathbf{P}$ from $\mathbf{C}$.
10. Calculate the total energy E.
11. Determine whether the procedure has converged, i.e., determine whether the difference between two successive total energy is less than a threshold (10^{-8}). If the procedure has not converged, return to step (5) with the new bond-order matrix. If the procedure has converged, then calculate and output the quantities of interest.

References