1 Coupled Perturbed Hatree-Fock (CPHF) Method

This is a summary of the article Pople et al., IJQC (1979).

The fock equation, subject to a perturbation ξ, in matrix notation:

$$\mathbf{F}(\xi)\mathbf{C}(\xi) = \mathbf{S}(\xi))\mathbf{C}(\xi)\mathbf{E}(\xi) \tag{1}$$

The spin-orbitals are required to be orthonormal for all values of ξ:

$$\mathbf{C}^\dagger(\xi)\mathbf{S}(\xi)\mathbf{C}(\xi) = \mathbf{I} \tag{2}$$

We would like to transform $\mathbf{C}(\xi)$ to unperturbed spin-orbital coefficients, i.e. $\mathbf{C}(0)$. Consider the transformation from AO to MO:

$$\psi_p(\xi) = \sum_\mu C_{\mu p}(\xi)\phi_\mu(\xi) \tag{3}$$

Suppose we have the basis functions $\{\phi_i(0)\}$ changed to $\{\phi_i(\xi)\}$ but the coefficients $\mathbf{C}(0)$ remains unperturbed:

$$\psi_p(\xi) = \sum_q U_{qp}(\xi)\big(\sum_\mu C_{\mu q}(0)\phi_\mu(\xi)\big) \tag{4}$$

The matrix $\mathbf{U}(\xi)$ transforms the spin-orbital coefficients $\mathbf{C}(0)$ to a perturbed basis:

$$C_{\mu p}(\xi) = \sum_q C_{\mu q}(0)U_{qp}(\xi) \tag{5}$$
$$\Updownarrow$$
$$\mathbf{C}(\xi) = \mathbf{C}(0)\mathbf{U}(\xi) \tag{6}$$

Now our aim is to find $\mathbf{U}(\xi)$ for perturbation ξ.

The Roothaan equations subject to perturbation are:

$$\mathbf{F}(\xi)\mathbf{C}(\xi) = \mathbf{S}(\xi)\mathbf{C}(\xi)\mathbf{E}(\xi) \tag{7}$$

Writing the equation in terms of unperturbed coefficients and left-multiply by $\mathbf{C}^\dagger(0)$:

$$\begin{aligned} \mathbf{F}(\xi)\mathbf{C}(0)\mathbf{U}(\xi) &= \mathbf{S}(\xi)\mathbf{C}(0)\mathbf{U}(\xi)\mathbf{E}(\xi) \\ \Leftrightarrow \mathbf{C}^\dagger(0)\mathbf{F}(\xi)\mathbf{C}(0)\mathbf{U}(\xi) &= \mathbf{C}(0)\mathbf{S}(\xi)\mathbf{C}(0)\mathbf{U}(\xi)\mathbf{E}(\xi) \end{aligned} \tag{8}$$

By defining:

$$\boldsymbol{\mathcal{F}}(\xi) = \mathbf{C}^\dagger(0)\mathbf{F}(\xi)\mathbf{C}(0) \tag{9}$$
$$\boldsymbol{\mathcal{S}}(\xi) = \mathbf{C}^\dagger(0)\mathbf{S}(\xi)\mathbf{C}(0) \tag{10}$$

the Roothaan equations become:

$$\boldsymbol{\mathcal{F}}(\xi)\mathbf{U}(\xi) = \boldsymbol{\mathcal{S}}(\xi)\mathbf{U}(\xi)\mathbf{E}(\xi) \tag{11}$$

and the orthonomality condition follows:

$$\mathbf{U}^\dagger(\xi)\boldsymbol{\mathcal{S}}(\xi)\mathbf{U}(\xi) = \mathbf{I} \tag{12}$$

Note here that, by definition, $\boldsymbol{\mathcal{S}}(0)$ and $\mathbf{U}(0)$ are the unit matrix $\mathbf{I}$:

$$\mathbf{C}(\xi = 0) = \mathbf{C}(0)\mathbf{U}(\xi = 0) \Longleftrightarrow \mathbf{U}(0) = \mathbf{I} \tag{13}$$

$$\boldsymbol{\mathcal{S}}(\xi = 0) = \mathbf{C}^{\dagger}(0)\mathbf{S}(\xi = 0)\mathbf{C}(0) = \mathbf{I} \tag{14}$$

Turn off the perturbation in the Roothaan equations subject to perturbation:

$$\boldsymbol{\mathcal{F}}(0)\mathbf{U}(0) = \boldsymbol{\mathcal{S}}(0)\mathbf{U}(0)\mathbf{E}(0) \tag{15}$$

$$\Updownarrow$$

$$\boldsymbol{\mathcal{F}}(0) = \mathbf{E}(0) \tag{16}$$

With the unperturbed case defined, we now try to solve the Roothaan equations subject to perturbation, with orthonomality condition, by expanding the perturbed matrices in power series:

$$\boldsymbol{\mathcal{F}}(\xi) = \mathbf{E}(0) + \xi\boldsymbol{\mathcal{F}}^{(1)} + \mathcal{O}\big(\xi^2\big) \tag{17}$$

$$\boldsymbol{\mathcal{S}}(\xi) = \mathbf{I} + \xi\boldsymbol{\mathcal{S}}^{(1)} + \mathcal{O}\big(\xi^2\big) \tag{18}$$

$$\mathbf{U}(\xi) = \mathbf{I} + \xi\mathbf{U}^{(1)} + \mathcal{O}\big(\xi^2\big) \tag{19}$$

$$\mathbf{E}(\xi) = \mathbf{E}(0) + \xi\mathbf{E}^{(1)} + \mathcal{O}\big(\xi^2\big) \tag{20}$$

Substitute these expansions into the Roothaan equations and normalisation condition, and collect linear terms in ξ:

$$\mathbf{E}(0)\mathbf{U}^{(1)} + \boldsymbol{\mathcal{F}}^{(1)} = \mathbf{E}^{(1)} + \mathbf{U}^{(1)}\mathbf{E}(0) + \boldsymbol{\mathcal{S}}^{(1)}\mathbf{E}(0) \tag{21}$$

$$\mathbf{0} = \mathbf{U}^{(1)\dagger} + \boldsymbol{\mathcal{S}}^{(1)} + \mathbf{U}^{(1)} \tag{22}$$

Now our aim is to solve for $\mathbf{U}^{(1)}$ and $\mathbf{E}^{(1)}$.
As adding a random phase factor to the wavefunction does not alter the physical observables (e.g. electron density), we can safely choose elements of $\mathbf{U}$ to be real, WLOG. Therefore, considering the diagonal terms in the orthonomality equation:

$$U_{pp} = -\frac{1}{2}\mathcal{S}_{pp} \tag{23}$$

By looking at the diagonal terms of the Roothaan equations:

$$\begin{aligned}
\big(\mathcal{F}^{(1)} + E(0)U^{(1)}\big)_{pp} &= \big(\mathcal{S}^{(1)}E(0) + U^{(1)}E(0) + E^{(1)}\big)_{pp} \\
\Leftrightarrow \mathcal{F}^{(1)}_{pp} + E_{pq}(0)U^{(1)}_{qp} &= \mathcal{S}^{(1)}_{pr}E^{(0)}_{rp} + U^{(1)}_{ps}E_{sp}(0) + E^{(1)}_{pp} \\
\Leftrightarrow \mathcal{F}^{(1)}_{pp} + E_p(0)\delta_{pq}U^{(1)}_{qp} &= \mathcal{S}^{(1)}_{pr}E_p(0)\delta_{rp} + U^{(1)}_{ps}E_p(0)\delta_{ps} + E^{(1)}_{pp} \\
\Leftrightarrow \mathcal{F}^{(1)}_{pp} + E_p(0)U^{(1)}_{pp} &= \mathcal{S}^{(1)}_{pp}E_p(0) + U^{(1)}_{pp}E_p(0) + E^{(1)}_{p} \\
&\Downarrow \\
E^{(1)}_p &= \mathcal{F}^{(1)}_{pp} - \mathcal{S}^{(1)}_{pp}E_p(0)
\end{aligned} \tag{24}$$

Einstein's summation convention are assumed here as well as in later sections, unless otherwise noted.
To find the off-diagonal element of $\mathbf{U}$, we look at the off-diagonal terms in the Roothaan equations:

$$\begin{aligned}
\big(\mathcal{F}^{(1)} + E(0)U^{(1)}\big)_{pq} &= \big(\mathcal{S}^{(1)}E(0) + U^{(1)}E(0) + E^{(1)}\big)_{pq} \\
\Leftrightarrow \mathcal{F}^{(1)}_{pq} + E_{pr}(0)U^{(1)}_{rq} &= \mathcal{S}^{(1)}_{ps}E_{sq}(0) + U^{(1)}_{pt}E_{tq}(0) + E^{(1)}_{pq}
\end{aligned}$$

$$\begin{aligned}\Leftrightarrow \mathcal{F}^{(1)}_{pq} + E_p(0)\delta_{pr}U^{(1)}_{rq} =& \mathcal{S}^{(1)}_{ps}E_q(0)\delta_{sq} + U^{(1)}_{pt}E_q(0)\delta_{tq} + E^{(1)}_{pq} \\ &\Downarrow \\ U^{(1)}_{pq} =& \frac{\mathcal{F}^{(1)}_{pq} - \mathcal{S}^{(1)}_{pq}E_q(0)}{E_q(0) - E_p(0)} \end{aligned} \tag{25}$$

TODO:This is unfinished.