I.   UHF NATURAL ORBITALS

The position space representation of the electron density operator is given by

$$\hat{\rho}(\mathbf{r}) = \sum_{i=1}^{n_e} \delta(\mathbf{r} - \mathbf{r}_i) \tag{1}$$

which adds up the probability for each electron to inhabit position $\mathbf{r}$. The density of a single determinant is

$$\rho(\mathbf{r}) = \langle\Phi|\hat{\rho}(\mathbf{r})|\Phi\rangle = n\langle\Phi|\delta(\mathbf{r} - \mathbf{r}_1)|\Phi\rangle = \sum_{i=1}^{n_e} \langle\psi_i(\mathbf{r}_1)|\delta(\mathbf{r} - \mathbf{r}_1)|\psi_i(\mathbf{r}_1)\rangle_{\mathbf{r}_1}$$
$$= \sum_{i_\alpha=1}^{n_\alpha} \phi_{i_\alpha}^{\alpha*}(\mathbf{r})\phi_{i_\alpha}^{\alpha}(\mathbf{r}) + \sum_{i_\beta=1}^{n_\beta} \phi_{i_\beta}^{\beta*}(\mathbf{r})\phi_{i_\beta}^{\beta}(\mathbf{r}) \tag{2}$$

which can be identified as the trace of the spatial one-particle density matrix

$$\operatorname*{tr}_{\mathbf{r}'\to\mathbf{r}} d(\mathbf{r},\mathbf{r}') = \int d^3\mathbf{r}'\,\delta(\mathbf{r}-\mathbf{r}')d(\mathbf{r},\mathbf{r}') = \rho(\mathbf{r}) \quad d(\mathbf{r},\mathbf{r}') \equiv \sum_{i_\alpha=1}^{n_\alpha} \phi_{i_\alpha}^{\alpha*}(\mathbf{r}')\phi_{i_\alpha}^{\alpha}(\mathbf{r}) + \sum_{i_\beta=1}^{n_\beta} \phi_{i_\beta}^{\beta*}(\mathbf{r}')\phi_{i_\beta}^{\beta}(\mathbf{r}) \tag{3}$$

From the position-space representation of the operator $d(\mathbf{r},\mathbf{r}') = \langle\mathbf{r}|\hat{d}|\mathbf{r}'\rangle$, we can back out an expression for the abstract density operator $\hat{d}$ as follows.

$$d(\mathbf{r},\mathbf{r}') = \sum_{i_\alpha=1}^{n_\alpha} \phi_{i_\alpha}^{\alpha*}(\mathbf{r}')\phi_{i_\alpha}^{\alpha}(\mathbf{r}) + \sum_{i_\beta=1}^{n_\beta} \phi_{i_\beta}^{\beta*}(\mathbf{r}')\phi_{i_\beta}^{\beta}(\mathbf{r}) = \langle\mathbf{r}| \left(\sum_{i_\alpha=1}^{n_\alpha} |\phi_{i_\alpha}^{\alpha}\rangle\langle\phi_{i_\alpha}^{\alpha}| + \sum_{i_\beta=1}^{n_\beta} |\phi_{i_\beta}^{\beta}\rangle\langle\phi_{i_\beta}^{\beta}| \right) |\mathbf{r}'\rangle$$
$$\implies \hat{d} = \sum_{i_\alpha=1}^{n_\alpha} |\phi_{i_\alpha}^{\alpha}\rangle\langle\phi_{i_\alpha}^{\alpha}| + \sum_{i_\beta=1}^{n_\beta} |\phi_{i_\beta}^{\beta}\rangle\langle\phi_{i_\beta}^{\beta}| \tag{4}$$

This is the spatial one-particle density operator of the determinant $\Phi = \det(\psi_1 \cdots \psi_{n_e})$. Expanding the molecular orbitals in terms of atomic orbital basis functions, $\phi_{p_\omega}^\omega = \sum_\mu \chi_\mu C_{\mu p}^\omega$ where $\omega \in \{\alpha, \beta\}$, the spatial density operator of Φ can be expressed in terms of the Hartree-Fock density matrices $D_{\mu\nu}^\omega = \sum_{i_\omega=1}^{n_\omega} C_{\mu i_\omega}^\omega C_{\nu i_\omega}^\omega$ as follows

$$\hat{d} = \sum_{i_\alpha=1}^{n_\alpha} \sum_{\mu\nu} C_{\mu i_\alpha}^{\alpha*} C_{\nu i_\alpha}^{\alpha} |\chi_\mu\rangle\langle\chi_\nu| + \sum_{i_\beta=1}^{n_\beta} \sum_{\mu\nu} C_{\mu i_\beta}^{\beta*} C_{\nu i_\beta}^{\beta} |\chi_\mu\rangle\langle\chi_\nu| = \sum_{\mu\nu} \left(D_{\mu\nu}^\alpha + D_{\mu\nu}^\beta\right) |\chi_\mu\rangle\langle\chi_\nu| \tag{5}$$

In general, the spatial natural orbitals of a wavefunction Ψ are the eigenfunctions of its spatial one-particle density operator

$$\hat{d}|\phi_p^{no}\rangle = n_p^{no}|\phi_p^{no}\rangle \tag{6}$$

Expanding the natural orbitals in terms of AO basis functions $\phi_p^{no} = \sum_\nu \chi_\nu C_{\nu p}^{no}$, projecting by $\langle\chi_\mu|$, and expanding $\hat{d}$ according to eq 5, the eigenvalue equation becomes

$$\sum_\nu \sum_{\rho\sigma} \langle\chi_\mu|\chi_\rho\rangle \left(D_{\rho\sigma}^\alpha + D_{\rho\sigma}^\beta\right) \langle\chi_\sigma|\chi_\nu\rangle C_{\nu p}^{no} = n_p^{no} \sum_\nu \langle\chi_\mu|\chi_\nu\rangle C_{\nu p}^{no} \tag{7}$$

which can be expressed in matrix notation as follows

$$\mathbf{SDSC}^{\mathrm{no}} = \mathbf{SC}^{\mathrm{no}}\tilde{\mathbf{D}}^{\mathrm{no}}$$
$$\mathbf{D} = \mathbf{D}^{\alpha} + \mathbf{D}^{\beta} = [D_{\mu\nu}^{\alpha} + D_{\mu\nu}^{\beta}]$$
$$\mathbf{C}^{\mathrm{no}} = [C_{\mu p}^{\mathrm{no}}]$$
$$\tilde{\mathbf{D}}^{\mathrm{no}} = [n_p^{\mathrm{no}}\delta_{pq}]$$

$$(8)$$

Multiplying both sides by the orthogonalizer $\mathbf{X} \equiv \mathbf{S}^{-\frac{1}{2}}$ reduces this equation to a standard symmetric matrix diagonalization

$$\overline{\mathbf{D}}\,\overline{\mathbf{C}}^{\mathrm{no}} = \overline{\mathbf{C}}^{\mathrm{no}}\tilde{\mathbf{D}}^{\mathrm{no}}$$
$$\overline{\mathbf{D}} = \mathbf{S}^{\frac{1}{2}}\mathbf{DS}^{\frac{1}{2}}$$
$$\overline{\mathbf{C}}^{\mathrm{no}} = \mathbf{S}^{\frac{1}{2}}\mathbf{C}^{\mathrm{no}}$$

$$(9)$$

II. NOTAS

Con un poco de calma me falta ver como transforma todo el operador de Fock para ver si hay que tocar algo en promolden.

Por otro lado creo que si eso proceso se hace separando lo cores podemos fijar la ocupacion de estos en 2.0 y luego hacer otra transformacion en las valencia y pasar de los virtuales, para esto habria que usar la base orbital MO en lugar de AO, esto se llama una semi-canonicalizacin y deja igualmente el operado de Fock diagonal, esto tengo que acabar de pensarlo mejor igual no tiene mucho sentido.