ROHF

Let ϕ_d, ϕ_s, and ϕ_v be column vectors of doubly occupied, singly occupied, and virtual orbitals. Each of these spatial functions corresponds to two spin-orbital vectors, $\phi_x\alpha$ and $\phi_x\beta$, and the SODS-ROHF effective Fock operator is given (in the Guest-Saunders approach) by the following

$$\hat{f}_{\text{eff}} \equiv \begin{pmatrix} \hat{1}_d & \hat{1}_s & \hat{1}_v \end{pmatrix} \begin{pmatrix} \hat{f}_{\text{avg}} & \hat{f}_\beta & \hat{f}_{\text{avg}} \\ \hat{f}_\beta & \hat{f}_{\text{avg}} & \hat{f}_\alpha \\ \hat{f}_{\text{avg}} & \hat{f}_\alpha & \hat{f}_{\text{avg}} \end{pmatrix} \begin{pmatrix} \hat{1}_d \\ \hat{1}_s \\ \hat{1}_v \end{pmatrix} \qquad \hat{f}_{\text{avg}} \equiv \tfrac{1}{2}(\hat{f}_\alpha + \hat{f}_\beta) \qquad \hat{1}_x \equiv |\psi_x\rangle\langle\psi_x| \qquad (1)$$

where $\hat{f}_\alpha$ and $\hat{f}_\beta$ are the usual Fock operators, defined in terms of $\hat{f}_{\text{eff}}$'s self-consistent densities.

Start with the canonical Hartree-Fock equation

$$\hat{f}_{\text{eff}}\phi_p = \epsilon_p\phi_p \qquad\qquad \hat{f}_{\text{eff}} = \sum_{x,y} \hat{1}_x \, \hat{f}_{\text{eff}}^{x,y} \, \hat{1}_y \qquad (2)$$

and expand it in the AO basis.

$$\langle\chi|\hat{f}_{\text{eff}}|\chi\rangle\mathbf{c}_p = \epsilon_p\langle\chi|\chi\rangle\mathbf{c}_p \qquad\qquad \hat{1}_x = |\phi_x\rangle\langle\phi_x| = |\chi\rangle\mathbf{C}_x\mathbf{C}_x^\dagger\langle\chi| \qquad (3)$$

Yields the following

$$\langle\chi|\hat{f}_{\text{eff}}|\chi\rangle = \sum_{x,y}\mathbf{P}_x^\dagger\langle\chi|\hat{f}_{\text{eff}}^{x,y}|\chi\rangle\mathbf{P}_y \qquad\qquad \mathbf{P}_x \equiv \mathbf{C}_x\mathbf{C}_x^\dagger\langle\chi|\chi\rangle \qquad (4)$$

designating the single occupations as alpha spins, we have the following relationships

$$\mathbf{P}_d = \mathbf{D}_\beta\mathbf{S} \qquad \mathbf{P}_{s+d} = \mathbf{D}_\alpha\mathbf{S} \qquad \hat{1}_s = \hat{1} - \hat{1}_d \qquad \hat{1}_v = \hat{1} - \hat{1}_{s+d} \qquad (5)$$

where $\mathbf{D}_\beta = \mathbf{C}_{o_\beta}\mathbf{C}_{o_\beta}^\dagger$ and $\mathbf{D}_\alpha = \mathbf{C}_{o_\alpha}\mathbf{C}_{o_\alpha}^\dagger$ are the UHF density matrices. This allows us to express the AO-basis pseudo-projection operators as follows.

$$\mathbf{P}_d = \mathbf{D}_\beta\mathbf{S} \qquad\qquad \mathbf{P}_s = (\mathbf{D}_\alpha - \mathbf{D}_\beta)\mathbf{S} \qquad\qquad \mathbf{P}_v = \mathbf{1} - \mathbf{D}_\alpha\mathbf{S} \qquad (6)$$

The final expression for the effective Fock matrix in terms of UHF Fock matrices is as follows.

$$\mathbf{F}_{\text{eff}} = \tfrac{1}{2}\sum_{\substack{x,y\in\{d,v\}\\x=y=s}}\mathbf{P}_x^\dagger(\mathbf{F}_\alpha + \mathbf{F}_\beta)\mathbf{P}_y + \sum_{x\neq y\in\{d,s\}}\mathbf{P}_x\mathbf{F}_\beta\mathbf{P}_y + \sum_{x\neq y\in\{s,v\}}\mathbf{P}_x\mathbf{F}_\alpha\mathbf{P}_y \qquad (7)$$

Apart from replacing the two UHF Fock matrices with this single effective Fock matrix, the algorithm for solving ROHF is the same. The residual (orbital gradient) condition is given by

$$\mathbf{R} = \mathbf{P}_s^\dagger\mathbf{F}_\beta\mathbf{P}_d + \tfrac{1}{2}\mathbf{P}_v^\dagger(\mathbf{F}_\alpha + \mathbf{F}_\beta)\mathbf{P}_d + \mathbf{P}_v^\dagger\mathbf{F}_\alpha\mathbf{P}_s \qquad (8)$$

$$- \mathbf{P}_d^\dagger\mathbf{F}_\beta\mathbf{P}_s - \tfrac{1}{2}\mathbf{P}_d^\dagger(\mathbf{F}_\alpha + \mathbf{F}_\beta)\mathbf{P}_v - \mathbf{P}_s^\dagger\mathbf{F}_\alpha\mathbf{P}_v \overset{!}{=} 0 \qquad (9)$$

which corresponds to the requirement that the off-diagonal blocks of $\mathbf{F}_{\text{eff}}$ vanish. This is analogous to the UHF residual condition.

$$\mathbf{R}_\alpha = \mathbf{P}_{v_\alpha}^\dagger\mathbf{F}_\alpha\mathbf{P}_{o_\alpha} - \mathbf{P}_{o_\alpha}^\dagger\mathbf{F}_\alpha\mathbf{P}_{v_\alpha} = \mathbf{F}_\alpha\mathbf{D}_\alpha\mathbf{S} - \mathbf{S}\mathbf{D}_\alpha\mathbf{F}_\alpha \overset{!}{=} 0 \qquad (10)$$