Programming Project 3 Theory (Part 2)
The Roothaan-Hall equations and the Pople-Nesbet equations

Spin and spin-orbitals

A spin-orbital ψ can be decomposed as $\psi(\mathbf{r}, s) = \phi(\mathbf{r})\omega(s)$, where $\phi(\mathbf{r})$ is a spatial orbital and $\omega(s)$ is a spin function. Spin functions live in a two-dimensional space spanned by $\{\alpha(s), \beta(s)\}$, which are orthonormal eigenfunctions of one component of $\hat{\mathbf{S}}$, the spin angular momentum operator.

$$\hat{S}_z\alpha = +\frac{1}{2}\alpha \qquad \hat{S}_z\beta = -\frac{1}{2}\beta \qquad \langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 1 \qquad \langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle = 0 \tag{1}$$

The "spin-coordinate" s is either $+$ or $-$, identifying the component of $\omega(s)$ along $\alpha(s)$ and $\beta(s)$. You can think of it as the index of a coordinate vector in spin space

$$\begin{bmatrix}\omega(+)\\ \omega(-)\end{bmatrix} = \begin{bmatrix}\langle\alpha|\omega\rangle\\ \langle\beta|\omega\rangle\end{bmatrix}$$

so that $\alpha(+) = \beta(-) = 1$ and $\alpha(-) = \beta(+) = 0$. Using this spin coordinate, the inner product in spin space can be defined explicitly as $\langle\omega|\omega'\rangle = \sum_s \omega^*(s)\omega'(s)$. It is typical to refer to the inner product of spin functions as a "spin integration".

A complete set of one-electron functions (spin-orbitals) comes in α, β-pairs.

$$\psi_{2p-1}(\mathbf{r}, s) = \phi_{p_\alpha}(\mathbf{r})\alpha(s) \qquad \psi_{2p}(\mathbf{r}, s) = \phi_{p_\beta}(\mathbf{r})\beta(s) \tag{2}$$

The spatial components of these functions can be expanded in terms of a set of AO basis functions $\{\chi_\nu\}$ as

$$\phi_{p_\alpha} = \sum_\mu \chi_\mu C_{\mu p_\alpha} \qquad \phi_{p_\beta} = \sum_\mu \chi_\mu C_{\mu p_\beta} \tag{3}$$

which are atom-centered Gaussian functions (cc-pVDZ, STO-3G, etc.).

Spin-integration of the canonical Hartree-Fock equations

For a system with n_α spin-up and n_β spin-down electrons, the spin-orbital canonical Hartree-Fock equation takes the form

$$\hat{f}\psi_p = \epsilon_p\psi_p \qquad \hat{f} = \hat{h} + \sum_{i_\alpha}^{n_\alpha}(\hat{J}_{i_\alpha} - \hat{K}_{i_\alpha}) + \sum_{i_\beta}^{n_\beta}(\hat{J}_{i_\beta} - \hat{K}_{i_\beta})\ . \tag{4}$$

This equation can be expanded in the spin basis as

$$\begin{bmatrix}\langle\alpha|\hat{f}|\alpha\rangle & \langle\alpha|\hat{f}|\beta\rangle\\ \langle\beta|\hat{f}|\alpha\rangle & \langle\beta|\hat{f}|\beta\rangle\end{bmatrix}\begin{bmatrix}\langle\alpha|\psi_p\rangle\\ \langle\beta|\psi_p\rangle\end{bmatrix} = \epsilon_p\begin{bmatrix}\langle\alpha|\psi_p\rangle\\ \langle\beta|\psi_p\rangle\end{bmatrix}$$

where we are integrating only over the spin coordinate. The operators in $\hat{f}$ then become

$$\hat{h} \mapsto \begin{bmatrix}\langle\alpha|\hat{h}|\alpha\rangle & 0\\ 0 & \langle\beta|\hat{h}|\beta\rangle\end{bmatrix} \qquad \hat{J}_{i_\alpha} \mapsto \begin{bmatrix}\langle\alpha|\hat{J}_{i_\alpha}|\alpha\rangle & 0\\ 0 & \langle\beta|\hat{J}_{i_\alpha}|\beta\rangle\end{bmatrix} \qquad \hat{K}_{i_\alpha} \mapsto \begin{bmatrix}\langle\alpha|\hat{K}_{i_\alpha}|\alpha\rangle & 0\\ 0 & 0\end{bmatrix}$$

$$\hat{J}_{i_\beta} \mapsto \begin{bmatrix}\langle\alpha|\hat{J}_{i_\beta}|\alpha\rangle & 0\\ 0 & \langle\beta|\hat{J}_{i_\beta}|\beta\rangle\end{bmatrix} \qquad \hat{K}_{i_\beta} \mapsto \begin{bmatrix}0 & 0\\ 0 & \langle\beta|\hat{K}_{i_\beta}|\beta\rangle\end{bmatrix}$$

where the core and Coulomb operators can be evaluated simply using $\langle\omega|\hat{h}|\omega'\rangle = \hat{h}\langle\omega|\omega'\rangle$, since these operators do not act on spin coordinates. The exchange operator, however, does act on spin coordinates by its coordinate-swapping operation. Hence, for example,

$$\hat{K}_{i_\beta}(\mathbf{r})\alpha(s) = \langle\phi_{i_\beta}(\mathbf{r}')|\hat{g}(\mathbf{r},\mathbf{r}')|\cdot(\mathbf{r}')\rangle\langle\beta|\alpha\rangle\ \phi_{i_\beta}(\mathbf{r})\beta(s) = 0$$

where the $\cdot$ represents "fill in spatial function here". This shows why $\langle\alpha|\hat{K}_{i_\beta}|\alpha\rangle = \langle\beta|\hat{K}_{i_\beta}|\alpha\rangle = 0$. The remaining components can be derived in the same way.

Since all of the off-diagonal blocks in the spin basis vanish, we can separate equation 4 into two spin-integrated equations.

$$\hat{f}_\alpha\phi_{p_\alpha} = \epsilon_{p_\alpha}\phi_{p_\alpha} \qquad \hat{f}_\alpha = \hat{h} + \sum_{i_\alpha}^{n_\alpha}(\hat{J}_{i_\alpha} - \hat{K}_{i_\alpha}) + \sum_{i_\beta}^{n_\beta}\hat{J}_{i_\beta} \tag{5}$$

$$\hat{f}_\beta\phi_{p_\beta} = \epsilon_{p_\beta}\phi_{p_\beta} \qquad \hat{f}_\beta = \hat{h} + \sum_{i_\alpha}^{n_\alpha}\hat{J}_{i_\alpha} + \sum_{i_\beta}^{n_\beta}(\hat{J}_{i_\beta} - \hat{K}_{i_\beta}) \tag{6}$$

RHF: The Roothaan-Hall Equations

Assuming a closed-shell system with $n_\alpha = n_\beta = n/2$, we can impose the restriction that $\phi_{i_\alpha} = \phi_{i_\beta}$ for each pair of electrons. Then equations 5 and 6 collapse into a single expression.

$$\hat{f}_\mathrm{R}\phi_p = \epsilon_p\phi_p \qquad \hat{f}_\mathrm{R} = \hat{h} + \sum_{i}^{n/2}(2\hat{J}_i - \hat{K}_i)$$

where the R stands for "restricted". Expanding ϕ_p in the AO basis and projecting by χ_μ, we get the Roothaan-Hall equations

$$\sum_\nu\langle\chi_\mu|\hat{f}_\mathrm{R}|\chi_\nu\rangle C_{\nu p} = \sum_\nu\langle\chi_\mu|\chi_\nu\rangle C_{\mu p}\epsilon_p$$

which can be written in matrix notation as

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\epsilon} \qquad F_{\mu\nu} = \langle\chi_\mu|\hat{f}_\mathrm{R}|\chi_\nu\rangle \qquad S_{\mu\nu} = \langle\chi_\mu|\chi_\nu\rangle \qquad (\boldsymbol{\epsilon})_{pq} = \epsilon_p\delta_{pq}\ . \tag{7}$$

Note that if the AO basis contains m functions, then $\mathbf{C} = [C_{\mu p}]$ is an $m \times m$ matrix with each column vector containing the expansion coefficients for an orbital ϕ_p. Also, note that only the $n/2$ MOs of lowest energy (ϵ_p) will be "occupied" – the remaining virtual orbitals will not enter into the Coulomb and exchange parts of $\hat{f}_\mathrm{R}$. Expanding $\hat{f}_\mathrm{R}$ in its core, Coulomb, and exchange parts, we find

$$\begin{aligned} F_{\mu\nu} &= \langle\chi_\mu|\hat{h}|\chi_\nu\rangle + \sum_i^{n/2}(2\langle\chi_\mu\phi_i|\chi_\nu\phi_i\rangle - \langle\chi_\mu\phi_i|\phi_i\chi_\nu\rangle) \\ &= \langle\chi_\mu|\hat{h}|\chi_\nu\rangle + \sum_i^{n/2}\sum_{\rho\sigma}^{m} C^*_{\rho i}C_{\sigma i}(2\langle\chi_\mu\chi_\rho|\chi_\nu\chi_\sigma\rangle - \langle\chi_\mu\chi_\rho|\chi_\sigma\chi_\nu\rangle) \end{aligned}$$

which is conveniently given in terms of a "density matrix" $D_{\mu\nu}$.

$$F_{\mu\nu} = \langle\chi_\mu|\hat{h}|\chi_\nu\rangle + \sum_{\rho\sigma}^{m} D_{\rho\sigma}(2\langle\chi_\mu\chi_\rho|\chi_\nu\chi_\sigma\rangle - \langle\chi_\mu\chi_\rho|\chi_\sigma\chi_\nu\rangle) \qquad D_{\mu\nu} = \sum_i^{n/2} C^*_{\mu i}C_{\nu i} \tag{8}$$

Solving the Roothaan-Hall Equations

Equation 7 would look like an ordinary eigenvalue problem if $\mathbf{S}$ were an identity matrix. This would be the case if the AO basis were orthogonal. We can get around this problem by an algebraic trick: if we multiply both sides of equation 7 by $\mathbf{S}^{-\frac{1}{2}}$ and insert $\mathbf{I} = \mathbf{S}^{-\frac{1}{2}}\mathbf{S}^{\frac{1}{2}}$ between $\mathbf{F}$ and $\mathbf{C}$, we get

$$\tilde{\mathbf{F}}\tilde{\mathbf{C}} = \tilde{\mathbf{C}}\boldsymbol{\epsilon} \qquad \tilde{\mathbf{F}} = \mathbf{S}^{-\frac{1}{2}}\mathbf{F}\mathbf{S}^{-\frac{1}{2}} \qquad \tilde{\mathbf{C}} = \mathbf{S}^{\frac{1}{2}}\mathbf{C}\ . \tag{9}$$

This is equivalent to a transformation to an orthogonalized AO basis $\tilde{\chi}_\mu = \sum_\nu \chi_\nu (\mathbf{S}^{-\frac{1}{2}})_{\nu\mu}$ which satisfies $\langle\tilde{\chi}_\mu|\tilde{\chi}_\nu\rangle = \delta_{\mu\nu}$. After diagonalizing $\tilde{\mathbf{F}}$, the ordinary MO coefficient matrix can be recovered as $\mathbf{C} = \mathbf{S}^{-\frac{1}{2}}\tilde{\mathbf{C}}$.

Recall, however, that equation 9 is still not an ordinary eigenvalue problem because $\mathbf{F}$ depends on the MOs via the density matrix $\mathbf{D}$. The standard procedure for solving the Roothan-Hall equations is as follows:

1. Get integrals $\langle\chi_\mu|\chi_\nu\rangle, \langle\chi_\mu|\hat{h}|\chi_\nu\rangle, \langle\chi_\mu\chi_\nu|\chi_\rho\chi_\sigma\rangle$ and form orthogonalizer $\mathbf{S}^{-\frac{1}{2}}$
2. Guess $\mathbf{D} = \mathbf{0}$
3. Build $\mathbf{F}$ (equation 8)
4. Diagonalize $\tilde{\mathbf{F}} = \mathbf{S}^{-\frac{1}{2}}\mathbf{F}\mathbf{S}^{-\frac{1}{2}}$, giving $\tilde{\mathbf{C}}$ and $\boldsymbol{\epsilon}$
5. Backtransform $\mathbf{C} = \mathbf{S}^{-\frac{1}{2}}\tilde{\mathbf{C}}$
6. Form new density matrix $D_{\mu\nu} = \sum_i^{n/2} C^*_{\mu i} C_{\nu i}$
7. If the new $\mathbf{D}$ differs from the old $\mathbf{D}$ by more than a threshold, return to step 3

UHF: The Pople-Nesbet Equations

For open-shell systems of arbitrary n_α, n_β, we can solve equations 5 and 6 without any spin restriction. By exactly the same procedure as was used for the Roothaan-Hall equations, we arrive at the Pople-Nesbet equations

$$\mathbf{F}^\alpha\mathbf{C}^\alpha = \mathbf{S}\mathbf{C}^\alpha\boldsymbol{\epsilon}^\alpha \qquad F^\alpha_{\mu\nu} = \langle\chi_\mu|\hat{f}_\alpha|\chi_\nu\rangle \qquad S_{\mu\nu} = \langle\chi_\mu|\chi_\nu\rangle \qquad (\boldsymbol{\epsilon}^\alpha)_{p_\alpha q_\alpha} = \epsilon_{p_\alpha}\delta_{p_\alpha q_\alpha}$$
$$\mathbf{F}^\beta\mathbf{C}^\beta = \mathbf{S}\mathbf{C}^\beta\boldsymbol{\epsilon}^\beta \qquad F^\beta_{\mu\nu} = \langle\chi_\mu|\hat{f}_\beta|\chi_\nu\rangle \qquad S_{\mu\nu} = \langle\chi_\mu|\chi_\nu\rangle \qquad (\boldsymbol{\epsilon}^\beta)_{p_\beta q_\beta} = \epsilon_{p_\beta}\delta_{p_\beta q_\beta}$$

where $\mathbf{C}^\alpha = [C_{\mu p_\alpha}]$ is an $m \times m$ matrix of MO coefficients for $\{\phi_{p_\alpha}\}$ and $\mathbf{C}^\beta = [C_{\mu p_\beta}]$ is an $m \times m$ matrix of MO coefficients for $\{\phi_{p_\beta}\}$. Expanding the α and β Fock matrices as in equation 8, we find

$$F^\alpha_{\mu\nu} = \langle\chi_\mu|\hat{h}|\chi_\nu\rangle + \sum_{\rho\sigma} D^\alpha_{\rho\sigma}\langle\chi_\mu\chi_\rho||\chi_\nu\chi_\sigma\rangle + \sum_{\rho\sigma} D^\beta_{\rho\sigma}\langle\chi_\mu\chi_\rho|\chi_\nu\chi_\sigma\rangle \qquad D^\alpha_{\mu\nu} = \sum_{i_\alpha}^{n_\alpha} C^*_{\mu i_\alpha} C_{\nu i_\alpha}$$
$$F^\beta_{\mu\nu} = \langle\chi_\mu|\hat{h}|\chi_\nu\rangle + \sum_{\rho\sigma} D^\alpha_{\rho\sigma}\langle\chi_\mu\chi_\rho|\chi_\nu\chi_\sigma\rangle + \sum_{\rho\sigma} D^\beta_{\rho\sigma}\langle\chi_\mu\chi_\rho||\chi_\nu\chi_\sigma\rangle \qquad D^\beta_{\mu\nu} = \sum_{i_\beta}^{n_\beta} C^*_{\mu i_\beta} C_{\nu i_\beta}$$

where $\mathbf{D}^\alpha$ and $\mathbf{D}^\beta$ are the α and β density matrices. The procedure for solving the Pople-Nesbet equations is identical to the one given for RHF. However, note that one must solve the α and β equations simultaneously because each Fock operator depends on both $\mathbf{C}^\alpha$ and $\mathbf{C}^\beta$ (via $\mathbf{D}^\alpha$ and $\mathbf{D}^\beta$).