0.1 Perturbed Brillouin Condition

The SCF density matrix is defined as:

$$D_{\mu\nu}^{\text{SCF}} = \sum_{i}^{N} C_{\mu i}^{*} C_{\nu i} \tag{1}$$

in which the MO coefficients are parameterized as:

$$\begin{aligned} C_{\mu p}(\lambda) =& \sum_{q} C_{\mu q}(0) U(\lambda)_{qp} && (2)\\ \mathbf{C}(\lambda) =& \mathbf{C}(0)\mathbf{U}(\lambda) && (3) \end{aligned}$$

Define the one- and two-electron parts of the fock matrix, in AO and MO basis, as:

$$\begin{aligned} h_{pq} =& \langle p|\hat{h}|q\rangle = \sum_{\mu\nu} C_{\mu p}^{*} h_{\mu\nu}^{\text{AO}} C_{\nu q} & g_{pq} =& \sum_{i}\langle pi||qi\rangle = \sum_{i}\sum_{\mu\nu} C_{\mu p}^{*}\langle \mu i||\nu i\rangle C_{\nu q} \qquad (4)\\ h_{\mu\nu}^{\text{AO}} =& \langle \mu|\hat{h}|\nu\rangle & g_{\mu\nu}^{\text{AO}} =& \sum_{i}\langle \mu i||\nu i\rangle = \sum_{\rho\sigma} D_{\rho\sigma}\langle \mu\rho||\nu\sigma\rangle\\ \mathbf{h} =& \mathbf{C}^{\dagger}\mathbf{h}^{\text{AO}}\mathbf{C} & \mathbf{g} =& \mathbf{C}^{\dagger}\mathbf{g}^{\text{AO}}\mathbf{C} \end{aligned}$$

Therefore, the Fock matrix could be expressed as (with the dependency on SCF density explicitly addressed):

$$\begin{aligned} f_{pq} =& h_{pq} + \sum_{i}\langle pi||qi\rangle\\ =& \sum_{\mu\nu} C_{\mu p}^{*} h_{\mu\nu}^{\text{AO}} C_{\nu q} + \sum_{\mu\nu} C_{\mu p}^{*} g_{\mu\nu}^{\text{AO}} C_{\nu q}\\ =& \sum_{\mu\nu} C_{\mu p}^{*}\langle \mu|\hat{h}|\nu\rangle C_{\nu q} + \sum_{\mu\nu} C_{\mu p}^{*}\big(\sum_{\rho\sigma} D_{\rho\sigma}\langle \mu\rho||\nu\sigma\rangle\big) C_{\nu q} && (5)\\ f_{\mu\nu}^{\text{AO}} =& h_{\mu\nu}^{\text{AO}} + g_{\mu\nu}^{\text{AO}} = \langle \mu|\hat{h}|\nu\rangle + \sum_{\rho\sigma} D_{\rho\sigma}\langle \mu\rho||\nu\sigma\rangle && (6)\\ \mathbf{f} =& \mathbf{h} + \mathbf{g}[\mathbf{D}^{\text{SCF}}]\\ =& \mathbf{C}^{\dagger}\mathbf{h}^{\text{AO}}\mathbf{C} + \mathbf{C}^{\dagger}\mathbf{g}^{\text{AO}}[\mathbf{D}^{\text{SCF}}]\mathbf{C}\\ =& \mathbf{C}^{\dagger}\mathbf{F}^{\text{AO}}[\mathbf{D}^{\text{SCF}}]\mathbf{C} && (7)\\ \mathbf{f}^{\text{AO}}[\mathbf{D}^{\text{SCF}}] =& \mathbf{h}^{\text{AO}} + \mathbf{g}^{\text{AO}}[\mathbf{D}^{\text{SCF}}] && (8) \end{aligned}$$

Evaluating the derivative at $\lambda = 0$, noting that $\mathbf{U}(0) = \mathbf{I}$:

$$\begin{aligned} \mathbf{f}^{\lambda} =& \frac{\mathrm{d}\mathbf{f}(\lambda)}{\mathrm{d}\lambda}\Big|_{\lambda=0} = \Big(\mathbf{C}^{\dagger}(\lambda)\mathbf{f}^{\text{AO}}[\mathbf{D}^{\text{SCF}}(\lambda)](\lambda)\mathbf{C}(\lambda)\Big)^{\lambda}\\ =& \mathbf{C}^{\lambda\dagger}(\lambda)\mathbf{f}^{\text{AO}}[\mathbf{D}^{\text{SCF}}(\lambda)](\lambda)\mathbf{C}(\lambda) + \mathbf{C}^{\dagger}(\lambda)\mathbf{f}^{\text{AO}}[\mathbf{D}^{\text{SCF}}(\lambda)](\lambda)\mathbf{C}^{\lambda}(\lambda)\\ &+ \mathbf{C}^{\dagger}(\lambda)\Big(\mathbf{h}^{\text{AO}}(\lambda) + \mathbf{g}^{\text{AO}}[\mathbf{D}^{\text{SCF}}(\lambda)](\lambda)\Big)^{\lambda}\mathbf{C}(\lambda)\\ =& \mathbf{U}^{\lambda\dagger}(\lambda)\underbrace{\mathbf{U}^{\dagger}(0)\mathbf{C}^{\dagger}(0)}_{\mathbf{C}^{\dagger}(\lambda=0)}\mathbf{f}^{\text{AO}}[\mathbf{D}^{\text{SCF}}(\lambda)](\lambda)\mathbf{C}(\lambda) + \mathbf{C}^{\dagger}(\lambda)\mathbf{f}^{\text{AO}}[\mathbf{D}^{\text{SCF}}(\lambda)](\lambda)\underbrace{\mathbf{C}(0)\mathbf{U}(0)}_{\mathbf{C}(\lambda=0)}\mathbf{U}^{\lambda}(\lambda)\\ &+ \mathbf{C}^{\dagger}(\lambda)\Big(\mathbf{h}^{\text{AO},\lambda}(\lambda) + \mathbf{g}^{\text{AO},\lambda}[\mathbf{D}^{\text{SCF}}(\lambda)](\lambda) + \mathbf{g}^{\text{AO}}[\mathbf{D}^{\text{SCF},\lambda}(\lambda)](\lambda)\Big)\mathbf{C}(\lambda)\\ =& \mathbf{U}^{\lambda\dagger}\mathbf{f} + \mathbf{f}\mathbf{U}^{\lambda} + \mathbf{C}^{\dagger}\mathbf{h}^{\text{AO},\lambda}\mathbf{C} + \mathbf{C}^{\dagger}\mathbf{g}^{\text{AO},\lambda}[\mathbf{D}^{\text{SCF}}]\mathbf{C} + \mathbf{C}^{\dagger}\mathbf{g}^{\text{AO}}[\mathbf{D}^{\text{SCF},\lambda}]\mathbf{C} && (9) \end{aligned}$$

The perturbed Brillouin condition is:

$$f_{ai}^{\lambda} = 0 \tag{10}$$

To evaluate the perturbed Fock matrix, we write the perturbed quantities in suffix notation as (assuming canonical orbitals, i.e. $f_{pq} = \delta_{pq}\varepsilon_p$):

$$(\mathbf{U}^{\lambda\dagger}\mathbf{f})_{ai} = U_{ia}^{\lambda *}\varepsilon_i = \frac{\mathrm{d}U_{ia}^{*}}{\mathrm{d}\lambda}\Big|_{\lambda=0}\varepsilon_i \tag{11}$$

$$(\mathbf{f}\mathbf{U}^{\lambda})_{ai} = \varepsilon_a U_{ai}^{\lambda} = \varepsilon_a \frac{\mathrm{d}U_{ai}}{\mathrm{d}\lambda}\Big|_{\lambda=0} \tag{12}$$

$$(\mathbf{C}^{\dagger}\mathbf{h}^{\mathrm{AO},\lambda}\mathbf{C})_{ai} = \sum_{\mu\nu} C_{\mu a}^{*} h_{\mu\nu}^{\lambda} C_{\nu i} = \sum_{\mu\nu} C_{\nu a}^{*} \frac{\mathrm{d}h_{\mu\nu}}{\mathrm{d}\lambda}\Big|_{\lambda=0} C_{\nu i} \tag{13}$$

$$\begin{aligned}(\mathbf{C}^{\dagger}\mathbf{g}^{\mathrm{AO},\lambda}[\mathbf{D}^{\mathrm{SCF}}]\mathbf{C})_{ai} &= \sum_{\mu\nu} C_{\mu a}^{*} (\sum_{\rho\sigma} D_{\rho\sigma} \langle\mu\rho||\nu\sigma\rangle^{\lambda}) C_{\nu i} \\ &= \sum_{\mu\nu} C_{\mu a}^{*} (\sum_{\rho\sigma} D_{\rho\sigma} \frac{\mathrm{d}\langle\mu\rho||\nu\sigma\rangle}{\mathrm{d}\lambda}\Big|_{\lambda=0}) C_{\nu i}\end{aligned} \tag{14}$$

$$\begin{aligned}(\mathbf{C}^{\dagger}\mathbf{g}^{\mathrm{AO}}[\mathbf{D}^{\mathrm{SCF},\lambda}]\mathbf{C})_{ai} &= \sum_{\mu\nu} C_{\mu a}^{*} (\sum_{\rho\sigma} D_{\rho\sigma}^{\lambda} \langle\mu\rho||\nu\sigma\rangle) C_{\nu i} \\ &= \sum_{\mu\nu} C_{\mu a}^{*} (\sum_{\rho\sigma} \frac{\mathrm{d}D_{\rho\sigma}}{\mathrm{d}\lambda}\Big|_{\lambda=0} \langle\mu\rho||\nu\sigma\rangle) C_{\nu i}\end{aligned} \tag{15}$$