ROHF

Let $\boldsymbol{\phi}_\mathrm{d}$, $\boldsymbol{\phi}_\mathrm{s}$, and $\boldsymbol{\phi}_\mathrm{v}$ be row vectors of doubly occupied, singly occupied, and virtual orbitals. Each of these spatial functions corresponds to two spin-orbital vectors, $\boldsymbol{\phi}_\mathrm{x}\alpha$ and $\boldsymbol{\phi}_\mathrm{x}\beta$, and the SODS-ROHF effective Fock operator is given (in the Guest-Saunders approach) by the following

$$\hat{f}_\mathrm{eff} \equiv \begin{pmatrix} \hat{1}_\mathrm{d} & \hat{1}_\mathrm{s} & \hat{1}_\mathrm{v} \end{pmatrix} \begin{pmatrix} \hat{f}_\mathrm{avg} & \hat{f}_\beta & \hat{f}_\mathrm{avg} \\ \hat{f}_\beta & \hat{f}_\mathrm{avg} & \hat{f}_\alpha \\ \hat{f}_\mathrm{avg} & \hat{f}_\alpha & \hat{f}_\mathrm{avg} \end{pmatrix} \begin{pmatrix} \hat{1}_\mathrm{d} \\ \hat{1}_\mathrm{s} \\ \hat{1}_\mathrm{v} \end{pmatrix} \qquad \hat{f}_\mathrm{avg} \equiv \tfrac{1}{2}(\hat{f}_\alpha + \hat{f}_\beta) \qquad \hat{1}_\mathrm{x} \equiv |\boldsymbol{\psi}_\mathrm{x}\rangle\langle\boldsymbol{\psi}_\mathrm{x}| \tag{1}$$

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

Starting with the canonical Hartree-Fock equation

$$\hat{f}_\mathrm{eff}\phi_p = \epsilon_p \phi_p \qquad \hat{f}_\mathrm{eff} = \sum_{\mathrm{x,y}} \hat{1}_\mathrm{x}\, \hat{f}_\mathrm{eff}^{\mathrm{x,y}}\, \hat{1}_\mathrm{y} \tag{2}$$

and expanding it in the AO basis

$$\langle\boldsymbol{\chi}|\hat{f}_\mathrm{eff}|\boldsymbol{\chi}\rangle\mathbf{c}_p = \epsilon_p\langle\boldsymbol{\chi}|\boldsymbol{\chi}\rangle\mathbf{c}_p \qquad \hat{1}_\mathrm{x} = |\boldsymbol{\phi}_\mathrm{x}\rangle\langle\boldsymbol{\phi}_\mathrm{x}| = |\boldsymbol{\chi}\rangle\mathbf{C}_\mathrm{x}\mathbf{C}_\mathrm{x}^\dagger\langle\boldsymbol{\chi}| \tag{3}$$

yields the following

$$\langle\boldsymbol{\chi}|\hat{f}_\mathrm{eff}|\boldsymbol{\chi}\rangle = \sum_{\mathrm{x,y}} \mathbf{P}_\mathrm{x}^\dagger\langle\boldsymbol{\chi}|\hat{f}_\mathrm{eff}^{\mathrm{x,y}}|\boldsymbol{\chi}\rangle\mathbf{P}_\mathrm{y} \qquad \mathbf{P}_\mathrm{x} \equiv \mathbf{C}_\mathrm{x}\mathbf{C}_\mathrm{x}^\dagger\langle\boldsymbol{\chi}|\boldsymbol{\chi}\rangle \tag{4}$$

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

$$\mathbf{P}_\mathrm{d} = \mathbf{D}_\beta\mathbf{S} \qquad \mathbf{P}_\mathrm{s+d} = \mathbf{D}_\alpha\mathbf{S} \qquad \hat{1}_\mathrm{s} = \hat{1} - \hat{1}_\mathrm{d} \qquad \hat{1}_\mathrm{v} = \hat{1} - \hat{1}_\mathrm{s+d} \tag{5}$$

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

$$\mathbf{P}_\mathrm{d} = \mathbf{D}_\beta\mathbf{S} \qquad \mathbf{P}_\mathrm{s} = (\mathbf{D}_\alpha - \mathbf{D}_\beta)\mathbf{S} \qquad \mathbf{P}_\mathrm{v} = \mathbf{1} - \mathbf{D}_\alpha\mathbf{S} \tag{6}$$

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

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

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

$$\mathbf{R} = \mathbf{P}_\mathrm{s}^\dagger\mathbf{F}_\beta\mathbf{P}_\mathrm{d} + \tfrac{1}{2}\mathbf{P}_\mathrm{v}^\dagger(\mathbf{F}_\alpha + \mathbf{F}_\beta)\mathbf{P}_\mathrm{d} + \mathbf{P}_\mathrm{v}^\dagger\mathbf{F}_\alpha\mathbf{P}_\mathrm{s} \tag{8}$$

$$- \mathbf{P}_\mathrm{d}^\dagger\mathbf{F}_\beta\mathbf{P}_\mathrm{s} - \tfrac{1}{2}\mathbf{P}_\mathrm{d}^\dagger(\mathbf{F}_\alpha + \mathbf{F}_\beta)\mathbf{P}_\mathrm{v} - \mathbf{P}_\mathrm{s}^\dagger\mathbf{F}_\alpha\mathbf{P}_\mathrm{v} \overset{!}{=} \mathbf{0} \tag{9}$$

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

$$\mathbf{R}_\alpha = \mathbf{P}_{\mathrm{v}_\alpha}^\dagger\mathbf{F}_\alpha\mathbf{P}_{\mathrm{o}_\alpha} - \mathbf{P}_{\mathrm{o}_\alpha}^\dagger\mathbf{F}_\alpha\mathbf{P}_{\mathrm{v}_\alpha} = \mathbf{F}_\alpha\mathbf{D}_\alpha\mathbf{S} - \mathbf{S}\mathbf{D}_\alpha\mathbf{F}_\alpha \overset{!}{=} \mathbf{0} \tag{10}$$