Unrestricted Hartree Fock - Pople-Nesbet Equations

UHF theory allows electrons of α and β spin to be individually described by different spatial functions. To solve this electronic structure problem analytically, the unrestricted molecular orbitals are expanded in a basis: $\{\phi_\mu|\ \mu= 1, 2,\ldots., K\}$.

$$\psi_a^\alpha = \sum_{\mu=1}^{K} \boldsymbol{C}_{\mu a}^{\alpha}\phi_\mu \quad with\ a = 1,2,\ldots,K$$

$$\psi_a^\beta = \sum_{\mu=1}^{K} \boldsymbol{C}_{\mu a}^{\beta}\phi_\mu \quad with\ a = 1,2,\ldots,K$$

The α and β charge densities are represented by the density matrices $\mathbf{P}^\alpha$ and $\mathbf{P}^\beta$ respectively. Likewise, it is possible to define a total density matrix $\boldsymbol{P}^{Total}$ and a spin density matrix $\boldsymbol{P}^{S}$. If the density matrices fulfill the relation: $\mathbf{P}^\alpha = \mathbf{P}^\beta = \frac{1}{2}\boldsymbol{P}^{Total}$, the RHF solution will be obtained. In order to generate unrestricted wave functions, proper initial densities with $\mathbf{P}^\alpha \neq \mathbf{P}^\beta$ should be used at the start of the SCF procedure. The set of expressions for the α and β Fock matrices are coupled to each other through the total density matrix, $\boldsymbol{F}^\alpha$ depends on $\mathbf{P}^\beta$ and $\boldsymbol{F}^\beta$ depends on $\mathbf{P}^\alpha$. The elements of the Fock matrices $\boldsymbol{F}^\alpha$ and $\boldsymbol{F}^\beta$ are derived below starting from matrix elements of the Fock operator in the basis $\{\phi_\mu\}$.

$$\boldsymbol{F}_{\mu\nu}^{\alpha} = \int d\boldsymbol{r}_1 \phi_\mu^*(1)\hat{f}^\alpha(1)\phi_\nu(1)$$

$$\boldsymbol{F}_{\mu\nu}^{\alpha} = \boldsymbol{H}_{\mu\nu}^{core} + \sum_{a}^{N^\alpha}[\left(\phi_\mu\phi_\nu\middle|\psi_a^\alpha\psi_a^\alpha\right) - (\phi_\mu\psi_a^\alpha|\psi_a^\alpha\phi_\nu)] + \sum_{a}^{N^\beta}\left(\phi_\mu\phi_\nu\middle|\psi_a^\alpha\psi_a^\alpha\right)$$

$$\boldsymbol{F}_{\mu\nu}^{\alpha} = \boldsymbol{H}_{\mu\nu}^{core} + \sum_{\lambda}\sum_{\sigma}\sum_{a}^{N^\alpha}\boldsymbol{C}_{\lambda a}^{\alpha}(\boldsymbol{C}_{\sigma a}^{\alpha})^*[(\mu\nu|\sigma\lambda) - (\mu\lambda|o\nu)] + \sum_{\lambda}\sum_{\sigma}\sum_{a}^{N^\beta}\boldsymbol{C}_{\lambda a}^{\beta}(\boldsymbol{C}_{\sigma a}^{\beta})^*(\mu\nu|\sigma\lambda)$$

$$\boldsymbol{F}_{\mu\nu}^{\alpha} = \boldsymbol{H}_{\mu\nu}^{core} + \sum_{\lambda}\sum_{\sigma}\boldsymbol{P}_{\lambda\sigma}^{\alpha}[(\mu\nu|\sigma\lambda) - (\mu\lambda|o\nu)] + \sum_{\lambda}\sum_{\sigma}\boldsymbol{P}_{\lambda\sigma}^{\beta}\,(\mu\nu|\sigma\lambda)$$

$$\boldsymbol{F}_{\mu\nu}^{\alpha} = \boldsymbol{H}_{\mu\nu}^{core} + \sum_{\lambda}\sum_{\sigma}\boldsymbol{P}_{\lambda\sigma}^{Total}\,(\mu\nu|\sigma\lambda) - \boldsymbol{P}_{\lambda\sigma}^{\alpha}(\mu\lambda|\sigma\nu)$$

For beta spin:

$$\boldsymbol{F}_{\mu\nu}^{\beta} = \int d\boldsymbol{r}_1 \phi_\mu^*(1)\hat{f}^\beta(1)\phi_\nu(1)$$

$$\boldsymbol{F}_{\mu\nu}^{\beta} = \boldsymbol{H}_{\mu\nu}^{core} + \sum_{a}^{N^\beta}[(\phi_\mu\phi_\nu\left|\psi_a^\beta\psi_a^\beta\right.) - (\phi_\mu\psi_a^\beta|\psi_a^\beta\phi_\nu)] + \sum_{a}^{N^\alpha}\left(\phi_\mu\phi_\nu\middle|\psi_a^\beta\psi_a^\beta\right)$$

$$\boldsymbol{F}_{\mu\nu}^{\beta} = \boldsymbol{H}_{\mu\nu}^{core} + \sum_{\lambda}\sum_{\sigma}\sum_{a}^{N^\beta}\boldsymbol{C}_{\lambda a}^{\beta}(\boldsymbol{C}_{\sigma a}^{\beta})^*[(\mu\nu|\sigma\lambda) - (\mu\lambda|o\nu)] + \sum_{\lambda}\sum_{\sigma}\sum_{a}^{N^\alpha}\boldsymbol{C}_{\lambda a}^{\alpha}(\boldsymbol{C}_{\sigma a}^{\alpha})^*(\mu\nu|\sigma\lambda)$$

$$\boldsymbol{F}_{\mu\nu}^{\beta} = \boldsymbol{H}_{\mu\nu}^{core} + \sum_{\lambda}\sum_{\sigma}\boldsymbol{P}_{\lambda\sigma}^{\beta}[(\mu\nu|\sigma\lambda) - (\mu\lambda|o\nu)] + \sum_{\lambda}\sum_{\sigma}\boldsymbol{P}_{\lambda\sigma}^{\alpha}\,(\mu\nu|\sigma\lambda)$$

$$\boldsymbol{F}_{\mu\nu}^{\beta} = \boldsymbol{H}_{\mu\nu}^{core} + \sum_{\lambda}\sum_{\sigma}\boldsymbol{P}_{\lambda\sigma}^{Total}\,(\mu\nu|\sigma\lambda) - \boldsymbol{P}_{\lambda\sigma}^{\beta}(\mu\lambda|o\nu)$$

Where is used: $\boldsymbol{P}^{Total} = \mathbf{P}^{\alpha} + \mathbf{P}^{\beta}$

The total electronic energy (without the nuclei-nuclei interaction) can be expressed as:

$$E_0 = \sum_{a}^{N^{\alpha}} \boldsymbol{h}_{aa}^{\alpha} + \sum_{a}^{N^{\beta}} \boldsymbol{h}_{aa}^{\beta} + \frac{1}{2}\sum_{a}^{N^{\alpha}}\sum_{b}^{N^{\alpha}} (\boldsymbol{J}_{ab}^{\alpha\alpha} - \boldsymbol{K}_{ab}^{\alpha\alpha}) + \frac{1}{2}\sum_{a}^{N^{\beta}}\sum_{b}^{N^{\beta}} (\boldsymbol{J}_{ab}^{\beta\beta} - \boldsymbol{K}_{ab}^{\beta\beta}) + \sum_{a}^{N^{\alpha}}\sum_{b}^{N^{\beta}} \boldsymbol{J}_{ab}^{\alpha\beta}$$

Alternatively, in terms of density matrices or matrix equation:

$$E_0 = \frac{1}{2}\sum_{\mu}\sum_{\nu} [\boldsymbol{P}_{\nu\mu}^{Total}\, \boldsymbol{H}_{\mu\nu}^{core} + \boldsymbol{P}_{\nu\mu}^{\alpha} \boldsymbol{F}_{\mu\nu}^{\alpha} + \boldsymbol{P}_{\nu\mu}^{\beta} \boldsymbol{F}_{\mu\nu}^{\beta}]$$

$$\begin{pmatrix} \boldsymbol{F}_{\alpha\alpha} & \boldsymbol{F}_{\alpha\beta} \\ \boldsymbol{F}_{\beta\alpha} & \boldsymbol{F}_{\beta\beta} \end{pmatrix} \begin{pmatrix} \boldsymbol{c}^{\alpha} \\ \boldsymbol{c}^{\beta} \end{pmatrix} = \epsilon \begin{pmatrix} \boldsymbol{c}^{\alpha} \\ \boldsymbol{c}^{\beta} \end{pmatrix} \; where \; \boldsymbol{F}_{\sigma\sigma'} = \delta \boldsymbol{h} + \boldsymbol{G}_{\sigma\sigma'}$$

References

1. Szabo, A; Ostlund, N. S. Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory, *McGraw-Hill Inc.*