

Self-Consistent Field (SCF) Method in Hartree-Fock Theory

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Introduction

The Self-Consistent Field (SCF) method is an iterative procedure used to solve the many-electron Schrödinger equation within the Hartree-Fock (HF) approximation. Instead of solving for all electrons simultaneously, SCF assumes that each electron moves in an average field created by all others.

SCF Overview

The goal is to determine a set of molecular orbitals (MOs) that minimize the total electronic energy of the system. These MOs are expressed as linear combinations of atomic orbitals (AOs), typically chosen from a basis set of Gaussian functions.

The general SCF procedure involves:

1. Guess the electron density or molecular orbitals
2. Build the Fock matrix from this guess
3. Solve the Roothaan-Hall equations to get new orbitals
4. Build a new density matrix from the new orbitals
5. Check for convergence; repeat if necessary

Step-by-Step Process

1. Molecular Input

The input includes:

- Nuclear coordinates
- Atomic numbers (Z_i)
- Charge and multiplicity (used to compute number of electrons)
- Basis set (e.g., STO-3G)

2. Basis Set Construction

Construct atomic orbitals using contracted Gaussian functions:

$$\chi_\mu(\vec{r}) = \sum_i d_i N_i e^{-\alpha_i |\vec{r}-\vec{A}|^2}$$

where:

- d_i are contraction coefficients
- N_i is a normalization factor
- α_i are primitive exponents
- \vec{A} is the center of the Gaussian

3. Integral Evaluation

Compute all required one- and two-electron integrals:

- Overlap: $S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle$
- Kinetic: $T_{\mu\nu} = \langle \chi_\mu | -\frac{1}{2} \nabla^2 | \chi_\nu \rangle$
- Nuclear attraction: $V_{\mu\nu} = \langle \chi_\mu | -\sum_A \frac{Z_A}{r_A} | \chi_\nu \rangle$
- Two-electron: $(\mu\nu|\lambda\sigma)$

4. Core Hamiltonian

$$H_{\mu\nu}^{\text{core}} = T_{\mu\nu} + V_{\mu\nu}$$

5. Initial Density Matrix

An initial guess $D^{(0)}$ is used. Often it is zero or obtained by diagonalizing the core Hamiltonian.

6. SCF Iteration

a. Build Fock Matrix

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} + \sum_{\lambda\sigma} D_{\lambda\sigma} \left[(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\sigma|\lambda\nu) \right]$$

b. Solve Roothaan-Hall Equation

$$FC = SC\varepsilon$$

This generalized eigenvalue problem yields orbital energies ε and coefficients C .

c. Build New Density Matrix

$$D_{\mu\nu} = \sum_i^{\text{occ}} C_{\mu i} C_{\nu i}$$

d. Compute SCF Energy

$$E_{\text{elec}} = \sum_{\mu\nu} D_{\mu\nu} (H_{\mu\nu}^{\text{core}} + F_{\mu\nu})$$
$$E_{\text{SCF}} = E_{\text{elec}} + E_{\text{nuc}}$$

e. Convergence Check

$$\Delta E = |E^{(n)} - E^{(n-1)}| < \epsilon \quad \text{and} \quad \Delta D = \|D^{(n)} - D^{(n-1)}\| < \delta$$

If not converged, repeat the loop.

Additional Notes

- For unrestricted Hartree-Fock (UHF), separate Fock and density matrices are built for α and β spins.
- DIIS (Direct Inversion of Iterative Subspace) is often used to speed up convergence.

Conclusion

The SCF procedure is a foundational technique in computational chemistry, allowing practical quantum-mechanical calculations for molecules using the Hartree-Fock approximation. It transforms the many-electron problem into a set of matrix operations that can be efficiently solved and iterated.