A Simple Hartree-Fock Self-Consistent Field Algorithm

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This document outlines the basic steps of a Hartree-Fock self-consistent field (SCF) program. The input integrals (overlap, kinetic and potential energy, and electron repulsion) are provided in external files, which are produced by the PSI3 programs. Additional details and theoretical background can be found in chapter 3 of *Modern Electronic Structure Theory*, by A. Szabo and N. S. Ostlund, 1st edition, revised, 1989, Macmilan, New York.

I. Integral Preprocessing

1. Read the nuclear repulsion energy (E_{nuc}) from the file `enuc.dat`.

2. Read the overlap integrals, $\mathbf{S}$, from the file `s.dat`:

$$S_{\mu\nu} \equiv \int \phi_\mu(\mathbf{r})\phi_\nu(\mathbf{r})d\mathbf{r},$$

   where ϕ_ρ denotes the ρ-th contracted (real) Gaussian-type orbital in the basis set and $\mathbf{r}$ the spatial coordinates of the electron.

3. Read the one-electron kinetic energy integrals, $\mathbf{T}$, from the file `t.dat`:

$$T_{\mu\nu} \equiv \int \phi_\mu(\mathbf{r})\left(-\frac{1}{2}\nabla^2_{\mathbf{r}}\right)\phi_\nu(\mathbf{r})d\mathbf{r}$$

4. Read the one-electron nuclear attraction integrals, $\mathbf{V}$, from the file `v.dat`:

$$V_{\mu\nu} \equiv \int \phi_\mu(\mathbf{r})\left(-\sum_A^N \frac{Z}{r_A}\right)\phi_\nu(\mathbf{r})d\mathbf{r},$$

   where r_A is the distance of the electron from nucleus A with atomic number Z.

5. Form the core Hamiltonian matrix, $\mathbf{H}$,

$$H^{\text{core}}_{\mu\nu} = T_{\mu\nu} + V_{\mu\nu}.$$

6. Read the two-electron repulsion integrals, $(\mu\nu|\lambda\sigma)$, from the file `eriout.dat`. Note that the two-electron integrals in this file are provided in Mulliken notation such that:

$$(\mu\nu|\lambda\sigma) \equiv \int \phi_\mu(\mathbf{r}_1)\phi_\nu(\mathbf{r}_1)r_{12}^{-1}\phi_\lambda(\mathbf{r}_2)\phi_\sigma(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2.$$

   These integrals obey the eight-fold permutational symmetry relationships:

$$(\mu\nu|\lambda\sigma) = (\nu\mu|\lambda\sigma) = (\mu\nu|\sigma\lambda) = (\nu\mu|\sigma\lambda) = (\lambda\sigma|\mu\nu) = (\sigma\lambda|\mu\nu) = (\lambda\sigma|\nu\mu) = (\sigma\lambda|\nu\mu),$$

and only the permutationally unique integrals are provided in the file with the restriction that, for each integral, the following relationships hold:

$$\mu \geq \nu, \quad \lambda \geq \sigma, \quad \text{and} \quad \mu\nu \geq \lambda\sigma,$$

where

$$\mu\nu \equiv \mu(\mu+1)/2 + \nu \quad \text{and} \quad \lambda\sigma \equiv \lambda(\lambda+1)/2 + \sigma.$$

Note that the two-electron integrals may be stored efficiently in a one-dimensional array and the above relationships used to map between given μ, ν, λ, and σ indices and a compound index defined as:

$$\mu\nu\lambda\sigma \equiv \mu\nu(\mu\nu+1)/2 + \lambda\sigma.$$

II. Orthogonalization of the Basis Set: The $S^{-1/2}$ Matrix

1. Diagonalize the overlap matrix, S,

$$SL_S = L_S\Lambda_S,$$

where L_S is the matrix of eigenvectors and Λ_S is a diagonal matrix containing the corresponding eigenvalues. Note that

$$L_S\tilde{L}_S = 1,$$

where the ˜ denotes transposition of the matrix.

2. Build the symmetric orthogonalization matrix, $S^{-1/2}$, defined as

$$S^{-1/2} \equiv L_S\Lambda^{-1/2}\tilde{L}_S$$

III. The Initial (Guess) Density Matrix

1. Form an initial Fock matrix, F'_0, in the orthonormal basis using the core Hamiltonian:

$$F'_0 \equiv \tilde{S}^{-1/2}H^{\text{core}}S^{-1/2}$$

2. Diagonalize F'_0, such that

$$F'_0C'_0 = C'_0\varepsilon_0$$

3. Transform the resulting eigenvectors into the original (non-orthonormal) basis,

$$C_0 = S^{-1/2}C'_0$$

4. Construct the initial-guess density matrix from C_0:

$$D^0_{\mu\nu} = \sum_m^{\text{occ.}} (C_0)^m_\mu (C_0)^m_\nu,$$

where m indexes columns of C_0 and the summation includes only the occupied (spatial) molecular orbitals (MOs).

5. Compute the electronic and total (Born-Oppenheimer) energies:

$$E_{\text{elec}}^0 = \sum_{\mu\nu}^{\text{AO}} D_{\mu\nu}^0 \left(H_{\mu\nu}^{\text{core}} + F_{\mu\nu} \right)$$

$$E_{\text{total}}^0 = E_{\text{elec}}^0 + E_{\text{nuc}},$$

where 0 denotes the initial SCF energy.

IV. The Self-Consistent Field Iteration

1. For a new Fock matrix, $\mathbf{F}$, that includes the two-electron integral contributions,

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

where the double summation runs over all the basis functions.

2. Transform the new Fock matrix to the orthonormal basis:

$$\mathbf{F}' \equiv \tilde{\mathbf{S}}^{-1/2} \mathbf{F} \mathbf{S}^{-1/2}.$$

3. Diagonalize the transformed Fock matrix:

$$\mathbf{F}'\mathbf{C}' = \mathbf{C}'\varepsilon.$$

4. Transform the resulting eigenvectors into the original (non-orthonormal) basis,

$$\mathbf{C} = \mathbf{S}^{-1/2}\mathbf{C}'.$$

5. Construct the new density matrix from $\mathbf{C}$:

$$D_{\mu\nu}^i = \sum_m^{\text{occ.}} (\mathbf{C})_\mu^m (\mathbf{C})_\nu^m.$$

where i denotes the current iteration density.

6. Compute the new electronic and total (Born-Oppenheimer) energies:

$$E_{\text{elec}}^i = \sum_{\mu\nu}^{\text{AO}} D_{\mu\nu}^i \left(H_{\mu\nu}^{\text{core}} + F_{\mu\nu} \right)$$

$$E_{\text{total}}^i = E_{\text{elec}}^i + E_{\text{nuc}},$$

where i denotes the SCF energy for the i-th iteration.

7. Test convergence of the density matrix and the electronic energy:

$$\text{rms}_D = \left[\sum_{\mu\nu}^{\text{AO}} \left(D_{\mu\nu}^i - D_{\mu\nu}^{i-1} \right)^2 \right]^{1/2} < \delta_1$$

$$\Delta E = E_{\text{elec}}^i - E_{\text{elec}}^{i-1} < \delta_2$$

If the root-mean-square (rms) difference in the densities and/or the change in the electronic energy does not fall below the chosen thresholds, δ_1 and δ_2, return to step 1 of this section.