

# An Introduction to SCF Theory

## Part II

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## Suggested procedure for an SCF program

### A. Preliminary Processing

- 1) Read in nuclear repulsion energy ( $E_{nuc}$ ).
- 2) Read in overlap integrals (S).
- 3) Read in kinetic energy integrals (T).
- 4) Read in potential energy integrals (V).
- 5) Form one electron integral matrix (H).

$$H_{\mu\nu} = T_{\mu\nu} + V_{\mu\nu} \quad (1)$$

- 6) Read in two-electron repulsion integrals ( $\mu\nu|\rho\sigma$ ).

**Note:**

$$\begin{aligned} (12|34) &= (12|43) = (21|34) = (21|43) = (34|12) = (34|21) = (43|12) \\ &= (43|21) \end{aligned} \quad (2)$$

$$\mu \geq \nu, \rho \geq \sigma, \text{ and } \mu\nu \geq \rho\sigma \quad (3)$$

$$\mu\nu = \mu * (\mu - 1) / 2 + \nu \quad (4)$$

$$\rho\sigma = \rho * (\rho - 1) / 2 + \sigma \quad (5)$$

$$\mu\nu\rho\sigma = \mu\nu * (\mu\nu - 1) / 2 + \rho\sigma \quad (6)$$

## B. Construction of the $S^{-1/2}$ Matrix

1) Diagonalize the S Matrix.

$$S L_s = L_s \Lambda_s \quad (7)$$

$$L_s \tilde{L}_s = L_s L_s^{-1} = 1 \quad (8)$$

2) Form the  $S^{-1/2}$  matrix.

$$S^{-1/2} = L_s \Lambda_s^{-1/2} \tilde{L}_s \quad (9)$$

### C. Construction of an Initial Density Matrix

1) Form an initial (transformed)  $F_o^\tau$  matrix using the H matrix.

$$F_o^\tau = \tilde{S}^{-1/2} H S^{-1/2} \quad (10)$$

2) Diagonalize the  $F_o^\tau$  matrix using a standard eigenvalue subroutine.

$$F_o^\tau C_o^\tau = C_o^\tau \epsilon \quad (11)$$

$$C_o^\tau \tilde{C}_o^\tau = C_o^\tau C_o^{\tau-1} = 1 \quad (12)$$

3) Form the SCF eigenvector matrix.

$$C = S^{-1/2} C_o^\tau \quad (13)$$

4) Form the first density matrix (D).

$$D_{\mu\nu} = \sum_m^{d.o.} C_\mu^m C_\nu^m \quad (14)$$

## D. The SCF Iteration

1) Form the new Fock matrix (**F**) including two-electron integrals.

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\rho\sigma}^{AO} D_{\rho\sigma} \left\{ 2(\mu\nu|\rho\sigma) - (\mu\rho|\nu\sigma) \right\} \quad (15)$$

2) Calculate the electronic and total energies.

$$E_{elec} = \sum_{\mu\nu}^{AO} D_{\mu\nu} (H_{\mu\nu} + F_{\mu\nu}) \quad (16)$$

$$E_{total} = E_{elec} + E_{nuc} \quad (17)$$

3) Transform the Fock matrix.

$$F^\tau = \tilde{S}^{-1/2} F S^{-1/2} \quad (18)$$

4) Diagonalize the Fock matrix.

$$F^\tau C^\tau = C^\tau \epsilon \quad (19)$$

5) Construct the new SCF eigenvector matrix.

$$C = S^{-1/2} C^\tau \quad (20)$$

6) Form the new density matrix.

$$D_{\mu\nu} = \sum_m^{d.o.} C_\mu^m C_\nu^m \quad (21)$$

7) Test convergency of density matrix and energy.

(i) RMS of density matrix elements :

$$rms = \left[ \sum_{\mu\nu}^{AO} (D_{\mu\nu}^n - D_{\mu\nu}^{n-1})^2 \right]^{1/2} < \delta_1 \quad (22)$$

(ii) Energy difference :

$$\Delta E = E_{SCF}^n - E_{SCF}^{n-1} < \delta_2 \quad (23)$$

8) If SCF is not attained go back to step D-1.