# An Introduction to SCF Theory

# Part II

Center for Computational
Quantum Chemistry
School of Chemical Sciences
The University of Georgia
Athens, Georgia 30602

Spring, 2008

**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).**

$$H_{\mu\nu} \quad = \quad T_{\mu\nu} \; + \; V_{\mu\nu} \tag{1}$$

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

**Note:**

$$(12|34) = (12|43) = (21|34) = (21|43) = (34|12) = (34|21) = (43|12) = (\mathbf{43}|\mathbf{21}) \tag{2}$$

$$\mu \; \geq \; \nu \; , \; \rho \; \geq \; \sigma \; , \; and \; \mu\nu \; \geq \; \rho\sigma \tag{3}$$

$$\mu\nu \quad = \quad \mu * (\mu - 1)/2 \; + \; \nu \tag{4}$$

$$\rho\sigma \quad = \quad \rho * (\rho - 1)/2 \; + \; \sigma \tag{5}$$

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

**B. Construction of the $\mathbf{S^{-1/2}}$ Matrix**

**1) Diagonalize the S Matrix.**

$$S\ L_s \quad = \quad L_s\ \Lambda_s \tag{7}$$

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

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

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

### C. Construction of an Initial Density Matrix

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

$$F_o^\tau \;=\; \tilde{S}^{-1/2}\; H\; S^{-1/2} \tag{10}$$

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

$$F_o^\tau\; C_o^\tau \;=\; C_o^\tau\; \epsilon \tag{11}$$

$$C_o^\tau\; \tilde{C}_o^\tau \;=\; C_o^\tau\; C_o^{\tau\,-1} \;=\; 1 \tag{12}$$

**3) Form the SCF eigenvector matrix.**

$$C \;=\; S^{-1/2}\; C_o^\tau \tag{13}$$

**4) Form the first density matrix (D).**

$$D_{\mu\nu} \;=\; \sum_{m}^{d.o.}\; C_\mu^m C_\nu^m \tag{14}$$

## D. The SCF Iteration

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

$$F_{\mu\nu} \;=\; H_{\mu\nu} \;+\; \sum_{\rho\sigma}^{AO} D_{\rho\sigma}\Big\{2(\mu\nu|\rho\sigma) \;-\; (\mu\rho|\nu\sigma)\Big\} \tag{15}$$

**2) Calculate the electronic and total energies.**

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

$$E_{total} = E_{elec} + E_{nuc} \tag{17}$$

**3) Transform the Fock matrix.**

$$F^{\tau} \;=\; \tilde{S}^{-1/2}\; F\; S^{-1/2} \tag{18}$$

**4) Diagonalize the Fock matrix.**

$$F^{\tau}\; C^{\tau} \;=\; C^{\tau}\; \epsilon \tag{19}$$

**5) Construct the new SCF eigenvector matrix.**

$$C \;=\; S^{-1/2}\; C^{\tau} \tag{20}$$

**6) Form the new density matrix.**

$$D_{\mu\nu} \;=\; \sum_{m}^{d.o.} C_{\mu}^{m} C_{\nu}^{m} \tag{21}$$

**7) Test convergency of density matrix and energy.**

(*i*) **RMS of density matrix elements :**

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

(*ii*) **Energy difference :**

$$\Delta E \;=\; E_{SCF}^{n} \;-\; E_{SCF}^{n-1} \;<\; \delta_2 \tag{23}$$

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