1 Lagrangian Method

The MP2 Lagrangian could be written as:

$$\begin{aligned}\mathcal{L}_{\text{MP2}} =& E_{\text{MP2}} + C_{\text{Bri}} \\ =& E_{\text{HF}} + E_{\text{H}} + C_{\text{Bri}}\end{aligned} \tag{1}$$

in which E_{H} is the Hylleraas functional, C_{Bri} is the Brillouin condition. The orthonormality condition is enforced implicitly by the anti-Hermitian condition on the orbital rotation paramer.

1.1 Hartree Fock Energy

The Hartree-Fock energy has contribution from zeroth- and first-order energies in MP2:

$$\begin{aligned}E_{\text{HF}} =& E^{(0)} + E^{(1)} \\ =& \sum_i h_{ii} + \sum_{ij} \langle ij||ij\rangle - \frac{1}{2}\sum_{ij}\langle ij||ij\rangle \\ =& \sum_i h_{ii} + \frac{1}{2}\sum_{ij}\langle ij||ij\rangle\end{aligned} \tag{2}$$

1.2 Hylleraas Functional

The Hylleraas functional is defined as:

$$\begin{aligned}E_{\text{H}} =& \langle\Psi^{(1)}|\hat{V} - E^{(1)}|\Phi_0\rangle + \langle\Phi_0|\hat{V} - E^{(1)}|\Psi^{(1)}\rangle + \langle\Psi^{(1)}|\hat{H}^{(0)} - E^{(0)}|\Psi^{(1)}\rangle \\ =& 2\,\text{Re}\langle\Psi^{(1)}|\hat{V} - E^{(1)}|\Phi_0\rangle + \langle\Psi^{(1)}|\hat{H}^{(0)} - E^{(0)}|\Psi^{(1)}\rangle\end{aligned} \tag{3}$$

in which the relevant operators and functions are:

$$\hat{V} - E^{(1)} = \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\} \tag{4}$$

$$\hat{H}^{(0)} - E^{(0)} = \sum_{pq} f_{pq}\{\hat{p}^\dagger\hat{q}\} = \sum_{pq} h_{pq}\{\hat{p}^\dagger\hat{q}\} + \sum_{pqi}\langle pi||qi\rangle\{\hat{p}^\dagger\hat{q}\} \tag{5}$$

$$|\Psi^{(1)}\rangle = \frac{1}{4}\sum_{ijab} T_{ij}^{ab}|\Phi_{ij}^{ab}\rangle \tag{6}$$

Therefore the Hylleraas functional could be written as:

$$\begin{aligned}E_{\text{H}} =& \frac{1}{8}\,\text{Re}\left\{\sum_{ijab}(T_{ij}^{ab})^*\sum_{pqrs}\langle pq||rs\rangle\langle\Phi_{ij}^{ab}|\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}|\Phi_0\rangle\right\} \\ &+ \frac{1}{16}\sum_{ijab}(T_{ij}^{ab})^*\sum_{klcd}T_{kl}^{cd}\sum_{pq}\langle\Phi_{ij}^{ab}|\{\hat{p}^\dagger\hat{q}\}|\Phi_{kl}^{cd}\rangle f_{pq}\end{aligned} \tag{7}$$

First, we need to work out the following expectations:

$$\langle\Phi_{ij}^{ab}|\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}|\Phi_0\rangle = \langle\Phi_0|\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\}\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}|\Phi_0\rangle \tag{8}$$

$$\langle\Phi_{ij}^{ab}|\{\hat{p}^\dagger\hat{q}\}|\Phi_{kl}^{cd}\rangle = \langle\Phi_0|\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\}\{\hat{p}^\dagger\hat{q}\}\{\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\}|\Phi_0\rangle \tag{9}$$

Using GWT, the non-zero contributions come from the fully contracted terms:

$$\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\}\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\} = \{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\} + \{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\} + \{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\} + \{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\} + \dots$$

$$=\delta_{ir}\delta_{js}\delta_{bq}\delta_{ap}+\delta_{is}\delta_{jr}\delta_{bp}\delta_{aq}-\delta_{ir}\delta_{js}\delta_{bp}\delta_{aq}-\delta_{is}\delta_{jr}\delta_{bq}\delta_{ap}+\dots \tag{10}$$

$$\begin{aligned}
&\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\}\{\hat{p}^\dagger\hat{q}\}\{\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\}\\
=&\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\hat{p}^\dagger\hat{q}\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\}+\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\hat{p}^\dagger\hat{q}\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\}+\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\hat{p}^\dagger\hat{q}\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\}+\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\hat{p}^\dagger\hat{q}\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\}\\
&+\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\hat{p}^\dagger\hat{q}\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\}+\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\hat{p}^\dagger\hat{q}\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\}+\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\hat{p}^\dagger\hat{q}\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\}+\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\hat{p}^\dagger\hat{q}\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\}\\
&+\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\hat{p}^\dagger\hat{q}\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\}+\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\hat{p}^\dagger\hat{q}\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\}+\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\hat{p}^\dagger\hat{q}\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\}+\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\hat{p}^\dagger\hat{q}\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\}\\
&+\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\hat{p}^\dagger\hat{q}\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\}+\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\hat{p}^\dagger\hat{q}\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\}+\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\hat{p}^\dagger\hat{q}\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\}+\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\hat{p}^\dagger\hat{q}\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\}+\dots\\
=&\delta_{iq}\delta_{jk}\delta_{bd}\delta_{ac}\delta_{pl}-\delta_{iq}\delta_{jk}\delta_{bc}\delta_{ad}\delta_{pl}-\delta_{iq}\delta_{jl}\delta_{bd}\delta_{ac}\delta_{pk}+\delta_{iq}\delta_{jl}\delta_{bc}\delta_{ad}\delta_{pk}\\
&-\delta_{ik}\delta_{jq}\delta_{bd}\delta_{ac}\delta_{pl}+\delta_{il}\delta_{jq}\delta_{bd}\delta_{ac}\delta_{pk}+\delta_{ik}\delta_{jq}\delta_{bc}\delta_{ad}\delta_{pl}-\delta_{il}\delta_{jq}\delta_{bc}\delta_{ad}\delta_{pk}\\
&+\delta_{ik}\delta_{jl}\delta_{bp}\delta_{ac}\delta_{qd}-\delta_{il}\delta_{jk}\delta_{bp}\delta_{ac}\delta_{qd}-\delta_{ik}\delta_{jl}\delta_{bp}\delta_{ad}\delta_{qc}+\delta_{il}\delta_{jk}\delta_{bp}\delta_{ad}\delta_{qc}\\
&+\delta_{ik}\delta_{jl}\delta_{bd}\delta_{ap}\delta_{qc}-\delta_{il}\delta_{jk}\delta_{bd}\delta_{ap}\delta_{qc}-\delta_{ik}\delta_{jl}\delta_{bc}\delta_{ap}\delta_{qd}+\delta_{il}\delta_{jk}\delta_{bc}\delta_{ap}\delta_{qd}+\dots
\end{aligned} \tag{11}$$

the terms not fully contrated are ommitted.
Therefore, the two parts of Hylleraas functional could be simplified as:

$$\begin{aligned}
&\frac{1}{8}\,\mathrm{Re}\left\{\sum_{ijab}(T_{ij}^{ab})^*\sum_{pqrs}\langle pq||rs\rangle\langle\Phi_{ij}^{ab}|\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}|\Phi_0\rangle\right\}\\
=&\frac{1}{8}\,\mathrm{Re}\left\{\sum_{ijab}(T_{ij}^{ab})^*(\langle ab||ij\rangle+\langle ba||ji\rangle-\langle ba||ij\rangle-\langle ab||ji\rangle)\right\}\\
=&\frac{1}{2}\,\mathrm{Re}\left\{\sum_{ijab}(T_{ij}^{ab})^*\langle ab||ij\rangle\right\}
\end{aligned} \tag{12}$$

$$\begin{aligned}
&\frac{1}{16}\sum_{ijab}(T_{ij}^{ab})^*\sum_{klcd}T_{kl}^{cd}\sum_{pq}\langle\Phi_{ij}^{ab}|\{\hat{p}^\dagger\hat{q}\}|\Phi_{kl}^{cd}\rangle f_{pq}\\
=&\frac{1}{16}\Big(\sum_{ijlab}f_{li}(T_{ij}^{ab})^*T_{jl}^{ab}-\sum_{ijlab}f_{li}(T_{ij}^{ab})^*T_{jl}^{ba}-\sum_{ijkab}f_{ki}(T_{ij}^{ab})^*T_{kj}^{ab}+\sum_{ijkab}f_{ki}(T_{ij}^{ab})^*T_{kj}^{ba}\\
&-\sum_{ijlab}f_{lj}(T_{ij}^{ab})^*T_{il}^{ab}+\sum_{ijlab}f_{lj}(T_{ij}^{ab})^*T_{il}^{ba}+\sum_{ijkab}f_{kj}(T_{ij}^{ab})^*T_{ki}^{ab}-\sum_{ijkab}f_{kj}(T_{ij}^{ab})^*T_{ki}^{ba}\\
&+\sum_{ijabd}f_{bd}(T_{ij}^{ab})^*T_{ij}^{ad}-\sum_{ijabd}f_{bd}(T_{ij}^{ab})^*T_{ji}^{ad}-\sum_{ijabc}f_{bc}(T_{ij}^{ab})^*T_{ij}^{ca}+\sum_{ijabc}f_{bc}(T_{ij}^{ab})^*T_{ji}^{ca}\\
&+\sum_{ijabc}f_{ac}(T_{ij}^{ab})^*T_{ij}^{cb}-\sum_{ijabc}f_{ac}(T_{ij}^{ab})^*T_{ji}^{cb}-\sum_{ijabd}f_{ad}(T_{ij}^{ab})^*T_{ij}^{bd}+\sum_{ijabd}f_{ad}(T_{ij}^{ab})^*T_{ji}^{bd}\Big)\\
=&\frac{1}{4}\Big(\sum_{ijkab}f_{ki}(T_{ij}^{ab})^*T_{jk}^{ab}-\sum_{ijkab}f_{ki}(T_{ji}^{ab})^*T_{jk}^{ab}+\sum_{ijabc}f_{ac}(T_{ij}^{ba})^*T_{ij}^{bc}-\sum_{ijabc}f_{ac}(T_{ij}^{ab})^*T_{ij}^{bc}\Big)\\
=&\frac{1}{2}\Big(\sum_{ijkab}f_{ki}(T_{ij}^{ab})^*T_{jk}^{ab}-\sum_{ijabc}f_{ac}(T_{ij}^{ab})^*T_{ij}^{bc}\Big)
\end{aligned} \tag{13}$$

Therefore, the Hylleraas functional, written in spin-orbital form, is:

$$E_{\mathrm{H}} = \frac{1}{2}\,\mathrm{Re}\left\{\sum_{ijab}(T_{ij}^{ab})^{*}\langle ab||ij\rangle\right\} + \frac{1}{2}\Big(\sum_{ijkab} f_{ki}(T_{ij}^{ab})^{*}T_{jk}^{ab} - \sum_{ijabc} f_{ac}(T_{ij}^{ab})^{*}T_{ij}^{bc}\Big) \tag{14}$$

To formulate the Hylleraas functional into density matrix representation, we write out dependencies on one- and two-electron integrals, i.e., h_{pq} and $\langle pq||rs\rangle$ explicitly.

$$\begin{aligned}
E_{\mathrm{H}} =&\frac{1}{2}\,\mathrm{Re}\left\{\sum_{ijab}(T_{ij}^{ab})^{*}\langle ab||ij\rangle\right\} + \frac{1}{2}\Big(\sum_{ijkab} h_{ki}(T_{ij}^{ab})^{*}T_{jk}^{ab} - \sum_{ijabc} h_{ac}(T_{ij}^{ab})^{*}T_{ij}^{bc}\Big)\\
&+\frac{1}{2}\Big(\sum_{ijklab}\langle kl||il\rangle(T_{ij}^{ab})^{*}T_{jk}^{ab} - \sum_{ijkabc}\langle ak||ck\rangle(T_{ij}^{ab})^{*}T_{ij}^{bc}\Big)\\
=&\frac{1}{2}\Big(\frac{1}{2}\sum_{ijab}(T_{ij}^{ab})^{*}\langle ab||ij\rangle + \frac{1}{2}\sum_{ijab}T_{ij}^{ab}\langle ij||ab\rangle\Big) + \frac{1}{2}\Big(\sum_{ijkab} h_{ki}(T_{ij}^{ab})^{*}T_{jk}^{ab} - \sum_{ijabc} h_{ac}(T_{ij}^{ab})^{*}T_{ij}^{bc}\Big)\\
&+\frac{1}{2}\Big(\sum_{ijklab}\langle kl||il\rangle(T_{ij}^{ab})^{*}T_{jk}^{ab} - \sum_{ijkabc}\langle ak||ck\rangle(T_{ij}^{ab})^{*}T_{ij}^{bc}\Big)\\
=&\sum_{ij} h_{ij}\gamma_{ij}^{\mathrm{H}} + \sum_{ab} h_{ab}\gamma_{ab}^{\mathrm{H}} + \sum_{ijab}\langle ab||ij\rangle(\Gamma^{\mathrm{H}})_{ij}^{ab} + \sum_{ijab}\langle ij||ab\rangle(\Gamma^{\mathrm{H}})_{ab}^{ij}\\
&+\sum_{ijkl}\langle ij||kl\rangle(\Gamma^{\mathrm{H}})_{kl}^{ij} + \sum_{ijab}\langle ai||bj\rangle(\Gamma^{\mathrm{H}})_{bj}^{ai}
\end{aligned} \tag{15}$$

in which

$$\gamma_{ij}^{\mathrm{H}} = \frac{1}{2}\sum_{kab}(T_{jk}^{ab})^{*}T_{ki}^{ab} \tag{16}$$

$$\gamma_{ab}^{\mathrm{H}} = -\frac{1}{2}\sum_{ijc}(T_{ij}^{ac})^{*}T_{ij}^{cb} \tag{17}$$

$$(\Gamma^{\mathrm{H}})_{ij}^{ab} = \frac{1}{4}(T_{ij}^{ab})^{*} \tag{18}$$

$$(\Gamma^{\mathrm{H}})_{ab}^{ij} = \frac{1}{4}T_{ij}^{ab} \tag{19}$$

$$(\Gamma^{\mathrm{H}})_{kl}^{ij} = \frac{1}{2}\sum_{mab}(T_{km}^{ab})^{*}T_{mi}^{ab}\delta_{jl} \tag{20}$$

$$(\Gamma^{\mathrm{H}})_{bj}^{ai} = -\frac{1}{2}\sum_{klc}(T_{kl}^{ac})^{*}T_{kl}^{cb}\delta_{ij} \tag{21}$$

1.3 Z-Vector Equation (Exponential Parameterization)

$$
\begin{aligned}
\mathbf{U} &= \exp(-\boldsymbol{\kappa}) \\
&= \sum_{n=0}^{\infty} (-1)^n \frac{\boldsymbol{\kappa}^n}{n!}
\end{aligned} \tag{22}
$$

The orbital rotation parameter $\boldsymbol{\kappa}$ is anti-Hermitian:

$$
\boldsymbol{\kappa}^\dagger = (\boldsymbol{\kappa}^*)^T = -\boldsymbol{\kappa} \tag{23}
$$

Therefore the matrix $\mathbf{U}$ is unitary:

$$
\mathbf{U}^\dagger \mathbf{U} = \exp\left(-\boldsymbol{\kappa}^\dagger\right) \exp(-\boldsymbol{\kappa}) = \exp(\boldsymbol{\kappa}) \exp(-\boldsymbol{\kappa}) = \mathbf{I} \tag{24}
$$

Let the matrix $\mathbf{U}$ be the parameter in CPSCF:

$$
\mathbf{C}(\lambda) = \mathbf{C}(0)\mathbf{U}(\lambda) = \mathbf{C}(0) \exp[-\boldsymbol{\kappa}(\lambda)] \tag{25}
$$

$$
C_{\mu p}(\lambda) = \sum_r C_{\mu r}(0) U_{rp}(\lambda) = \sum_r C_{\mu r}(0) (\exp[-\boldsymbol{\kappa}(\lambda)])_{rp} \tag{26}
$$

$$
\begin{aligned}
[\exp(-\boldsymbol{\kappa})]_{rp} =& (\mathbf{I} - \boldsymbol{\kappa} + \frac{1}{2!}\boldsymbol{\kappa}^2 - \frac{1}{3!}\boldsymbol{\kappa}^3 + \dots)_{rp} \\
=& \delta_{rp} - \kappa_{rp} + \frac{1}{2!} \sum_x k_{rx} k_{xp} - \frac{1}{3!} \sum_{xy} k_{rx} k_{xy} k_{yp} + \dots
\end{aligned} \tag{27}
$$

$$
\begin{aligned}
\mathbf{S}(\lambda) =& \mathbf{C}^\dagger(\lambda) \mathbf{S}^{\text{AO}}(\lambda) \mathbf{C}(\lambda) \\
=& (\mathbf{C}(0) \exp[-\boldsymbol{\kappa}(\lambda)])^\dagger \mathbf{S}^{\text{AO}}(\lambda) \mathbf{C}(0) \exp[-\boldsymbol{\kappa}(\lambda)] \\
=& \exp\left[-\boldsymbol{\kappa}^\dagger(\lambda)\right] \mathbf{C}^\dagger(0) \mathbf{S}^{\text{AO}}(\lambda) \mathbf{C}(0) \exp[-\boldsymbol{\kappa}(\lambda)] \\
=& \exp[\boldsymbol{\kappa}(\lambda)] \boldsymbol{\mathcal{S}}(\lambda) \exp[-\boldsymbol{\kappa}(\lambda)] \\
=& \left[\mathbf{I} + \boldsymbol{\kappa}(\lambda) + \frac{1}{2}\boldsymbol{\kappa}^2(\lambda) + \dots\right] \boldsymbol{\mathcal{S}}(\lambda) \left[\mathbf{I} - \boldsymbol{\kappa}(\lambda) + \frac{1}{2}\boldsymbol{\kappa}^2(\lambda) + \dots\right]
\end{aligned} \tag{28}
$$

$$
\begin{aligned}
\Leftrightarrow S_{pq} =& \sum_{\mu\nu} C^*_{\mu p}(\lambda) S^{\text{AO}}_{\mu\nu}(\lambda) C_{\nu q}(\lambda) \\
=& \sum_{\mu\nu} \big(\sum_r C^*_{\mu r}(0) \exp[-\boldsymbol{\kappa}(\lambda)]^*_{rp}\big) S^{\text{AO}}_{\mu\nu}(\lambda) \big(\sum_s C_{\nu s} \exp[-\boldsymbol{\kappa}(\lambda)]_{sq}\big) \\
=& \sum_{\mu\nu rs} \exp[\boldsymbol{\kappa}(\lambda)]_{pr} \big(C^*_{\mu r}(0) S^{\text{AO}}_{\mu\nu}(\lambda) C_{\nu s}(0)\big) \exp[-\boldsymbol{\kappa}(\lambda)]_{sq} \\
=& \sum_{rs} \exp[\boldsymbol{\kappa}(\lambda)]_{pr} \mathcal{S}_{rs}(\lambda) \exp[-\boldsymbol{\kappa}(\lambda)]_{sq} \\
=& \sum_{rs} \left[\delta_{pr} + \kappa_{pr}(\lambda) + \frac{1}{2} \sum_x \kappa_{px}(\lambda) \kappa_{xr}(\lambda)\right] \mathcal{S}_{rs}(\lambda) \left[\delta_{sq} - \kappa_{sq}(\lambda) + \frac{1}{2} \sum_y \kappa_{sy}(\lambda) \kappa_{yq}(\lambda)\right]
\end{aligned} \tag{29}
$$

For derivative of ON condition, only first order expansion is needed.

$$
\begin{aligned}
S_{pq} =& \sum_{rs} \left[\delta_{pr} + \kappa_{pr}(\lambda)\right] \mathcal{S}_{rs}(\lambda) \left[\delta_{sq} - \kappa_{sq}(\lambda)\right] \\
=& \sum_{rs} \delta_{pr} \mathcal{S}_{rs}(\lambda) \delta_{sq} - \sum_{rs} \delta_{pr} \mathcal{S}_{rs}(\lambda) \kappa_{sq}(\lambda) + \sum_{rs} \kappa_{pr}(\lambda) \mathcal{S}_{rs}(\lambda) \delta_{sq} - \sum_{rs} \kappa_{pr}(\lambda) \mathcal{S}_{rs}(\lambda) \kappa_{sq}(\lambda)
\end{aligned} \tag{30}
$$

Taking derivative w.r.t. perturbation on both sides (noting that $\boldsymbol{\mathcal{S}}(0) = \mathbf{I}$ and $\boldsymbol{\kappa}(\lambda = 0) = \mathbf{0}$):

$$\begin{aligned}\frac{\partial S_{pq}}{\partial \lambda}\Big|_{\lambda=0} =& \sum_{rs} \delta_{pr}\delta_{sq}\frac{\partial \mathcal{S}_{rs}}{\partial \lambda}\Big|_{\lambda=0} - \sum_{rs} \delta_{pr}\mathcal{S}_{rs}(\lambda)\frac{\partial \kappa_{sq}}{\partial \lambda}\Big|_{\lambda=0} + \sum_{rs} \frac{\partial \kappa_{pr}}{\partial \lambda}\mathcal{S}_{rs}(\lambda)\delta_{sq}\Big|_{\lambda=0} \\ =& \mathcal{S}^{\lambda}_{pq} - \sum_{s} \mathcal{S}_{ps}\kappa^{\lambda}_{sq}\Big|_{\lambda=0} + \sum_{r} \kappa^{\lambda}_{pr}\mathcal{S}_{rq}\Big|_{\lambda=0} \\ =& \mathcal{S}^{\lambda}_{pq} - \kappa^{\lambda}_{pq} + \kappa^{\lambda}_{pq} \\ =& \mathcal{S}^{\lambda}_{pq} \end{aligned} \tag{31}$$

Hence the perturbed orthonormality becomes (need to enforce this explicitly):

$$\boldsymbol{\mathcal{S}}^{\lambda} = \mathbf{C}^{\dagger}(0)\mathbf{S}^{\mathrm{AO},\lambda}\mathbf{C}(0) = \mathbf{0} \tag{32}$$

This looks weird.

1.4 Z-Vector Equation (Improved Exponential Parameterization)

$$\begin{aligned}\mathbf{C}(\lambda) =& \mathbf{C}(0)\mathbf{U}(\lambda) && (33)\\ \mathbf{U}(\lambda) =& \boldsymbol{\mathcal{S}}^{-\frac{1}{2}}(\lambda)\exp[-\boldsymbol{\kappa}(\lambda)] && (34)\\ \boldsymbol{\mathcal{S}}(\lambda) =& \mathbf{C}^{\dagger}(0)\mathbf{S}^{\mathrm{AO}}(\lambda)\mathbf{C}(0) && (35)\end{aligned}$$

We need to consider the fact that the canonical AO basis is no longer normalised upon external perturbation. The $\boldsymbol{\mathcal{S}}^{-\frac{1}{2}}$ part takes care of the normalisation, and the exponential part ensures the MO rotation is unitary (i.e. preserves orthonormality).

Only up to second derivative is needed, hence we can truncate the exponential expansion in $\boldsymbol{\kappa}$ to quadratic term:

$$\exp(-\boldsymbol{\kappa}) = \mathbf{I} - \boldsymbol{\kappa} + \frac{1}{2}\boldsymbol{\kappa}^2 \tag{36}$$

Then the relevant integrals could be expressed as:

$$\begin{aligned}\mathbf{h} =& \mathbf{C}^{\dagger}(\lambda)\mathbf{h}^{\mathrm{AO}}(\lambda)\mathbf{C}(\lambda)\\ =& \exp[\boldsymbol{\kappa}(\lambda)]\boldsymbol{\mathcal{S}}^{-\frac{1}{2}\dagger}(\lambda)\mathbf{C}^{\dagger}(0)\mathbf{h}^{\mathrm{AO}}(\lambda)\mathbf{C}(0)\boldsymbol{\mathcal{S}}^{-\frac{1}{2}}(\lambda)\exp[-\boldsymbol{\kappa}(\lambda)]\\ =& \big(\mathbf{I}+\boldsymbol{\kappa}+\frac{1}{2}\boldsymbol{\kappa}^2\big)\boldsymbol{\mathcal{S}}^{-\frac{1}{2}\dagger}(\lambda)\mathbf{C}^{\dagger}(0)\mathbf{h}^{\mathrm{AO}}(\lambda)\mathbf{C}(0)\boldsymbol{\mathcal{S}}^{-\frac{1}{2}}(\lambda)\big(\mathbf{I}-\boldsymbol{\kappa}+\frac{1}{2}\boldsymbol{\kappa}^2\big) && (37)\end{aligned}$$

$$\big(\mathbf{I}+\boldsymbol{\kappa}+\frac{1}{2}\boldsymbol{\kappa}^2\big)_{pq} = \delta_{pq} + \kappa_{pq} + \frac{1}{2}\sum_x \kappa_{px}\kappa_{xq} \tag{38}$$

$$\begin{aligned}\frac{\partial \delta_{pq}}{\partial \kappa_{rs}} =& 0 && (39)\\ \frac{\partial \kappa_{pq}}{\partial \kappa_{rs}} =& \delta_{pr}\delta_{qs} && (40)\end{aligned}$$

$$\begin{aligned}h_{pq} =& \sum_{\mu\nu} C^*_{\mu p}(\lambda)h^{\mathrm{AO}}_{\mu\nu}(\lambda)C_{\nu q}(\lambda)\\ =& \sum_{\mu\nu rs} C^*_{\mu r}(0)U^*_{rp}(\lambda)h^{\mathrm{AO}}_{\mu\nu}(\lambda)C_{vs}(0)U_{sq}(\lambda)\\ =& \sum_{\mu\nu rstu} C^*_{\mu r}\mathcal{S}_{rt}^{-\frac{1}{2}*}\exp[-\boldsymbol{\kappa}]^*_{tp}h^{\mathrm{AO}}_{\mu\nu}C_{\nu s}\mathcal{S}_{su}^{-\frac{1}{2}}\exp[-\boldsymbol{\kappa}]_{uq} && (41)\\ =& \sum_{\mu\nu rstu} C^*_{\mu r}\mathcal{S}_{rt}^{-\frac{1}{2}*}\exp[\boldsymbol{\kappa}]_{pt}h^{\mathrm{AO}}_{\mu\nu}C_{\nu s}\mathcal{S}_{su}^{-\frac{1}{2}}\exp[-\boldsymbol{\kappa}]_{uq}\\ =& \sum_{\mu\nu rstu} C^*_{\mu r}\mathcal{S}_{rt}^{-\frac{1}{2}*}\left[\delta_{pt}+\kappa_{pt}+\dots\right]h^{\mathrm{AO}}_{\mu\nu}C_{\nu s}\mathcal{S}_{su}^{-\frac{1}{2}}\left[\delta_{uq}-\kappa_{uq}+\dots\right]\\ =& \sum_{\mu\nu rstu} C^*_{\mu r}\mathcal{S}_{rt}^{-\frac{1}{2}*}h^{\mathrm{AO}}_{\mu\nu}C_{\nu s}\mathcal{S}_{su}^{-\frac{1}{2}}\left[\delta_{pt}\delta_{uq}-\delta_{pt}\kappa_{uq}+\delta_{uq}\kappa_{pt}-\kappa_{pt}\kappa_{uq}\right] && (42)\end{aligned}$$

By $\boldsymbol{\kappa}(\lambda=0)=\mathbf{0}$, we only need to expand the exponential to first order when taking derivative w.r.t. $\boldsymbol{\kappa}$:

$$\frac{\partial h_{pq}}{\partial \kappa_{vw}}\Big|_{\lambda=0} = \sum_{\mu\nu rstu} C^*_{\mu r}\mathcal{S}_{rt}^{-\frac{1}{2}*}h^{\mathrm{AO}}_{\mu\nu}C_{\nu s}\mathcal{S}_{su}^{-\frac{1}{2}}\left(0-\delta_{pt}\frac{\partial\kappa_{uq}}{\partial\kappa_{vw}}\Big|_{\lambda=0}+\delta_{uq}\frac{\partial\kappa_{pt}}{\partial\kappa_{vw}}\Big|_{\lambda=0}\right)$$

$$= \sum_{\mu\nu rstu} C^*_{\mu r}\mathcal{S}^{-\frac{1}{2}*}_{rt} h^{\mathrm{AO}}_{\mu\nu} C_{\nu s}\mathcal{S}^{-\frac{1}{2}}_{su}\left(-\delta_{pt}\delta_{uv}\delta_{qw} + \delta_{uq}\delta_{pv}\delta_{tw}\right) \tag{43}$$

Note that $\boldsymbol{\mathcal{S}}(\lambda=0) = \mathbf{U}(\lambda=0) = \mathbf{I}$, then:

$$\begin{aligned}
\frac{\partial h_{pq}}{\partial \kappa_{vw}}\Big|_{\lambda=0} &= \sum_{\mu\nu rstu} C^*_{\mu r}\delta_{rt} h^{\mathrm{AO}}_{\mu\nu} C_{vs}\delta_{su}\delta_{uq}\delta_{pv}\delta_{tw} - \sum_{\mu\nu rstu} C^*_{\mu r}\delta_{rt} h^{\mathrm{AO}}_{\mu\nu} C_{\nu s}\delta_{su}\delta_{pt}\delta_{uv}\delta_{qw} \\
&= \sum_{\mu\nu} C^*_{\mu w} h^{\mathrm{AO}}_{\mu\nu} C_{\nu q}\delta_{pv} - \sum_{\mu\nu} C^*_{\mu p} h^{\mathrm{AO}}_{\mu\nu} C_{\nu v}\delta_{qw} \\
&= h_{wq}\delta_{pv} - h_{pv}\delta_{qw}
\end{aligned} \tag{44}$$

Change the indices for convenience (and using the fact that the Hamiltonian is Hermitian):

$$\frac{\partial h_{pq}}{\partial \kappa_{rs}}\Big|_{\lambda=0} = h_{qs}\delta_{pr} - h_{pr}\delta_{qs} \tag{45}$$

hence:

$$\sum_{pq}\frac{\partial h_{pq}}{\partial \kappa_{rs}}\Big|_{\lambda=0} = \sum_{pq} h_{qs}\delta_{pr} - h_{pr}\delta_{qs} \tag{46}$$

Now the two-electron integral:

$$\begin{aligned}
\langle pq||rs\rangle &= \sum_{\mu\nu\sigma\tau} C^*_{\mu p}C^*_{\nu q}\langle\mu\nu||\sigma\tau\rangle C_{\sigma r}C_{\tau s} \\
&= \sum_{\mu\nu\sigma\tau}\sum_{tuvw} C^*_{\mu t}U^*_{tp}C^*_{\nu u}U^*_{uq}\langle\mu\nu||\sigma\tau\rangle C_{\sigma v}U_{vr}C_{\tau w}U_{ws} \\
&= \sum_{\mu\nu\sigma\tau}\sum_{tuvw}\sum_{ghmn} C^*_{\mu t}\mathcal{S}^{-\frac{1}{2}*}_{tg}\exp[-\boldsymbol{\kappa}]^*_{gp} C^*_{\nu u}\mathcal{S}^{-\frac{1}{2}*}_{uh}\exp[-\boldsymbol{\kappa}]^*_{hq} \\
&\quad \langle\mu\nu||\sigma\tau\rangle C_{\sigma v}\mathcal{S}^{-\frac{1}{2}}_{vm}\exp[-\boldsymbol{\kappa}]_{mr} C_{\tau w}\mathcal{S}^{-\frac{1}{2}}_{wn}\exp[-\boldsymbol{\kappa}]_{ns} \\
&= \sum_{\mu\nu\sigma\tau}\sum_{tuvw}\sum_{ghmn} C^*_{\mu t}\mathcal{S}^{-\frac{1}{2}*}_{tg}\left(\delta_{pg}+\kappa_{pg}\right) C^*_{\nu u}\mathcal{S}^{-\frac{1}{2}*}_{uh}\left(\delta_{qh}+\kappa_{qh}\right) \\
&\quad \langle\mu\nu||\sigma\tau\rangle C_{\sigma v}\mathcal{S}^{-\frac{1}{2}}_{vm}\left(\delta_{mr}-\kappa_{mr}\right) C_{\tau w}\mathcal{S}^{-\frac{1}{2}}_{wn}\left(\delta_{ns}-\kappa_{ns}\right) \\
&= \sum_{\mu\nu\sigma\tau}\sum_{tuvw}\sum_{ghmn} C^*_{\mu t}\mathcal{S}^{-\frac{1}{2}*}_{tg} C^*_{\nu u}\mathcal{S}^{-\frac{1}{2}*}_{uh}\langle\mu\nu||\sigma\tau\rangle C_{\sigma v}\mathcal{S}^{-\frac{1}{2}}_{vm} C_{\tau w}\mathcal{S}^{-\frac{1}{2}}_{wn}\big(\kappa_{pg}\delta_{qh}\delta_{mr}\delta_{ns} \\
&\quad + \kappa_{qh}\delta_{pg}\delta_{mr}\delta_{ns} - \kappa_{mr}\delta_{pg}\delta_{qh}\delta_{ns} - \kappa_{ns}\delta_{pg}\delta_{qh}\delta_{mr} + \ldots\big)
\end{aligned} \tag{47}$$

now take derivative w.r.t. $\boldsymbol{\kappa}$, noting that $\mathbf{U}(\lambda=0) = \boldsymbol{\mathcal{S}}(\lambda=0) = \mathbf{I}$:

$$\begin{aligned}
\frac{\partial\langle pq||rs\rangle}{\partial \kappa_{xy}}\Big|_{\lambda=0} &= \sum_{\mu\nu\sigma\tau}\sum_{tuvw}\sum_{ghmn} C^*_{\mu t}C^*_{\nu u}\langle\mu\nu||\sigma\tau\rangle C_{\sigma v}C_{\tau w}\delta_{tg}\delta_{uh}\delta_{vm}\delta_{wn}\Big(\frac{\partial \kappa_{pg}}{\partial \kappa_{xy}}\Big|_{\lambda=0}\delta_{qh}\delta_{mr}\delta_{ns} \\
&\quad + \frac{\partial \kappa_{qh}}{\partial \kappa_{xy}}\Big|_{\lambda=0}\delta_{pg}\delta_{mr}\delta_{ns} - \frac{\partial \kappa_{mr}}{\partial \kappa_{xy}}\Big|_{\lambda=0}\delta_{pg}\delta_{qh}\delta_{ns} - \frac{\partial \kappa_{ns}}{\partial \kappa_{xy}}\delta_{pg}\delta_{qh}\delta_{mr}\Big) \\
&= \sum_{\mu\nu\sigma\tau}\sum_{tuvw}\sum_{ghmn} C^*_{\mu t}C^*_{\nu u}\langle\mu\nu||\sigma\tau\rangle C_{\sigma v}C_{\tau w}\delta_{tg}\delta_{uh}\delta_{vm}\delta_{wn}\delta_{px}\delta_{gy}\delta_{qh}\delta_{mr}\delta_{ns} \\
&\quad + \sum_{\mu\nu\sigma\tau}\sum_{tuvw}\sum_{ghmn} C^*_{\mu t}C^*_{\nu u}\langle\mu\nu||\sigma\tau\rangle C_{\sigma v}C_{\tau w}\delta_{tg}\delta_{uh}\delta_{vm}\delta_{wn}\delta_{qx}\delta_{hy}\delta_{pg}\delta_{mr}\delta_{ns} \\
&\quad - \sum_{\mu\nu\sigma\tau}\sum_{tuvw}\sum_{ghmn} C^*_{\mu t}C^*_{\nu u}\langle\mu\nu||\sigma\tau\rangle C_{\sigma v}C_{\tau w}\delta_{tg}\delta_{uh}\delta_{vm}\delta_{wn}\delta_{mx}\delta_{ry}\delta_{pg}\delta_{qh}\delta_{ns}
\end{aligned}$$

$$
\begin{aligned}
&-\sum_{\mu\nu\sigma\tau}\sum_{tuvw}\sum_{ghmn} C^*_{\mu t}C^*_{\nu u}\langle\mu\nu||\sigma\tau\rangle C_{\sigma v}C_{\tau w}\delta_{tg}\delta_{uh}\delta_{vm}\delta_{wn}\delta_{nx}\delta_{sy}\delta_{pg}\delta_{qh}\delta_{mr}\\
=&\sum_{\mu\nu\sigma\tau} C^*_{\mu y}C^*_{\nu q}\langle\mu\nu||\sigma\tau\rangle C_{\sigma r}C_{\tau s}\delta_{px} + \sum_{\mu\nu\sigma\tau} C^*_{\mu p}C^*_{\nu y}\langle\mu\nu||\sigma\tau\rangle C_{\sigma r}C_{\tau s}\delta_{qx}\\
&-\sum_{\mu\nu\sigma\tau} C^*_{\mu p}C^*_{\nu q}\langle\mu\nu||\sigma\tau\rangle C_{\sigma x}C_{\tau s}\delta_{ry} - \sum_{\mu\nu\sigma\tau} C^*_{\mu p}C^*_{\nu q}\langle\mu\nu||\sigma\tau\rangle C_{\sigma r}C_{\tau x}\delta_{sy}\\
=&\langle yq||rs\rangle\delta_{px} + \langle py||rs\rangle\delta_{qx} - \langle pq||xs\rangle\delta_{ry} - \langle pq||rx\rangle\delta_{sy}
\end{aligned}
\tag{48}
$$

Therefore, the orbital response for fock matrix is:

$$
\begin{aligned}
\frac{\partial f_{ai}}{\partial\kappa_{pq}}\Big|_{\lambda=0} =&\frac{\partial h_{ai}}{\partial\kappa_{pq}}\Big|_{\lambda=0} + \sum_k \frac{\partial\langle ak||ik\rangle}{\partial\kappa_{pq}}\Big|_{\lambda=0}\\
=&h_{iq}\delta_{ap} - h_{ap}\delta_{iq} + \sum_k\langle qk||ik\rangle\delta_{ap} + \sum_k\langle aq||ik\rangle\delta_{pk}\\
&-\sum_k\langle ak||pk\rangle\delta_{iq} - \sum_k\langle ak||ip\rangle\delta_{kq}\\
=&\delta_{ap}\Big(h_{iq} + \sum_k\langle qk||ik\rangle\Big) - \delta_{iq}\Big(h_{ap} + \sum_k\langle ak||pk\rangle\Big)\\
&+\sum_k\langle aq||ik\rangle\delta_{pk} - \sum_k\langle ak||ip\rangle\delta_{qk}\\
=&\delta_{ap}f_{iq} - \delta_{iq}f_{ap} + \langle aq||ip\rangle - \langle aq||ip\rangle\\
=&\delta_{ap}\delta_{iq}\varepsilon_i - \delta_{iq}\delta_{ap}\varepsilon_a\\
=&(\varepsilon_i - \varepsilon_a)\delta_{ap}\delta_{iq}
\end{aligned}
\tag{49}
$$

thus the only non-redundant orbital response is:

$$
\frac{\partial f_{ai}}{\partial\kappa_{bj}}\Big|_{\lambda=0} = (\varepsilon_i - \varepsilon_a)\delta_{ab}\delta_{ij}
\tag{50}
$$

Then, the orbital response for the Hylleraas functional:

$$
\begin{aligned}
E_{\mathrm{H}} =&\sum_{ij} h_{ij}\gamma^{\mathrm{H}}_{ij} + \sum_{ab} h_{ab}\gamma^{\mathrm{H}}_{ab} + \sum_{ijab}\langle ab||ij\rangle(\Gamma^{\mathrm{H}})^{ab}_{ij} + \sum_{ijab}\langle ij||ab\rangle(\Gamma^{\mathrm{H}})^{ij}_{ab}\\
&+\sum_{ijkl}\langle ij||kl\rangle(\Gamma^{\mathrm{H}})^{ij}_{kl} + \sum_{ijab}\langle ai||bj\rangle(\Gamma^{\mathrm{H}})^{ai}_{bj}
\end{aligned}
\tag{51}
$$

$$
\frac{\partial h_{ij}}{\partial\kappa_{pq}}\Big|_{\lambda=0} = h_{jq}\delta_{ip} - h_{ip}\delta_{jq}
\tag{52}
$$

$$
\frac{\partial h_{ab}}{\partial\kappa_{pq}}\Big|_{\lambda=0} = h_{bq}\delta_{ap} - h_{ap}\delta_{bq}
\tag{53}
$$

$$
\frac{\partial\langle ab||ij\rangle}{\partial\kappa_{pq}}\Big|_{\lambda=0} = \langle qb||ij\rangle\delta_{ap} + \langle aq||ij\rangle\delta_{bp} - \langle ab||pj\rangle\delta_{iq} - \langle ab||ip\rangle\delta_{jq}
\tag{54}
$$

$$
\frac{\partial\langle ij||ab\rangle}{\partial\kappa_{pq}}\Big|_{\lambda=0} = \langle qj||ab\rangle\delta_{ip} + \langle iq||ab\rangle\delta_{jp} - \langle ij||pb\rangle\delta_{aq} - \langle ij||ap\rangle\delta_{bq}
\tag{55}
$$

$$
\frac{\partial\langle ij||kl\rangle}{\partial\kappa_{pq}}\Big|_{\lambda=0} = \langle qj||kl\rangle\delta_{ip} + \langle iq||kl\rangle\delta_{jp} - \langle ij||pl\rangle\delta_{kq} - \langle ij||kp\rangle\delta_{lq}
\tag{56}
$$

$$\frac{\partial\langle ai||bj\rangle}{\partial\kappa_{pq}}\Big|_{\lambda=0} = \langle qi||bj\rangle\delta_{ap} + \langle aq||bj\rangle\delta_{ip} - \langle ai||pj\rangle\delta_{bq} - \langle ai||bp\rangle\delta_{jq} \tag{57}$$

Evaluating the constituent parts of Hylleraas functional response to orbital rotation ($e \in$ external and $m \in$ internal):

$$\begin{aligned}\sum_{ij}\frac{\partial h_{ij}}{\partial\kappa_{em}}\gamma^{\mathrm{H}}_{ij}\Big|_{\lambda=0} &= \sum_{ij}(\cancel{h_{jm}\delta_{ie}} - h_{ie}\delta_{jm})\gamma^{\mathrm{H}}_{ij} \\ &= -\sum_{i} h_{ie}\gamma^{\mathrm{H}}_{im}\end{aligned} \tag{58}$$

$$\begin{aligned}\sum_{ij}\frac{\partial h_{ij}}{\partial\kappa^*_{em}}\gamma^{\mathrm{H}}_{ij}\Big|_{\lambda=0} &= -\sum_{ij}\frac{\partial h_{ij}}{\partial\kappa_{me}}\gamma^{\mathrm{H}}_{ij}\Big|_{\lambda=0} \\ &= -\sum_{ij}(h_{je}\delta_{im} - \cancel{h_{im}\delta_{je}})\gamma^{\mathrm{H}}_{ij} \\ &= -\sum_{j} h_{je}\gamma^{\mathrm{H}}_{mj} = -\sum_{i} h_{ie}\gamma^{\mathrm{H}}_{mi}\end{aligned} \tag{59}$$

$$\begin{aligned}\sum_{ab}\frac{\partial h_{ab}}{\partial\kappa_{em}}\gamma^{\mathrm{H}}_{ab}\Big|_{\lambda=0} &= \sum_{ab}(h_{bm}\delta_{ae} - \cancel{h_{ae}\delta_{bm}})\gamma^{\mathrm{H}}_{ab} \\ &= \sum_{b} h_{bm}\gamma^{\mathrm{H}}_{eb} = \sum_{a} h_{am}\gamma^{\mathrm{H}}_{ea}\end{aligned} \tag{60}$$

$$\begin{aligned}\sum_{ab}\frac{\partial h_{ab}}{\partial\kappa^*_{em}}\gamma^{\mathrm{H}}_{ab}\Big|_{\lambda=0} &= -\sum_{ab}\frac{\partial h_{ab}}{\partial\kappa_{me}}\gamma^{\mathrm{H}}_{ab}\Big|_{\lambda=0} \\ &= -\sum_{ab}(\cancel{h_{be}\delta_{am}} - h_{am}\delta_{be})\gamma^{\mathrm{H}}_{ab} \\ &= \sum_{a} h_{am}\gamma^{\mathrm{H}}_{ae}\end{aligned} \tag{61}$$

$$\begin{aligned}&\sum_{ijab}\frac{\partial\langle ab||ij\rangle}{\partial\kappa_{em}}\left(\Gamma^{\mathrm{H}}\right)^{ab}_{ij}\Big|_{\lambda=0} \\ =&\sum_{ijab}\Big(\langle mb||ij\rangle\delta_{ae} + \langle am||ij\rangle\delta_{be} - \langle ab||ej\rangle\delta_{im} - \langle ab||ie\rangle\delta_{jm}\Big)(\Gamma^{\mathrm{H}})^{ab}_{ij} \\ =&\sum_{ijb}\langle mb||ij\rangle(\Gamma^{\mathrm{H}})^{eb}_{ij} + \sum_{ija}\langle am||ij\rangle(\Gamma^{\mathrm{H}})^{ae}_{ij} - \sum_{jab}\langle ab||ej\rangle(\Gamma^{\mathrm{H}})^{ab}_{mj} - \sum_{iab}\langle ab||ie\rangle(\Gamma^{\mathrm{H}})^{ab}_{im} \\ =&\sum_{ija}\langle ma||ij\rangle(\Gamma^{\mathrm{H}})^{ea}_{ij} + \sum_{ija}\langle am||ij\rangle(\Gamma^{\mathrm{H}})^{ae}_{ij} - \sum_{iab}\langle ab||ei\rangle(\Gamma^{\mathrm{H}})^{ab}_{mi} - \sum_{iab}\langle ab||ie\rangle(\Gamma^{\mathrm{H}})^{ab}_{im} \\ =&\sum_{ija}\langle am||ji\rangle(\Gamma^{\mathrm{H}})^{ea}_{ij} + \sum_{ija}\langle am||ji\rangle(\Gamma^{\mathrm{H}})^{ae}_{ji} - \sum_{iab}\langle ab||ei\rangle(\Gamma^{\mathrm{H}})^{ab}_{mi} - \sum_{iab}\langle ab||ei\rangle(\Gamma^{\mathrm{H}})^{ba}_{im} \\ =&2\sum_{ija}\langle am||ji\rangle(\Gamma^{\mathrm{H}})^{ea}_{ij} - 2\sum_{iab}\langle ab||ei\rangle(\Gamma^{\mathrm{H}})^{ab}_{mi}\end{aligned} \tag{62}$$

in which the symmetry of MP2 amplitudes is exploited:

$$T^{ab}_{ij} = T^{ba}_{ji} \Leftrightarrow (\Gamma^{\mathrm{H}})^{ab}_{ij} = (\Gamma^{\mathrm{H}})^{ba}_{ji} \tag{63}$$

$$\sum_{ijab}\frac{\partial\langle ab||ij\rangle}{\partial\kappa^*_{em}}\left(\Gamma^{\mathrm{H}}\right)^{ab}_{ij}\Big|_{\lambda=0}$$

$$
\begin{aligned}
&= -\sum_{ijab} \frac{\partial\langle ab||ij\rangle}{\partial\kappa_{me}} \left(\Gamma^{\mathrm{H}}\right)^{ab}_{ij}\Big|_{\lambda=0} \\
&= \sum_{ijab} \Big(\Big)
\end{aligned}
\tag{64}
$$

Similarly:

$$
\begin{aligned}
\sum_{ijab} \frac{\partial\langle ij||ab\rangle}{\partial\kappa_{em}} \Gamma^{ij}_{ab}\Big|_{\lambda=0} =& \sum_{ijab} \Big(\cancel{\langle mj||ab\rangle}\delta_{ie} + \cancel{\langle im||ab\rangle}\delta_{je} - \cancel{\langle ij||eb\rangle}\delta_{am} - \cancel{\langle ij||ae\rangle}\delta_{bm} \Big) \Gamma^{ij}_{ab} \\
=& 0
\end{aligned}
\tag{65}
$$

Then:

$$
\begin{aligned}
\sum_{ijkl} \frac{\partial\langle ij||kl\rangle}{\partial\kappa_{em}} \Gamma^{ij}_{kl}\Big|_{\lambda=0} =& \sum_{ijkl} \Big(\cancel{\langle mj||kl\rangle}\delta_{ie} + \cancel{\langle im||kl\rangle}\delta_{je} - \langle ij||el\rangle\delta_{km} - \langle ij||ke\rangle\delta_{lm} \Big) \Gamma^{ij}_{kl} \\
=& -\sum_{ijl} \langle ij||el\rangle \Gamma^{ij}_{ml} - \sum_{ijk} \langle ij||ke\rangle \Gamma^{ij}_{km} \\
=& -\sum_{ijk} \langle ij||ek\rangle \Gamma^{ij}_{mk} - \sum_{ijk} \langle ij||ek\rangle \Gamma^{ji}_{km}
\end{aligned}
\tag{66}
$$

No symmetry for Γ^{ij}_{kl} could be used to simplify the expression.

$$
\begin{aligned}
\sum_{ijab} \frac{\partial\langle ai||bj\rangle}{\partial\kappa_{em}} \Gamma^{ai}_{bj}\Big|_{\lambda=0} =& \sum_{ijab} \Big(\langle mi||bj\rangle\delta_{ae} + \cancel{\langle am||bj\rangle}\delta_{ie} - \cancel{\langle ai||ej\rangle}\delta_{bm} - \langle ai||be\rangle\delta_{jm} \Big) \Gamma^{ai}_{bj} \\
=& \sum_{ijb} \langle mi||bj\rangle \Gamma^{ei}_{bj} - \sum_{iab} \langle ai||be\rangle \Gamma^{ai}_{bm}
\end{aligned}
\tag{67}
$$

Therefore, the overall Hylleraas response is:

$$
\begin{aligned}
\frac{\partial E_{\mathrm{H}}}{\partial\kappa_{bj}}\Big|_{\lambda=0} =& \sum_{a} h_{aj}\gamma_{ba} - \sum_{i} h_{ib}\gamma_{ij} \\
&+ 2\sum_{ika} \langle aj||ki\rangle \Gamma^{ba}_{ik} - 2\sum_{iac} \langle ac||bi\rangle \Gamma^{ac}_{ji} \\
&- \sum_{ikl} \langle ik||bl\rangle \Gamma^{ik}_{jl} - \sum_{ikl} \langle ik||bl\rangle \Gamma^{ki}_{lj} \\
&+ \sum_{ikc} \langle ji||ck\rangle \Gamma^{bi}_{ck} - \sum_{iac} \langle ai||cb\rangle \Gamma^{ai}_{cj}
\end{aligned}
\tag{68}
$$

For the sake of completeness, we can verify that E_{HF} response to orbital rotation is zero, as HF energy is variationally determined.

$$
E_{\mathrm{HF}} = \sum_{i} h_{ii} + \frac{1}{2}\sum_{ik} \langle ik||ik\rangle \tag{69}
$$

$$
\begin{aligned}
\frac{\partial E_{\mathrm{HF}}}{\partial\kappa_{bj}}\Big|_{\lambda=0} =& \sum_{i} \frac{\partial h_{ii}}{\partial\kappa_{bj}}\Big|_{\lambda=0} + \frac{1}{2}\sum_{ik} \frac{\partial\langle ik||ik\rangle}{\partial\kappa_{bj}}\Big|_{\lambda=0} \\
=& \sum_{i} \left(\cancel{h_{ij}\delta_{ib}} - h_{ib}\delta_{ij} \right)
\end{aligned}
$$

$$
\begin{aligned}
&+\frac{1}{2}\sum_{ik}\left(\cancel{\langle jk||ik\rangle\delta_{ib}}+\cancel{\langle ij||ik\rangle\delta_{kb}}-\langle ik||bk\rangle\delta_{ij}-\langle ik||ib\rangle\delta_{kj}\right)\\
=&-h_{jb}-\frac{1}{2}\sum_{k}\langle jk||bk\rangle-\frac{1}{2}\sum_{i}\langle ij||ib\rangle\\
=&-h_{jb}-\sum_{i}\langle ji||bi\rangle\\
=&-f_{jb}\\
=&0
\end{aligned}
\tag{70}
$$

The Lagrangian constraint on orbital rotation:

$$
\frac{\partial\mathcal{L}_{\text{MP2}}}{\partial\kappa_{bj}}\Big|_{\lambda=0}=\frac{\partial E_{\text{HF}}}{\partial\kappa_{bj}}\Big|_{\lambda=0}+\frac{\partial E_{\text{H}}}{\partial\kappa_{bj}}\Big|_{\lambda=0}+\sum_{ai}z_{ai}\frac{\partial f_{ai}}{\partial\kappa_{bj}}\Big|_{\lambda=0}=0
\tag{71}
$$

Now the Z-Vector equation becomes:

$$
\sum_{ai}z_{ai}\frac{\partial f_{ai}}{\partial\kappa_{bj}}\Big|_{\lambda=0}=-\frac{\partial E_{\text{H}}}{\partial\kappa_{bj}}\Big|_{\lambda=0}
\tag{72}
$$

in which the RHS is the orbital gradient for MP2.

$$
\begin{aligned}
\text{LHS}=&\sum_{ai}(\varepsilon_i-\varepsilon_a)\delta_{ab}\delta_{ij}z_{ai}\\
=&(\varepsilon_j-\varepsilon_b)z_{bj}
\end{aligned}
\tag{73}
$$

The RHS (Hylleraas response) has been worked out previously. Hence the Z-Vector equation:

$$
\begin{aligned}
(\varepsilon_b-\varepsilon_j)z_{bj}=&\sum_{a}h_{aj}\gamma_{ba}-\sum_{i}h_{ib}\gamma_{ij}\\
&+2\sum_{ika}\langle aj||ki\rangle\Gamma^{ba}_{ik}-2\sum_{iac}\langle ac||bi\rangle\Gamma^{ac}_{ji}\\
&-\sum_{ikl}\langle ik||bl\rangle\Gamma^{ik}_{jl}-\sum_{ikl}\langle ik||bl\rangle\Gamma^{ki}_{lj}\\
&+\sum_{ikc}\langle ji||ck\rangle\Gamma^{bi}_{ck}-\sum_{iac}\langle ai||cb\rangle\Gamma^{ai}_{cj}
\end{aligned}
\tag{74}
$$

2 !!EUREKA: Summary of MP2 Gradient

The Lagrangian for MP2 could be written as (with $z_{ai} = z_{ia}^*$):

$$\begin{aligned}\mathcal{L}_{\text{MP2}} =& E_{\text{HF}} + E_{\text{H}} + \frac{1}{2}\sum_{ai}\left(z_{ai}f_{ai} + z_{ai}^* f_{ai}^*\right) \\ =& \sum_{pq} h_{pq}\gamma_{pq} + \sum_{pqrs}\Gamma_{rs}^{pq}\langle pq||rs\rangle + \frac{1}{2}\sum_{ai}\left(z_{ai}f_{ai} + z_{ai}^* f_{ai}^*\right)\end{aligned} \tag{75}$$

Constraints:

$$\frac{\partial\mathcal{L}_{\text{MP2}}}{\partial z_{ai}} = f_{ai} = 0 \qquad \text{Hatree-Fock Condition} \tag{76}$$

$$\frac{\partial\mathcal{L}_{\text{MP2}}}{\partial T_{ij}^{ab}} = \frac{\partial E_{\text{H}}}{\partial T_{ij}^{ab}} = 0 \qquad \text{MP2 Condition} \tag{77}$$

$$\frac{\partial\mathcal{L}_{\text{MP2}}}{\partial \kappa_{bj}} = \frac{\partial E_{\text{H}}}{\partial \kappa_{bj}} + \frac{1}{2}\sum_{ai}\left(z_{ai}\frac{\partial f_{ai}}{\partial \kappa_{bj}} + \bar{z}_{ai}\frac{\partial f_{ai}^*}{\partial \kappa_{bj}}\right) = 0 \qquad \text{Z-Vector Equations} \tag{78}$$

Densities:

$$\gamma_{pq} = \gamma_{pq}^{\text{HF}} + \gamma_{pq}^{\text{H}} \tag{79}$$

$$\Gamma_{rs}^{pq} = (\Gamma^{\text{HF}})_{rs}^{pq} + (\Gamma^{\text{H}})_{rs}^{pq} \tag{80}$$

$$\gamma_{ij}^{\text{H}} = \frac{1}{2}\sum_{kab}(T_{jk}^{ab})^* T_{ki}^{ab} \qquad \gamma_{ij}^{\text{HF}} = \delta_{ij} \tag{81}$$

$$\gamma_{ab}^{\text{H}} = -\frac{1}{2}\sum_{ijc}(T_{ij}^{ac})^* T_{ij}^{cb} \tag{82}$$

$$(\Gamma^{\text{H}})_{ij}^{ab} = \frac{1}{2}(T_{ij}^{ab})^* \tag{83}$$

$$(\Gamma^{\text{H}})_{kl}^{ij} = \frac{1}{2}\sum_{mab}(T_{km}^{ab})^* T_{mi}^{ab}\delta_{jl} \qquad (\Gamma^{\text{HF}})_{kl}^{ij} = \frac{1}{2}\delta_{ik}\delta_{jl} \tag{84}$$

$$(\Gamma^{\text{H}})_{bj}^{ai} = -\frac{1}{2}\sum_{klc}(T_{kl}^{ac})^* T_{kl}^{cb}\delta_{ij} \tag{85}$$

2.1 Hartree-Fock

$$f_{ai} = h_{ai} + \sum_j \langle aj||ij\rangle = 0 \tag{86}$$

$$\begin{aligned}E_{\text{HF}} =& \sum_i h_{ii} + \frac{1}{2}\sum_{ij}\langle ij||ij\rangle \\ =& \sum_{i\mu\nu} C_{\mu i}^* C_{\nu i} h_{\mu\nu} + \frac{1}{2}\sum_{ij}\sum_{\mu\nu\sigma\tau} C_{\mu i}^* C_{\nu j}^* C_{\sigma i} C_{\tau j}\langle\mu\nu||\sigma\tau\rangle \\ =& \sum_{\mu\nu} D_{\mu\nu}^{\text{HF}} h_{\mu\nu} + \frac{1}{2}\sum_{\mu\nu\sigma\tau} D_{\mu\sigma}^{\text{HF}} D_{\nu\tau}^{\text{HF}}\langle\mu\nu||\sigma\tau\rangle\end{aligned} \tag{87}$$

2.2 MP2

$$E_{\mathrm{H}} = \sum_{ij} h_{ij}\gamma^{\mathrm{H}}_{ij} + \sum_{ab} h_{ab}\gamma^{\mathrm{H}}_{ab} + \sum_{ijab} \langle ab||ij\rangle (\Gamma^{\mathrm{H}})^{ab}_{ij} + \sum_{ijkl} \langle ij||kl\rangle (\Gamma^{\mathrm{H}})^{ij}_{kl} + \sum_{ijab} \langle ai||bj\rangle (\Gamma^{\mathrm{H}})^{ai}_{bj} \tag{88}$$

$$\sum_{ij} h_{ij}\gamma^{\mathrm{H}}_{ij} = \sum_{ij\mu\nu} C^*_{\mu i} C_{\nu j} h_{\mu\nu}\gamma^{\mathrm{H}}_{ij} \tag{89}$$

$$\sum_{ab} h_{ab}\gamma^{\mathrm{H}}_{ab} = \sum_{ab\mu\nu} C^*_{\mu a} C_{\nu b} h_{\mu\nu}\gamma^{\mathrm{H}}_{ab} \tag{90}$$

$$D^{\mathrm{H}}_{\mu\nu} = \sum_{ij} C^*_{\mu i} C_{\nu j}\gamma^{\mathrm{H}}_{ij} + \sum_{ab} C^*_{\mu a} C_{\nu b}\gamma^{\mathrm{H}}_{ab} \tag{91}$$

$$\frac{\partial \gamma^{\mathrm{H}}_{ij}}{\partial T^{ab}_{ij}} = \tag{92}$$