Extra Programming Project Theory
UHF Natural Orbitals

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

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

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

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

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

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

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.

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

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.

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

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

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

Expanding the natural orbitals in terms of AO basis functions $\phi_p^{\mathrm{no}} = \sum_\nu \chi_\nu C_{\nu p}^{\mathrm{no}}$, projecting by $\langle\chi_\mu|$, and expanding $\hat{d}$ according to eq 1, the eigenvalue equation becomes

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

which can be expressed in matrix notation as follows.

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

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

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