

1 Perturbed Orthonormality Condition

1.1 Matrix Parameterization

We have the general orthonormality condition, subject to perturbation, as:

$$S_{pq} = \langle p|q \rangle = \delta_{pq} \quad (1)$$

$$\sum_{\mu\nu} C_{\mu p}^* S_{\mu\nu} C_{\nu q} = \delta_{pq} \quad (2)$$

Parameterization of the MO coefficients:

$$\mathbf{C}(\lambda) = \mathbf{C}(0)\mathbf{U}(\lambda) \quad (3)$$

$$C_{\mu p}(\lambda) = \sum_r C_{\mu r}(0) U_{rp}(\lambda) \quad (4)$$

in which $\mathbf{U}(\lambda)$ is the solution to the CPHF equations.

Now the orthonormality condition using this parameterization:

$$\sum_{\mu\nu} \left(\sum_r U_{rp}^*(\lambda) C_{\mu r}^*(0) \right) S_{\mu\nu}(\lambda) \left(\sum_s C_{\nu s}(0) U_{sq}(\lambda) \right) = \delta_{pq} \quad (5)$$

Introducing the transformed overlap matrix:

$$S_{pq}^{00}(\lambda) = \sum_{\mu\nu} C_{\mu p}^*(0) S_{\mu\nu}(\lambda) C_{\nu q}(0) \quad (6)$$

we have:

$$\sum_{rs} U_{rp}^*(\lambda) S_{rs}^{00}(\lambda) U_{sq}(\lambda) = \delta_{pq} \quad (7)$$

differentiating both sides of the equation gives:

$$\sum_{rs} \frac{dU_{rp}^*(\lambda)}{d\lambda} S_{rs}^{00}(\lambda) U_{sq}(\lambda) + \sum_{rs} U_{rp}^*(\lambda) \frac{dS_{rs}^{00}(\lambda)}{d\lambda} U_{sq}(\lambda) + \sum_{rs} U_{rp}^*(\lambda) S_{rs}^{00}(\lambda) \frac{dU_{sq}(\lambda)}{d\lambda} = 0 \quad (8)$$

Noting that $\mathbf{S}^{00}(0) = \mathbf{I}$ because the unperturbed spin-orbitals are orthonormal, and it is trivial that $\mathbf{U}(0) = \mathbf{I}$.

Therefore evaluating the derivative at $\lambda = 0$, and denoting $A^\lambda = (\frac{dA}{d\lambda})|_{\lambda=0}$ results in:

$$\sum_{rs} (U_{rp}^\lambda)^* \delta_{rs} \delta_{sq} + \sum_{rs} \delta_{rp} S_{rs}^{00,\lambda} \delta_{sq} + \sum_{rs} \delta_{rp} \delta_{rs} U_{sq}^\lambda = 0 \quad (9)$$

contracting the Kronecker delta tensors we get the perturbed orthonormality condition:

$$(U_{qp}^\lambda)^* + S_{pq}^{00,\lambda} + U_{pq}^\lambda = 0 \quad (10)$$

1.2 Exponential Parameterization

$$\mathbf{C}(\lambda) = \mathbf{C}(0)\mathbf{U}(\lambda) \quad (11)$$

$$\mathbf{U}(\lambda) = (\mathbf{S}^{00})^{-\frac{1}{2}}(\lambda) \exp[-\kappa(\lambda)] \quad (12)$$

$$\mathbf{S}^{00}(\lambda) = \mathbf{C}^\dagger(0)\mathbf{S}^{\text{AO}}(\lambda)\mathbf{C}(0) \quad (13)$$

In this way:

$$\begin{aligned} \mathbf{S}(\lambda) &= \mathbf{C}^\dagger(\lambda)\mathbf{S}^{\text{AO}}(\lambda)\mathbf{C}(\lambda) \\ &= \mathbf{U}^\dagger(\lambda)\mathbf{C}^\dagger(0)\mathbf{S}^{\text{AO}}(\lambda)\mathbf{C}(0)\mathbf{U}(\lambda) \\ &= \mathbf{U}^\dagger(\lambda)(\mathbf{S}^{00})(\lambda)\mathbf{U}(\lambda) \\ &= \exp[-\kappa(\lambda)]^\dagger(\mathbf{S}^{00})^{-\frac{1}{2}\dagger}(\lambda)\mathbf{S}^{00}(\lambda)(\mathbf{S}^{00})^{-\frac{1}{2}}(\lambda)\exp[-\kappa(\lambda)] \\ &= \exp[\kappa(\lambda)]\exp[-\kappa(\lambda)] \\ &= \mathbf{I} \end{aligned} \quad (14)$$

the orthonormality is ensured by $(\mathbf{S}^{00})^{-\frac{1}{2}\dagger}\mathbf{S}^{00}(\mathbf{S}^{00})^{-\frac{1}{2}} = \mathbf{I}$, as \mathbf{S}^{AO} thus \mathbf{S}^{00} matrix is Hermitian. The perturbed orthonormality condition is then trivial:

$$\mathbf{S}^\lambda = \frac{\partial \mathbf{S}(\lambda)}{\partial \lambda} \Big|_{\lambda=0} = \mathbf{0} \quad (15)$$

With this new parameterization, the orthonormality condition and perturbed orthonormality condition come naturally, hence do not need to be included explicitly in the Lagrangian.

The derivative of $(\mathbf{S}^{00})^{-\frac{1}{2}}(\lambda)$ (needed for \mathbf{U}^λ appearing in second derivative) could be solved by taking derivative on this equation:

$$(\mathbf{S}^{00})^{-\frac{1}{2}\dagger}\mathbf{S}^{00}(\mathbf{S}^{00})^{-\frac{1}{2}} = \mathbf{I} \quad (16)$$

i.e. (note that $\mathbf{S}^{00,\dagger} = \mathbf{S}^{00}$ and $\mathbf{S}^{00}(\lambda = 0) = \mathbf{I}$):

$$\begin{aligned} \mathbf{0} &= \frac{\partial(\mathbf{S}^{00})^{-\frac{1}{2}}}{\partial \lambda} \mathbf{S}^{00}(\mathbf{S}^{00})^{-\frac{1}{2}} \Big|_{\lambda=0} + (\mathbf{S}^{00})^{-\frac{1}{2}} \frac{\partial \mathbf{S}^{00}}{\partial \lambda} (\mathbf{S}^{00})^{-\frac{1}{2}} \Big|_{\lambda=0} + (\mathbf{S}^{00})^{-\frac{1}{2}} \mathbf{S}^{00} \frac{\partial(\mathbf{S}^{00})^{-\frac{1}{2}}}{\partial \lambda} \Big|_{\lambda=0} \\ &= 2(\mathbf{S}^{00})^{-\frac{1}{2},\lambda} + \mathbf{S}^{00,\lambda} \end{aligned} \quad (17)$$

$$\Leftrightarrow (\mathbf{S}^{00})^{-\frac{1}{2},\lambda} = -\frac{1}{2}\mathbf{S}^{00,\lambda} \quad (18)$$