# 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 $E_{\text{H}}$ is the Hylleraas functional, $C_{\text{Bri}}$ 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:

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

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:

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

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:

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

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

$$\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:

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

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

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

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

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

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

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

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

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

## 1.3 MP2 Stationary Condition

$$\begin{aligned}
0 =& \frac{\partial\mathcal{L}_{\mathrm{MP2}}}{\partial T_{mn}^{ef}}\Big|_{\lambda=0} = \frac{\partial E_{\mathrm{H}}}{\partial T_{mn}^{ef}}\Big|_{\lambda=0}\\
=& \sum_{ij} h_{ij}\frac{\partial\gamma_{ij}^{\mathrm{H}}}{\partial T_{mn}^{ef}}\Big|_{\lambda=0} + \sum_{ab} h_{ab}\frac{\partial\gamma_{ab}^{\mathrm{H}}}{\partial T_{mn}^{ef}}\Big|_{\lambda=0} + \sum_{ijab}\langle ab||ij\rangle\frac{\partial(\Gamma^{\mathrm{H}})_{ij}^{ab}}{\partial T_{mn}^{ef}}\Big|_{\lambda=0}\\
&+ \sum_{ijab}\langle ij||ab\rangle\frac{\partial(\Gamma^{\mathrm{H}})_{ab}^{ij}}{\partial T_{mn}^{ef}}\Big|_{\lambda=0} + \sum_{ijkl}\langle ij||kl\rangle\frac{\partial(\Gamma^{\mathrm{H}})_{kl}^{ij}}{\partial T_{mn}^{ef}}\Big|_{\lambda=0} + \sum_{ijab}\langle ai||bj\rangle\frac{\partial(\Gamma^{\mathrm{H}})_{bj}^{ai}}{\partial T_{mn}^{ef}}\Big|_{\lambda=0}
\end{aligned} \tag{22}$$

$$0 = \frac{\partial\mathcal{L}_{\mathrm{MP2}}}{\partial(T_{mn}^{ef})^*}\Big|_{\lambda=0} = \frac{\partial E_{\mathrm{H}}}{\partial(T_{mn}^{ef})^*}\Big|_{\lambda=0}$$

$$
\begin{aligned}
&= \sum_{ij} h_{ij} \frac{\partial \gamma^{\mathrm{H}}_{ij}}{\partial (T^{ef}_{mn})^*}\Big|_{\lambda=0} + \sum_{ab} h_{ab} \frac{\partial \gamma^{\mathrm{H}}_{ab}}{\partial (T^{ef}_{mn})^*}\Big|_{\lambda=0} + \sum_{ijab} \langle ab||ij\rangle \frac{\partial (\Gamma^{\mathrm{H}})^{ab}_{ij}}{\partial (T^{ef}_{mn})^*}\Big|_{\lambda=0} \\
&\quad + \sum_{ijab} \langle ij||ab\rangle \frac{\partial (\Gamma^{\mathrm{H}})^{ij}_{ab}}{\partial (T^{ef}_{mn})^*}\Big|_{\lambda=0} + \sum_{ijkl} \langle ij||kl\rangle \frac{\partial (\Gamma^{\mathrm{H}})^{ij}_{kl}}{\partial (T^{ef}_{mn})^*}\Big|_{\lambda=0} + \sum_{ijab} \langle ai||bj\rangle \frac{\partial (\Gamma^{\mathrm{H}})^{ai}_{bj}}{\partial (T^{ef}_{mn})^*}\Big|_{\lambda=0}
\end{aligned} \tag{23}
$$

By the permutational symmetry of MP2 amplitudes, i.e. $T^{ab}_{ij} = -T^{ba}_{ij} = -T^{ab}_{ji} = T^{ba}_{ji}$, the amplitude derivative expands as:

$$
\frac{\partial T^{ab}_{ij}}{\partial T^{cd}_{kl}} = \delta_{ac}\delta_{bd}\delta_{ik}\delta_{jl} - \delta_{ac}\delta_{bd}\delta_{il}\delta_{jk} - \delta_{ad}\delta_{bc}\delta_{ik}\delta_{jl} + \delta_{ad}\delta_{bc}\delta_{il}\delta_{jk} \tag{24}
$$

$$
\frac{\partial (T^{ab}_{ij})^*}{\partial (T^{cd}_{kl})^*} = \delta_{ac}\delta_{bd}\delta_{ik}\delta_{jl} - \delta_{ac}\delta_{bd}\delta_{il}\delta_{jk} - \delta_{ad}\delta_{bc}\delta_{ik}\delta_{jl} + \delta_{ad}\delta_{bc}\delta_{il}\delta_{jk} \tag{25}
$$

$$
\frac{\partial T^{ab}_{ij}}{\partial (T^{cd}_{kl})^*} = \frac{\partial (T^{ab}_{ij})^*}{\partial T^{cd}_{kl}} = 0 \tag{26}
$$

Density derivatives:

$$
\begin{aligned}
\frac{\partial \gamma^{\mathrm{H}}_{ij}}{\partial T^{ef}_{mn}} &= \frac{1}{2}\sum_{kab} (T^{ab}_{jk})^* \frac{\partial T^{ab}_{ki}}{\partial T^{ef}_{mn}} \\
&= \frac{1}{2}\sum_{kab} (T^{ab}_{jk})^* \left(\delta_{ae}\delta_{bf}\delta_{km}\delta_{in} - \delta_{af}\delta_{be}\delta_{km}\delta_{in} - \delta_{ae}\delta_{bf}\delta_{kn}\delta_{im} + \delta_{af}\delta_{be}\delta_{kn}\delta_{im}\right) \\
&= \frac{1}{2}(T^{ef}_{jm})^*\delta_{in} - \frac{1}{2}(T^{fe}_{jm})^*\delta_{in} - \frac{1}{2}(T^{ef}_{jn})^*\delta_{im} + \frac{1}{2}(T^{fe}_{jn})^*\delta_{im} \\
&= (T^{ef}_{jm})^*\delta_{in} - (T^{ef}_{jn})^*\delta_{im}
\end{aligned} \tag{27}
$$

$$
\begin{aligned}
\frac{\partial \gamma^{\mathrm{H}}_{ij}}{\partial (T^{ef}_{mn})^*} &= \frac{1}{2}\sum_{kab} \frac{\partial (T^{ab}_{jk})^*}{\partial (T^{ef}_{mn})^*} T^{ab}_{ki} \\
&= \frac{1}{2}\sum_{kab} T^{ab}_{ki} \left(\delta_{ae}\delta_{bf}\delta_{jm}\delta_{kn} - \delta_{af}\delta_{be}\delta_{jm}\delta_{kn} - \delta_{ae}\delta_{bf}\delta_{jn}\delta_{km} + \delta_{af}\delta_{be}\delta_{jn}\delta_{km}\right) \\
&= \frac{1}{2}T^{ef}_{ni}\delta_{jm} - \frac{1}{2}T^{fe}_{ni}\delta_{jm} - \frac{1}{2}T^{ef}_{mi}\delta_{jn} + \frac{1}{2}T^{fe}_{mi}\delta_{jn} \\
&= T^{ef}_{ni}\delta_{jm} - T^{ef}_{mi}\delta_{jn}
\end{aligned} \tag{28}
$$

$$
\begin{aligned}
\frac{\partial \gamma^{\mathrm{H}}_{ab}}{\partial T^{ef}_{mn}} &= -\frac{1}{2}\sum_{ijc} (T^{ac}_{ij})^* \frac{\partial T^{cb}_{ij}}{\partial T^{ef}_{mn}} \\
&= -\frac{1}{2}\sum_{ijc} (T^{ac}_{ij})^* \left(\delta_{ce}\delta_{bf}\delta_{im}\delta_{jn} - \delta_{cf}\delta_{be}\delta_{im}\delta_{jn} - \delta_{ce}\delta_{bf}\delta_{in}\delta_{jm} + \delta_{cf}\delta_{be}\delta_{in}\delta_{jm}\right) \\
&= -\frac{1}{2}(T^{ae}_{mn})^*\delta_{bf} + \frac{1}{2}(T^{af}_{mn})^*\delta_{be} + \frac{1}{2}(T^{ae}_{nm})^*\delta_{bf} - \frac{1}{2}(T^{af}_{nm})^*\delta_{be} \\
&= (T^{af}_{mn})^*\delta_{be} - (T^{ae}_{mn})^*\delta_{bf}
\end{aligned} \tag{29}
$$

$$
\begin{aligned}
\frac{\partial \gamma^{\mathrm{H}}_{ab}}{\partial (T^{ef}_{mn})^*} &= -\frac{1}{2}\sum_{ijc} \frac{\partial (T^{ac}_{ij})^*}{\partial (T^{ef}_{mn})^*} T^{cb}_{ij} \\
&= -\frac{1}{2}\sum_{ijc} T^{cb}_{ij} \left(\delta_{ae}\delta_{cf}\delta_{im}\delta_{jn} - \delta_{af}\delta_{ce}\delta_{im}\delta_{jn} - \delta_{ae}\delta_{cf}\delta_{in}\delta_{jm} + \delta_{af}\delta_{ce}\delta_{in}\delta_{jm}\right) \\
&= -\frac{1}{2}T^{fb}_{mn}\delta_{ae} + \frac{1}{2}T^{eb}_{mn}\delta_{af} + \frac{1}{2}T^{fb}_{nm}\delta_{ae} - \frac{1}{2}T^{eb}_{nm}\delta_{af} \\
&= T^{eb}_{mn}\delta_{af} - T^{fb}_{mn}\delta_{ae}
\end{aligned} \tag{30}
$$

$$\frac{\partial (\Gamma^{\mathrm{H}})_{ij}^{ab}}{\partial T_{mn}^{ef}} = 0 \tag{31}$$

$$\begin{aligned}
\frac{\partial (\Gamma^{\mathrm{H}})_{ij}^{ab}}{\partial (T_{mn}^{ef})^*} &= \frac{1}{4}\frac{\partial (T_{ij}^{ab})^*}{\partial (T_{mn}^{ef})^*} \\
&= \frac{1}{4}\left(\delta_{ae}\delta_{bf}\delta_{im}\delta_{jn} - \delta_{af}\delta_{be}\delta_{im}\delta_{jn} - \delta_{ae}\delta_{bf}\delta_{in}\delta_{jm} + \delta_{af}\delta_{be}\delta_{in}\delta_{jm}\right)
\end{aligned} \tag{32}$$

$$\begin{aligned}
\frac{\partial (\Gamma^{\mathrm{H}})_{ab}^{ij}}{\partial T_{mn}^{ef}} &= \frac{1}{4}\frac{\partial T_{ij}^{ab}}{\partial T_{mn}^{ef}} \\
&= \frac{1}{4}\left(\delta_{ae}\delta_{bf}\delta_{im}\delta_{jn} - \delta_{af}\delta_{be}\delta_{im}\delta_{jn} - \delta_{ae}\delta_{bf}\delta_{in}\delta_{jm} + \delta_{af}\delta_{be}\delta_{in}\delta_{jm}\right)
\end{aligned} \tag{33}$$

$$\frac{\partial (\Gamma^{\mathrm{H}})_{ab}^{ij}}{\partial (T_{mn}^{ef})^*} = 0 \tag{34}$$

$$\begin{aligned}
\frac{\partial (\Gamma^{\mathrm{H}})_{kl}^{ij}}{\partial T_{mn}^{ef}} &= \frac{1}{2}\sum_{m'ab}(T_{km'}^{ab})^*\frac{\partial T_{m'i}^{ab}}{\partial T_{mn}^{ef}}\delta_{jl} \\
&= \frac{1}{2}\sum_{m'ab}(T_{km'}^{ab})^*(\delta_{ae}\delta_{bf}\delta_{m'm}\delta_{in} - \delta_{af}\delta_{be}\delta_{m'm}\delta_{in} - \delta_{ae}\delta_{bf}\delta_{m'n}\delta_{im} + \delta_{af}\delta_{be}\delta_{m'n}\delta_{im})\delta_{jl} \\
&= \frac{1}{2}(T_{km}^{ef})^*\delta_{in}\delta_{jl} - \frac{1}{2}(T_{km}^{fe})^*\delta_{in}\delta_{jl} - \frac{1}{2}(T_{kn}^{ef})^*\delta_{im}\delta_{jl} + \frac{1}{2}(T_{kn}^{fe})^*\delta_{im}\delta_{jl} \\
&= (T_{km}^{ef})^*\delta_{in}\delta_{jl} - (T_{kn}^{ef})^*\delta_{im}\delta_{jl}
\end{aligned} \tag{35}$$

$$\begin{aligned}
\frac{\partial (\Gamma^{\mathrm{H}})_{kl}^{ij}}{\partial (T_{mn}^{ef})^*} &= \frac{1}{2}\sum_{m'ab}\frac{\partial (T_{km'}^{ab})^*}{\partial (T_{mn}^{ef})^*}T_{m'i}^{ab}\delta_{jl} \\
&= \frac{1}{2}\sum_{m'ab}T_{m'i}^{ab}\left(\delta_{ae}\delta_{bf}\delta_{km}\delta_{m'n} - \delta_{af}\delta_{be}\delta_{km}\delta_{m'n} - \delta_{ae}\delta_{bf}\delta_{kn}\delta_{m'm} + \delta_{af}\delta_{be}\delta_{kn}\delta_{m'm}\right)\delta_{jl} \\
&= \frac{1}{2}T_{ni}^{ef}\delta_{km}\delta_{jl} - \frac{1}{2}T_{ni}^{fe}\delta_{km}\delta_{jl} - \frac{1}{2}T_{mi}^{ef}\delta_{kn}\delta_{jl} + \frac{1}{2}T_{mi}^{fe}\delta_{kn}\delta_{jl} \\
&= T_{ni}^{ef}\delta_{km}\delta_{jl} - T_{mi}^{ef}\delta_{kn}\delta_{jl}
\end{aligned} \tag{36}$$

$$\begin{aligned}
\frac{\partial (\Gamma^{\mathrm{H}})_{bj}^{ai}}{\partial T_{mn}^{ef}} &= -\frac{1}{2}\sum_{klc}(T_{kl}^{ac})^*\frac{\partial T_{kl}^{cb}}{\partial T_{mn}^{ef}}\delta_{ij} \\
&= -\frac{1}{2}\sum_{klc}(T_{kl}^{ac})^*\left(\delta_{ce}\delta_{bf}\delta_{km}\delta_{ln} - \delta_{cf}\delta_{be}\delta_{km}\delta_{ln} - \delta_{ce}\delta_{bf}\delta_{kn}\delta_{lm} + \delta_{cf}\delta_{be}\delta_{kn}\delta_{lm}\right)\delta_{ij} \\
&= -\frac{1}{2}(T_{mn}^{ae})^*\delta_{bf}\delta_{ij} + \frac{1}{2}(T_{mn}^{af})^*\delta_{be}\delta_{ij} + \frac{1}{2}(T_{nm}^{ae})^*\delta_{bf}\delta_{ij} - \frac{1}{2}(T_{nm}^{af})^*\delta_{be}\delta_{ij} \\
&= (T_{mn}^{af})^*\delta_{be}\delta_{ij} - (T_{mn}^{ae})^*\delta_{bf}\delta_{ij}
\end{aligned} \tag{37}$$

$$\begin{aligned}
\frac{\partial (\Gamma^{\mathrm{H}})_{bj}^{ai}}{\partial (T_{mn}^{ef})^*} &= -\frac{1}{2}\sum_{klc}\frac{\partial (T_{kl}^{ac})^*}{\partial (T_{mn}^{ef})^*}T_{kl}^{cb}\delta_{ij} \\
&= -\frac{1}{2}\sum_{klc}T_{kl}^{cb}\left(\delta_{ae}\delta_{cf}\delta_{km}\delta_{ln} - \delta_{af}\delta_{ce}\delta_{km}\delta_{ln} - \delta_{ae}\delta_{cf}\delta_{kn}\delta_{lm} + \delta_{af}\delta_{ce}\delta_{kn}\delta_{lm}\right)\delta_{ij} \\
&= -\frac{1}{2}T_{mn}^{fb}\delta_{ae}\delta_{ij} + \frac{1}{2}T_{mn}^{eb}\delta_{af}\delta_{ij} + \frac{1}{2}T_{nm}^{fb}\delta_{ae}\delta_{ij} - \frac{1}{2}T_{nm}^{eb}\delta_{af}\delta_{ij} \\
&= T_{mn}^{eb}\delta_{af}\delta_{ij} - T_{mn}^{fb}\delta_{ae}\delta_{ij}
\end{aligned} \tag{38}$$

Contraction with electron integrals:

$$\sum_{ij} h_{ij}\frac{\partial \gamma_{ij}^{\mathrm{H}}}{\partial T_{mn}^{ef}}\Big|_{\lambda=0} = \sum_{ij} h_{ij}(T_{jm}^{ef})^*\delta_{in} - \sum_{ij} h_{ij}(T_{jn}^{ef})^*\delta_{im}$$

$$
\begin{aligned}
&= \sum_j h_{nj}(T_{jm}^{ef})^* - \sum_j h_{mj}(T_{jn}^{ef})^* \\
&= \sum_j \mathscr{P}_{mn}^- h_{nj}(T_{jm}^{ef})^*
\end{aligned} \tag{39}
$$

$$
\begin{aligned}
\sum_{ij} h_{ij} \frac{\partial \gamma_{ij}^{\mathrm{H}}}{\partial (T_{mn}^{ef})^*}\Big|_{\lambda=0} &= \sum_{ij} h_{ij} T_{ni}^{ef} \delta_{jm} - \sum_{ij} h_{ij} T_{mi}^{ef} \delta_{jn} \\
&= \sum_i h_{im} T_{ni}^{ef} - \sum_i h_{in} T_{mi}^{ef} \\
&= \sum_i \mathscr{P}_{mn}^- h_{im} T_{ni}^{ef}
\end{aligned} \tag{40}
$$

$$
\begin{aligned}
\sum_{ab} h_{ab} \frac{\partial \gamma_{ab}^{\mathrm{H}}}{\partial T_{mn}^{ef}}\Big|_{\lambda=0} &= \sum_{ab} h_{ab} (T_{mn}^{af})^* \delta_{be} - \sum_{ab} h_{ab} (T_{mn}^{ae})^* \delta_{bf} \\
&= \sum_a h_{ae} (T_{mn}^{af})^* - \sum_a h_{af} (T_{mn}^{ae})^* \\
&= \sum_a \mathscr{P}_{ef}^- h_{ae} (T_{mn}^{af})^*
\end{aligned} \tag{41}
$$

$$
\begin{aligned}
\sum_{ab} h_{ab} \frac{\partial \gamma_{ab}^{\mathrm{H}}}{\partial (T_{mn}^{ef})^*}\Big|_{\lambda=0} &= \sum_{ab} h_{ab} T_{mn}^{eb} \delta_{af} - \sum_{ab} h_{ab} T_{mn}^{fb} \delta_{ae} \\
&= \sum_b h_{fb} T_{mn}^{eb} - \sum_b h_{eb} T_{mn}^{fb} \\
&= \sum_b \mathscr{P}_{ef}^- h_{fb} T_{mn}^{eb}
\end{aligned} \tag{42}
$$

$$
\sum_{ijab} \langle ab||ij\rangle \frac{\partial (\Gamma^{\mathrm{H}})_{ij}^{ab}}{\partial T_{mn}^{ef}}\Big|_{\lambda=0} = 0 \tag{43}
$$

$$
\begin{aligned}
\sum_{ijab} \langle ab||ij\rangle \frac{\partial (\Gamma^{\mathrm{H}})_{ij}^{ab}}{\partial (T_{mn}^{ef})^*}\Big|_{\lambda=0} =& \frac{1}{4} \sum_{ijab} \langle ab||ij\rangle \big(\delta_{ae}\delta_{bf}\delta_{im}\delta_{jn} - \delta_{af}\delta_{be}\delta_{im}\delta_{jn} \\
&- \delta_{ae}\delta_{bf}\delta_{in}\delta_{jm} + \delta_{af}\delta_{be}\delta_{in}\delta_{jm}\big) \\
=& \frac{1}{4} \left(\langle ef||mn\rangle - \langle fe||mn\rangle - \langle ef||nm\rangle + \langle fe||nm\rangle\right) \\
=& \langle ef||mn\rangle
\end{aligned} \tag{44}
$$

$$
\begin{aligned}
\sum_{ijab} \langle ij||ab\rangle \frac{\partial (\Gamma^{\mathrm{H}})_{ab}^{ij}}{\partial T_{mn}^{ef}}\Big|_{\lambda=0} =& \frac{1}{4} \sum_{ijab} \langle ij||ab\rangle \big(\delta_{ae}\delta_{bf}\delta_{im}\delta_{jn} - \delta_{af}\delta_{be}\delta_{im}\delta_{jn} \\
&- \delta_{ae}\delta_{bf}\delta_{in}\delta_{jm} + \delta_{af}\delta_{be}\delta_{in}\delta_{jm}\big) \\
=& \frac{1}{4} \left(\langle mn||ef\rangle - \langle mn||fe\rangle - \langle nm||ef\rangle + \langle nm||fe\rangle\right) \\
=& \langle mn||ef\rangle
\end{aligned} \tag{45}
$$

$$\sum_{ijab} \langle ij||ab\rangle \frac{\partial(\Gamma^{\mathrm{H}})^{ij}_{ab}}{\partial(T^{ef}_{mn})^*}\Big|_{\lambda=0} = 0 \tag{46}$$

$$\begin{aligned}
\sum_{ijkl} \langle ij||kl\rangle \frac{\partial(\Gamma^{\mathrm{H}})^{ij}_{kl}}{\partial T^{ef}_{mn}}\Big|_{\lambda=0} &= \sum_{ijkl} \langle ij||kl\rangle (T^{ef}_{km})^* \delta_{in}\delta_{jl} - \sum_{ijkl} \langle ij||kl\rangle (T^{ef}_{kn})^* \delta_{im}\delta_{jl} \\
&= \sum_{jk} \langle nj||kj\rangle (T^{ef}_{km})^* - \sum_{jk} \langle mj||kj\rangle (T^{ef}_{kn})^* \\
&= \sum_{jk} \mathscr{P}^-_{mn} \langle nj||kj\rangle (T^{ef}_{km})^*
\end{aligned} \tag{47}$$

$$\begin{aligned}
\sum_{ijkl} \langle ij||kl\rangle \frac{\partial(\Gamma^{\mathrm{H}})^{ij}_{kl}}{\partial (T^{ef}_{mn})^*}\Big|_{\lambda=0} &= \sum_{ijkl} \langle ij||kl\rangle T^{ef}_{ni} \delta_{km}\delta_{jl} - \sum_{ijkl} \langle ij||kl\rangle T^{ef}_{mi} \delta_{kn}\delta_{jl} \\
&= \sum_{ij} \langle ij||mj\rangle T^{ef}_{ni} - \sum_{ij} \langle ij||nj\rangle T^{ef}_{mi} \\
&= \sum_{ij} \mathscr{P}^-_{mn} \langle ij||mj\rangle T^{ef}_{ni}
\end{aligned} \tag{48}$$

$$\begin{aligned}
\sum_{ijab} \langle ai||bj\rangle \frac{\partial(\Gamma^{\mathrm{H}})^{ai}_{bj}}{\partial T^{ef}_{mn}}\Big|_{\lambda=0} &= \sum_{ijab} \langle ai||bj\rangle (T^{af}_{mn})^* \delta_{be}\delta_{ij} - \sum_{ijab} \langle ai||bj\rangle (T^{ae}_{mn})^* \delta_{bf}\delta_{ij} \\
&= \sum_{ia} \langle ai||ei\rangle (T^{af}_{mn})^* - \sum_{ia} \langle ai||fi\rangle (T^{ae}_{mn})^* \\
&= \sum_{ia} \mathscr{P}^-_{ef} \langle ai||ei\rangle (T^{af}_{mn})^*
\end{aligned} \tag{49}$$

$$\begin{aligned}
\sum_{ijab} \langle ai||bj\rangle \frac{\partial(\Gamma^{\mathrm{H}})^{ai}_{bj}}{\partial (T^{ef}_{mn})^*}\Big|_{\lambda=0} &= \sum_{ijab} \langle ai||bj\rangle T^{eb}_{mn} \delta_{af}\delta_{ij} - \sum_{ijab} \langle ai||bj\rangle T^{fb}_{mn} \delta_{ae}\delta_{ij} \\
&= \sum_{ib} \langle fi||bi\rangle T^{eb}_{mn} - \sum_{ib} \langle ei||bi\rangle T^{fb}_{mn} \\
&= \sum_{ib} \mathscr{P}^-_{ef} \langle fi||bi\rangle T^{eb}_{mn}
\end{aligned} \tag{50}$$

Therefore the MP2 stationary condition is constructed as:

$$\begin{aligned}
0 =& \frac{\partial \mathcal{L}_{\mathrm{MP2}}}{\partial T^{ef}_{mn}}\Big|_{\lambda=0} = \frac{\partial E_{\mathrm{H}}}{\partial T^{ef}_{mn}}\Big|_{\lambda=0} \\
=& \sum_{j} \mathscr{P}^-_{mn} h_{nj} (T^{ef}_{jm})^* + \sum_{a} \mathscr{P}^-_{ef} h_{ae} (T^{af}_{mn})^* + \langle mn||ef\rangle \\
&+ \sum_{jk} \mathscr{P}^-_{mn} \langle nj||kj\rangle (T^{ef}_{km})^* + \sum_{ia} \mathscr{P}^-_{ef} \langle ai||ei\rangle (T^{af}_{mn})^* \\
=& \sum_{j} \mathscr{P}^-_{mn} h_{nj} (T^{ef}_{jm})^* + \sum_{a} \mathscr{P}^-_{ef} h_{ae} (T^{af}_{mn})^* + \langle mn||ef\rangle \\
&+ \sum_{jk} \mathscr{P}^-_{mn} \langle nk||jk\rangle (T^{ef}_{jm})^* + \sum_{ia} \mathscr{P}^-_{ef} \langle ai||ei\rangle (T^{af}_{mn})^*
\end{aligned}$$

$$
= \sum_j \mathscr{P}^{-}_{mn} f_{nj} (T^{ef}_{jm})^* + \sum_a \mathscr{P}^{-}_{ef} f_{ae} (T^{af}_{mn})^* + \langle mn||ef\rangle \tag{51}
$$

$$
\begin{aligned}
0 =& \frac{\partial \mathcal{L}_{\text{MP2}}}{\partial (T^{ef}_{mn})^*}\Big|_{\lambda=0} = \frac{\partial E_{\text{H}}}{\partial (T^{ef}_{mn})^*}\Big|_{\lambda=0} \\
=& \sum_i \mathscr{P}^{-}_{mn} h_{im} T^{ef}_{ni} + \sum_b \mathscr{P}^{-}_{ef} h_{fb} T^{eb}_{mn} + \langle ef||mn\rangle \\
&+ \sum_{ij} \mathscr{P}^{-}_{mn} \langle ij||mj\rangle T^{ef}_{ni} + \sum_{ib} \mathscr{P}^{-}_{ef} \langle fi||bi\rangle T^{eb}_{mn} \\
=& \sum_i \mathscr{P}^{-}_{mn} f_{im} T^{ef}_{ni} + \sum_b \mathscr{P}^{-}_{ef} f_{fb} T^{eb}_{mn} + \langle ef||mn\rangle
\end{aligned} \tag{52}
$$

The fock matrix is diagonal in canonical basis, i.e. $f_{pq} = \varepsilon_p \delta_{pq}$, hence we obtain:

$$
\begin{aligned}
0 =& \sum_j \mathscr{P}^{-}_{mn} \varepsilon_n \delta_{nj} (T^{ef}_{jm})^* + \sum_a \mathscr{P}^{-}_{ef} \varepsilon_e \delta_{ae} (T^{af}_{mn})^* + \langle mn||ef\rangle \\
=& \mathscr{P}^{-}_{mn} \varepsilon_n (T^{ef}_{nm})^* + \mathscr{P}^{-}_{ef} \varepsilon_e (T^{ef}_{mn})^* + \langle mn||ef\rangle \\
=& -(T^{ef}_{mn})^* \varepsilon_n - (T^{ef}_{mn})^* \varepsilon_m + (T^{ef}_{mn})^* \varepsilon_e + (T^{ef}_{mn})^* \varepsilon_f + \langle mn||ef\rangle
\end{aligned}
$$

$$
(T^{ef}_{mn})^* = \frac{\langle mn||ef\rangle}{\varepsilon_m + \varepsilon_n - \varepsilon_e - \varepsilon_f} \tag{53}
$$

$$
\begin{aligned}
0 =& \sum_i \mathscr{P}^{-}_{mn} \varepsilon_m \delta_{im} T^{ef}_{ni} + \sum_b \mathscr{P}^{-}_{ef} \varepsilon_f \delta_{fb} T^{eb}_{mn} + \langle ef||mn\rangle \\
=& \mathscr{P}^{-}_{mn} \varepsilon_m T^{ef}_{nm} + \mathscr{P}^{-}_{ef} \varepsilon_f T^{ef}_{mn} + \langle ef||mn\rangle \\
=& -T^{ef}_{mn} \varepsilon_m - T^{ef}_{mn} \varepsilon_n + T^{ef}_{mn} \varepsilon_f + T^{ef}_{mn} \varepsilon_e + \langle ef||mn\rangle
\end{aligned}
$$

$$
T^{ef}_{mn} = \frac{\langle ef||mn\rangle}{\varepsilon_m + \varepsilon_n - \varepsilon_e - \varepsilon_f} \tag{54}
$$

as the familiar MP2 amplitude expressions.

## 1.4 Z-Vector Equation (Exponential Parameterization)

$$\begin{aligned}\mathbf{U} &= \exp(-\boldsymbol{\kappa}) \\ &= \sum_{n=0}^{\infty}(-1)^n \frac{\boldsymbol{\kappa}^n}{n!}\end{aligned} \tag{55}$$

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

$$\boldsymbol{\kappa}^\dagger = (\boldsymbol{\kappa}^*)^T = -\boldsymbol{\kappa} \tag{56}$$

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

$$\mathbf{U}^\dagger\mathbf{U} = \exp\left(-\boldsymbol{\kappa}^\dagger\right)\exp(-\boldsymbol{\kappa}) = \exp(\boldsymbol{\kappa})\exp(-\boldsymbol{\kappa}) = \mathbf{I} \tag{57}$$

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

$$\mathbf{C}(\lambda) = \mathbf{C}(0)\mathbf{U}(\lambda) = \mathbf{C}(0)\exp[-\boldsymbol{\kappa}(\lambda)] \tag{58}$$

$$C_{\mu p}(\lambda) = \sum_r C_{\mu r}(0)U_{rp}(\lambda) = \sum_r C_{\mu r}(0)(\exp[-\boldsymbol{\kappa}(\lambda)])_{rp} \tag{59}$$

$$\begin{aligned}[\exp(-\boldsymbol{\kappa})]_{rp} &= (\mathbf{I} - \boldsymbol{\kappa} + \frac{1}{2!}\boldsymbol{\kappa}^2 - \frac{1}{3!}\boldsymbol{\kappa}^3 + \dots)_{rp} \\ &= \delta_{rp} - \kappa_{rp} + \frac{1}{2!}\sum_x k_{rx}k_{xp} - \frac{1}{3!}\sum_{xy} k_{rx}k_{xy}k_{yp} + \dots\end{aligned} \tag{60}$$

$$\begin{aligned}\mathbf{S}(\lambda) &= \mathbf{C}^\dagger(\lambda)\mathbf{S}^{\mathrm{AO}}(\lambda)\mathbf{C}(\lambda) \\ &= (\mathbf{C}(0)\exp[-\boldsymbol{\kappa}(\lambda)])^\dagger\mathbf{S}^{\mathrm{AO}}(\lambda)\mathbf{C}(0)\exp[-\boldsymbol{\kappa}(\lambda)] \\ &= \exp\left[-\boldsymbol{\kappa}^\dagger(\lambda)\right]\mathbf{C}^\dagger(0)\mathbf{S}^{\mathrm{AO}}(\lambda)\mathbf{C}(0)\exp[-\boldsymbol{\kappa}(\lambda)] \\ &= \exp[\boldsymbol{\kappa}(\lambda)]\boldsymbol{\mathcal{S}}(\lambda)\exp[-\boldsymbol{\kappa}(\lambda)] \\ &= \left[\mathbf{I} + \boldsymbol{\kappa}(\lambda) + \frac{1}{2}\boldsymbol{\kappa}^2(\lambda) + \dots\right]\boldsymbol{\mathcal{S}}(\lambda)\left[\mathbf{I} - \boldsymbol{\kappa}(\lambda) + \frac{1}{2}\boldsymbol{\kappa}^2(\lambda) + \dots\right]\end{aligned} \tag{61}$$

$$\begin{aligned}\Leftrightarrow S_{pq} &= \sum_{\mu\nu} C^*_{\mu p}(\lambda)S^{\mathrm{AO}}_{\mu\nu}(\lambda)C_{\nu q}(\lambda) \\ &= \sum_{\mu\nu}\big(\sum_r C^*_{\mu r}(0)\exp[-\boldsymbol{\kappa}(\lambda)]^*_{rp}\big)S^{\mathrm{AO}}_{\mu\nu}(\lambda)\big(\sum_s C_{\nu s}\exp[-\boldsymbol{\kappa}(\lambda)]_{sq}\big) \\ &= \sum_{\mu\nu rs}\exp[\boldsymbol{\kappa}(\lambda)]_{pr}\big(C^*_{\mu r}(0)S^{\mathrm{AO}}_{\mu\nu}(\lambda)C_{\nu s}(0)\big)\exp[-\boldsymbol{\kappa}(\lambda)]_{sq} \\ &= \sum_{rs}\exp[\boldsymbol{\kappa}(\lambda)]_{pr}\mathcal{S}_{rs}(\lambda)\exp[-\boldsymbol{\kappa}(\lambda)]_{sq} \\ &= \sum_{rs}\left[\delta_{pr} + \kappa_{pr}(\lambda) + \frac{1}{2}\sum_x \kappa_{px}(\lambda)\kappa_{xr}(\lambda)\right]\mathcal{S}_{rs}(\lambda)\left[\delta_{sq} - \kappa_{sq}(\lambda) + \frac{1}{2}\sum_y \kappa_{sy}(\lambda)\kappa_{yq}(\lambda)\right]\end{aligned} \tag{62}$$

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

$$\begin{aligned}S_{pq} &= \sum_{rs}\left[\delta_{pr} + \kappa_{pr}(\lambda)\right]\mathcal{S}_{rs}(\lambda)\left[\delta_{sq} - \kappa_{sq}(\lambda)\right] \\ &= \sum_{rs}\delta_{pr}\mathcal{S}_{rs}(\lambda)\delta_{sq} - \sum_{rs}\delta_{pr}\mathcal{S}_{rs}(\lambda)\kappa_{sq}(\lambda) + \sum_{rs}\kappa_{pr}(\lambda)\mathcal{S}_{rs}(\lambda)\delta_{sq} - \sum_{rs}\kappa_{pr}(\lambda)\mathcal{S}_{rs}(\lambda)\kappa_{sq}(\lambda)\end{aligned} \tag{63}$$

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

$$\begin{aligned}\frac{\partial S_{pq}}{\partial \lambda}\Big|_{\lambda=0} =& \sum_{rs} \delta_{pr}\delta_{sq}\frac{\partial \mathcal{S}_{rs}}{\partial \lambda}\Big|_{\lambda=0} - \sum_{rs} \delta_{pr}\mathcal{S}_{rs}(\lambda)\frac{\partial \kappa_{sq}}{\partial \lambda}\Big|_{\lambda=0} + \sum_{rs} \frac{\partial \kappa_{pr}}{\partial \lambda}\mathcal{S}_{rs}(\lambda)\delta_{sq}\Big|_{\lambda=0} \\ =& \mathcal{S}^{\lambda}_{pq} - \sum_{s} \mathcal{S}_{ps}\kappa^{\lambda}_{sq}\Big|_{\lambda=0} + \sum_{r} \kappa^{\lambda}_{pr}\mathcal{S}_{rq}\Big|_{\lambda=0} \\ =& \mathcal{S}^{\lambda}_{pq} - \kappa^{\lambda}_{pq} + \kappa^{\lambda}_{pq} \\ =& \mathcal{S}^{\lambda}_{pq} \end{aligned} \tag{64}$$

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

$$\boldsymbol{\mathcal{S}}^{\lambda} = \mathbf{C}^{\dagger}(0)\mathbf{S}^{\mathrm{AO},\lambda}\mathbf{C}(0) = \mathbf{0} \tag{65}$$

This looks weird.

## 1.5 Z-Vector Equation (Improved Exponential Parameterization)

$$\begin{aligned}\mathbf{C}(\lambda) =& \mathbf{C}(0)\mathbf{U}(\lambda) & (66)\\ \mathbf{U}(\lambda) =& \boldsymbol{\mathcal{S}}^{-\frac{1}{2}}(\lambda)\exp[-\boldsymbol{\kappa}(\lambda)] & (67)\\ \boldsymbol{\mathcal{S}}(\lambda) =& \mathbf{C}^\dagger(0)\mathbf{S}^{\text{AO}}(\lambda)\mathbf{C}(0) & (68)\end{aligned}$$

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:

$$\exp(-\boldsymbol{\kappa}) = \mathbf{I} - \boldsymbol{\kappa} + \frac{1}{2}\boldsymbol{\kappa}^2 \tag{69}$$

Then the relevant integrals could be expressed as:

$$\begin{aligned}\mathbf{h} =& \mathbf{C}^\dagger(\lambda)\mathbf{h}^{\text{AO}}(\lambda)\mathbf{C}(\lambda)\\ =& \exp[\boldsymbol{\kappa}(\lambda)]\boldsymbol{\mathcal{S}}^{-\frac{1}{2}\dagger}(\lambda)\mathbf{C}^\dagger(0)\mathbf{h}^{\text{AO}}(\lambda)\mathbf{C}(0)\boldsymbol{\mathcal{S}}^{-\frac{1}{2}}(\lambda)\exp[-\boldsymbol{\kappa}(\lambda)]\\ =& \big(\mathbf{I} + \boldsymbol{\kappa} + \frac{1}{2}\boldsymbol{\kappa}^2\big)\boldsymbol{\mathcal{S}}^{-\frac{1}{2}\dagger}(\lambda)\mathbf{C}^\dagger(0)\mathbf{h}^{\text{AO}}(\lambda)\mathbf{C}(0)\boldsymbol{\mathcal{S}}^{-\frac{1}{2}}(\lambda)\big(\mathbf{I} - \boldsymbol{\kappa} + \frac{1}{2}\boldsymbol{\kappa}^2\big) & (70)\end{aligned}$$

$$\big(\mathbf{I} + \boldsymbol{\kappa} + \frac{1}{2}\boldsymbol{\kappa}^2\big)_{pq} = \delta_{pq} + \kappa_{pq} + \frac{1}{2}\sum_x \kappa_{px}\kappa_{xq} \tag{71}$$

$$\begin{aligned}\frac{\partial \delta_{pq}}{\partial \kappa_{rs}} =& 0 & (72)\\ \frac{\partial \kappa_{pq}}{\partial \kappa_{rs}} =& \delta_{pr}\delta_{qs} & (73)\end{aligned}$$

$$\begin{aligned}h_{pq} =& \sum_{\mu\nu} C^*_{\mu p}(\lambda)h^{\text{AO}}_{\mu\nu}(\lambda)C_{\nu q}(\lambda)\\ =& \sum_{\mu\nu rs} C^*_{\mu r}(0)U^*_{rp}(\lambda)h^{\text{AO}}_{\mu\nu}(\lambda)C_{\nu s}(0)U_{sq}(\lambda)\\ =& \sum_{\mu\nu rstu} C^*_{\mu r}\mathcal{S}_{rt}^{-\frac{1}{2}*}\exp[-\boldsymbol{\kappa}]^*_{tp}h^{\text{AO}}_{\mu\nu}C_{\nu s}\mathcal{S}_{su}^{-\frac{1}{2}}\exp[-\boldsymbol{\kappa}]_{uq} & (74)\\ =& \sum_{\mu\nu rstu} C^*_{\mu r}\mathcal{S}_{rt}^{-\frac{1}{2}*}\exp[\boldsymbol{\kappa}]_{pt}h^{\text{AO}}_{\mu\nu}C_{\nu s}\mathcal{S}_{su}^{-\frac{1}{2}}\exp[-\boldsymbol{\kappa}]_{uq}\\ =& \sum_{\mu\nu rstu} C^*_{\mu r}\mathcal{S}_{rt}^{-\frac{1}{2}*}\left[\delta_{pt} + \kappa_{pt} + \ldots\right]h^{\text{AO}}_{\mu\nu}C_{\nu s}\mathcal{S}_{su}^{-\frac{1}{2}}\left[\delta_{uq} - \kappa_{uq} + \ldots\right]\\ =& \sum_{\mu\nu rstu} C^*_{\mu r}\mathcal{S}_{rt}^{-\frac{1}{2}*}h^{\text{AO}}_{\mu\nu}C_{\nu s}\mathcal{S}_{su}^{-\frac{1}{2}}\left[\delta_{pt}\delta_{uq} - \delta_{pt}\kappa_{uq} + \delta_{uq}\kappa_{pt} - \kappa_{pt}\kappa_{uq}\right] & (75)\end{aligned}$$

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

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

$$= \sum_{\mu\nu rstu} C_{\mu r}^{*} \mathcal{S}_{rt}^{-\frac{1}{2}*} h_{\mu\nu}^{\text{AO}} C_{\nu s} \mathcal{S}_{su}^{-\frac{1}{2}} \left(-\delta_{pt}\delta_{uv}\delta_{qw} + \delta_{uq}\delta_{pv}\delta_{tw}\right) \tag{76}$$

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

$$\begin{aligned}
\frac{\partial h_{pq}}{\partial \kappa_{vw}}\Big|_{\lambda=0} &= \sum_{\mu\nu rstu} C_{\mu r}^{*} \delta_{rt} h_{\mu\nu}^{\text{AO}} C_{vs} \delta_{su} \delta_{uq} \delta_{pv} \delta_{tw} - \sum_{\mu\nu rstu} C_{\mu r}^{*} \delta_{rt} h_{\mu\nu}^{\text{AO}} C_{\nu s} \delta_{su} \delta_{pt} \delta_{uv} \delta_{qw} \\
&= \sum_{\mu\nu} C_{\mu w}^{*} h_{\mu\nu}^{\text{AO}} C_{\nu q} \delta_{pv} - \sum_{\mu\nu} C_{\mu p}^{*} h_{\mu\nu}^{\text{AO}} C_{\nu v} \delta_{qw} \\
&= h_{wq}\delta_{pv} - h_{pv}\delta_{wq}
\end{aligned} \tag{77}$$

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

$$\frac{\partial h_{pq}}{\partial \kappa_{rs}}\Big|_{\lambda=0} = h_{sq}\delta_{pr} - h_{pr}\delta_{sq} \tag{78}$$

hence:

$$\sum_{pq} \frac{\partial h_{pq}}{\partial \kappa_{rs}}\Big|_{\lambda=0} = \sum_{pq} h_{sq}\delta_{pr} - h_{pr}\delta_{qs} \tag{79}$$

Now the two-electron integral:

$$\begin{aligned}
\langle pq||rs\rangle &= \sum_{\mu\nu\sigma\tau} C_{\mu p}^{*} C_{\nu q}^{*} \langle \mu\nu||\sigma\tau\rangle C_{\sigma r} C_{\tau s} \\
&= \sum_{\mu\nu\sigma\tau} \sum_{tuvw} C_{\mu t}^{*} U_{tp}^{*} C_{\nu u}^{*} U_{uq}^{*} \langle \mu\nu||\sigma\tau\rangle C_{\sigma v} U_{vr} C_{\tau w} U_{ws} \\
&= \sum_{\mu\nu\sigma\tau} \sum_{tuvw} \sum_{ghmn} C_{\mu t}^{*} \mathcal{S}_{tg}^{-\frac{1}{2}*} \exp[-\boldsymbol{\kappa}]_{gp}^{*} C_{\nu u}^{*} \mathcal{S}_{uh}^{-\frac{1}{2}*} \exp[-\boldsymbol{\kappa}]_{hq}^{*} \\
&\quad \langle \mu\nu||\sigma\tau\rangle C_{\sigma v} \mathcal{S}_{vm}^{-\frac{1}{2}} \exp[-\boldsymbol{\kappa}]_{mr} C_{\tau w} \mathcal{S}_{wn}^{-\frac{1}{2}} \exp[-\boldsymbol{\kappa}]_{ns} \\
&= \sum_{\mu\nu\sigma\tau} \sum_{tuvw} \sum_{ghmn} C_{\mu t}^{*} \mathcal{S}_{tg}^{-\frac{1}{2}*} \left(\delta_{pg} + \kappa_{pg}\right) C_{\nu u}^{*} \mathcal{S}_{uh}^{-\frac{1}{2}*} \left(\delta_{qh} + \kappa_{qh}\right) \\
&\quad \langle \mu\nu||\sigma\tau\rangle C_{\sigma v} \mathcal{S}_{vm}^{-\frac{1}{2}} \left(\delta_{mr} - \kappa_{mr}\right) C_{\tau w} \mathcal{S}_{wn}^{-\frac{1}{2}} \left(\delta_{ns} - \kappa_{ns}\right) \\
&= \sum_{\mu\nu\sigma\tau} \sum_{tuvw} \sum_{ghmn} C_{\mu t}^{*} \mathcal{S}_{tg}^{-\frac{1}{2}*} C_{\nu u}^{*} \mathcal{S}_{uh}^{-\frac{1}{2}*} \langle \mu\nu||\sigma\tau\rangle C_{\sigma v} \mathcal{S}_{vm}^{-\frac{1}{2}} C_{\tau w} \mathcal{S}_{wn}^{-\frac{1}{2}} (\kappa_{pg}\delta_{qh}\delta_{mr}\delta_{ns} \\
&\quad + \kappa_{qh}\delta_{pg}\delta_{mr}\delta_{ns} - \kappa_{mr}\delta_{pg}\delta_{qh}\delta_{ns} - \kappa_{ns}\delta_{pg}\delta_{qh}\delta_{mr} + \dots)
\end{aligned} \tag{80}$$

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

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

$$
\begin{aligned}
&- \sum_{\mu\nu\sigma\tau} \sum_{tuvw} \sum_{ghmn} C^*_{\mu t} C^*_{\nu u} \langle \mu\nu || \sigma\tau \rangle C_{\sigma v} C_{\tau w} \delta_{tg} \delta_{uh} \delta_{vm} \delta_{wn} \delta_{nx} \delta_{sy} \delta_{pg} \delta_{qh} \delta_{mr} \\
=& \sum_{\mu\nu\sigma\tau} C^*_{\mu y} C^*_{\nu q} \langle \mu\nu || \sigma\tau \rangle C_{\sigma r} C_{\tau s} \delta_{px} + \sum_{\mu\nu\sigma\tau} C^*_{\mu p} C^*_{\nu y} \langle \mu\nu || \sigma\tau \rangle C_{\sigma r} C_{\tau s} \delta_{qx} \\
&- \sum_{\mu\nu\sigma\tau} C^*_{\mu p} C^*_{\nu q} \langle \mu\nu || \sigma\tau \rangle C_{\sigma x} C_{\tau s} \delta_{ry} - \sum_{\mu\nu\sigma\tau} C^*_{\mu p} C^*_{\nu q} \langle \mu\nu || \sigma\tau \rangle C_{\sigma r} C_{\tau x} \delta_{sy} \\
=& \langle yq || rs \rangle \delta_{px} + \langle py || rs \rangle \delta_{qx} - \langle pq || xs \rangle \delta_{ry} - \langle pq || rx \rangle \delta_{sy}
\end{aligned}
\tag{81}
$$

Therefore, the orbital response for fock matrix is:

$$
\begin{aligned}
\frac{\partial f_{ai}}{\partial \kappa_{pq}}\Big|_{\lambda=0} =& \frac{\partial h_{ai}}{\partial \kappa_{pq}}\Big|_{\lambda=0} + \sum_k \frac{\partial \langle ak || ik \rangle}{\partial \kappa_{pq}}\Big|_{\lambda=0} \\
=& h_{qi}\delta_{ap} - h_{ap}\delta_{qi} + \sum_k \langle qk || ik \rangle \delta_{ap} + \sum_k \langle aq || ik \rangle \delta_{pk} \\
&- \sum_k \langle ak || pk \rangle \delta_{iq} - \sum_k \langle ak || ip \rangle \delta_{kq} \\
=& \delta_{ap}\Big( h_{qi} + \sum_k \langle qk || ik \rangle \Big) - \delta_{qi}\Big( h_{ap} + \sum_k \langle ak || pk \rangle \Big) \\
&+ \sum_k \langle aq || ik \rangle \delta_{pk} - \sum_k \langle ak || ip \rangle \delta_{qk} \\
=& \delta_{ap} f_{qi} - \delta_{iq} f_{ap} + \langle aq || ip \rangle - \langle aq || ip \rangle \\
=& \delta_{ap}\delta_{qi}\varepsilon_i - \delta_{qi}\delta_{ap}\varepsilon_a \\
=& (\varepsilon_i - \varepsilon_a)\delta_{ap}\delta_{qi}
\end{aligned}
\tag{82}
$$

$$
\begin{aligned}
\frac{\partial f^*_{ai}}{\partial \kappa_{pq}}\Big|_{\lambda=0} =& \frac{\partial f_{ia}}{\partial \kappa_{pq}}\Big|_{\lambda=0} = \frac{\partial h_{ia}}{\partial \kappa_{pq}}\Big|_{\lambda=0} + \sum_k \frac{\partial \langle ik || ak \rangle}{\partial \kappa_{pq}}\Big|_{\lambda=0} \\
=& h_{qa}\delta_{ip} - h_{ip}\delta_{qa} + \sum_k \langle qk || ak \rangle \delta_{ip} + \sum_k \langle iq || ak \rangle \delta_{kp} \\
&- \sum_k \langle ik || pk \rangle \delta_{aq} - \sum_k \langle ik || ap \rangle \delta_{kq} \\
=& \delta_{ip}\Big( h_{qa} + \sum_k \langle qk || ak \rangle \Big) - \delta_{qa}\Big( h_{ip} + \sum_k \langle ik || pk \rangle \Big) + \langle iq || ap \rangle - \langle iq || ap \rangle \\
=& \delta_{ip} f_{qa} - \delta_{qa} f_{ip} \\
=& \delta_{ip}\delta_{qa}\varepsilon_a - \delta_{qa}\delta_{ip}\varepsilon_i \\
=& (\varepsilon_a - \varepsilon_i)\delta_{ip}\delta_{qa}
\end{aligned}
\tag{83}
$$

thus the only non-redundant orbital response is:

$$
\frac{\partial f_{ai}}{\partial \kappa_{bj}}\Big|_{\lambda=0} = (\varepsilon_i - \varepsilon_a)\delta_{ab}\delta_{ij}
\tag{84}
$$

Then, the orbital response for the Hylleraas functional:

$$
\begin{aligned}
E_{\mathrm{H}} =& \sum_{ij} h_{ij}\gamma^{\mathrm{H}}_{ij} + \sum_{ab} h_{ab}\gamma^{\mathrm{H}}_{ab} + \sum_{ijab} \langle ab || ij \rangle (\Gamma^{\mathrm{H}})^{ab}_{ij} + \sum_{ijab} \langle ij || ab \rangle (\Gamma^{\mathrm{H}})^{ij}_{ab} \\
&+ \sum_{ijkl} \langle ij || kl \rangle (\Gamma^{\mathrm{H}})^{ij}_{kl} + \sum_{ijab} \langle ai || bj \rangle (\Gamma^{\mathrm{H}})^{ai}_{bj}
\end{aligned}
\tag{85}
$$

$$\frac{\partial h_{ij}}{\partial \kappa_{pq}}\Big|_{\lambda=0} = h_{qj}\delta_{ip} - h_{ip}\delta_{qj} \tag{86}$$

$$\frac{\partial h_{ab}}{\partial \kappa_{pq}}\Big|_{\lambda=0} = h_{qb}\delta_{ap} - h_{ap}\delta_{qb} \tag{87}$$

$$\frac{\partial \langle ab||ij\rangle}{\partial \kappa_{pq}}\Big|_{\lambda=0} = \langle qb||ij\rangle\delta_{ap} + \langle aq||ij\rangle\delta_{bp} - \langle ab||pj\rangle\delta_{iq} - \langle ab||ip\rangle\delta_{jq} \tag{88}$$

$$\frac{\partial \langle ij||ab\rangle}{\partial \kappa_{pq}}\Big|_{\lambda=0} = \langle qj||ab\rangle\delta_{ip} + \langle iq||ab\rangle\delta_{jp} - \langle ij||pb\rangle\delta_{aq} - \langle ij||ap\rangle\delta_{bq} \tag{89}$$

$$\frac{\partial \langle ij||kl\rangle}{\partial \kappa_{pq}}\Big|_{\lambda=0} = \langle qj||kl\rangle\delta_{ip} + \langle iq||kl\rangle\delta_{jp} - \langle ij||pl\rangle\delta_{kq} - \langle ij||kp\rangle\delta_{lq} \tag{90}$$

$$\frac{\partial \langle ai||bj\rangle}{\partial \kappa_{pq}}\Big|_{\lambda=0} = \langle qi||bj\rangle\delta_{ap} + \langle aq||bj\rangle\delta_{ip} - \langle ai||pj\rangle\delta_{bq} - \langle ai||bp\rangle\delta_{jq} \tag{91}$$

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

$$\begin{aligned}\sum_{ij}\frac{\partial h_{ij}}{\partial \kappa_{em}}\gamma^{\mathrm{H}}_{ij}\Big|_{\lambda=0} &= \sum_{ij}(\cancel{h_{mj}\delta_{ie}} - h_{ie}\delta_{mj})\gamma^{\mathrm{H}}_{ij} \\ &= -\sum_{i} h_{ie}\gamma^{\mathrm{H}}_{im}\end{aligned} \tag{92}$$

$$\begin{aligned}\sum_{ij}\frac{\partial h_{ij}}{\partial \kappa^*_{em}}\gamma^{\mathrm{H}}_{ij}\Big|_{\lambda=0} &= -\sum_{ij}\frac{\partial h_{ij}}{\partial \kappa_{me}}\gamma^{\mathrm{H}}_{ij}\Big|_{\lambda=0} \\ &= -\sum_{ij}(h_{ej}\delta_{im} - \cancel{h_{im}\delta_{ej}})\gamma^{\mathrm{H}}_{ij} \\ &= -\sum_{j} h_{ej}\gamma^{\mathrm{H}}_{mj} = -\sum_{i} h_{ei}\gamma^{\mathrm{H}}_{mi}\end{aligned} \tag{93}$$

$$\begin{aligned}\sum_{ab}\frac{\partial h_{ab}}{\partial \kappa_{em}}\gamma^{\mathrm{H}}_{ab}\Big|_{\lambda=0} &= \sum_{ab}(h_{mb}\delta_{ae} - \cancel{h_{ae}\delta_{mb}})\gamma^{\mathrm{H}}_{ab} \\ &= \sum_{b} h_{mb}\gamma^{\mathrm{H}}_{eb} = \sum_{a} h_{ma}\gamma^{\mathrm{H}}_{ea}\end{aligned} \tag{94}$$

$$\begin{aligned}\sum_{ab}\frac{\partial h_{ab}}{\partial \kappa^*_{em}}\gamma^{\mathrm{H}}_{ab}\Big|_{\lambda=0} &= -\sum_{ab}\frac{\partial h_{ab}}{\partial \kappa_{me}}\gamma^{\mathrm{H}}_{ab}\Big|_{\lambda=0} \\ &= -\sum_{ab}(\cancel{h_{eb}\delta_{am}} - h_{am}\delta_{eb})\gamma^{\mathrm{H}}_{ab} \\ &= \sum_{a} h_{am}\gamma^{\mathrm{H}}_{ae}\end{aligned} \tag{95}$$

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

$$
\begin{aligned}
&=\sum_{ija}\langle am||ji\rangle(\Gamma^{\mathrm{H}})^{ea}_{ij}+\sum_{ija}\langle am||ji\rangle(\Gamma^{\mathrm{H}})^{ae}_{ji}-\sum_{iab}\langle ab||ei\rangle(\Gamma^{\mathrm{H}})^{ab}_{mi}-\sum_{iab}\langle ab||ei\rangle(\Gamma^{\mathrm{H}})^{ba}_{im}\\
&=2\sum_{ija}\langle am||ji\rangle(\Gamma^{\mathrm{H}})^{ea}_{ij}-2\sum_{iab}\langle ab||ei\rangle(\Gamma^{\mathrm{H}})^{ab}_{mi} \qquad (96)
\end{aligned}
$$

in which the symmetry of MP2 amplitudes is exploited:

$$
T^{ab}_{ij}=T^{ba}_{ji}\Leftrightarrow(\Gamma^{\mathrm{H}})^{ab}_{ij}=(\Gamma^{\mathrm{H}})^{ba}_{ji} \qquad (97)
$$

$$
\begin{aligned}
&\sum_{ijab}\frac{\partial\langle ab||ij\rangle}{\partial\kappa^*_{em}}\left(\Gamma^{\mathrm{H}}\right)^{ab}_{ij}\Big|_{\lambda=0}=-\sum_{ijab}\frac{\partial\langle ab||ij\rangle}{\partial\kappa_{me}}\left(\Gamma^{\mathrm{H}}\right)^{ab}_{ij}\Big|_{\lambda=0}\\
=&-\sum_{ijab}\Big(\cancel{\langle eb||ij\rangle\delta_{am}}+\cancel{\langle ae||ij\rangle\delta_{bm}}-\cancel{\langle ab||mj\rangle\delta_{ie}}-\cancel{\langle ab||im\rangle\delta_{je}}\Big)(\Gamma^{\mathrm{H}})^{ab}_{ij}\\
=&0 \qquad (98)
\end{aligned}
$$

Similarly:

$$
\begin{aligned}
&\sum_{ijab}\frac{\partial\langle ij||ab\rangle}{\partial\kappa_{em}}\left(\Gamma^{\mathrm{H}}\right)^{ij}_{ab}\Big|_{\lambda=0}\\
=&\sum_{ijab}\Big(\cancel{\langle mj||ab\rangle\delta_{ie}}+\cancel{\langle im||ab\rangle\delta_{je}}-\cancel{\langle ij||eb\rangle\delta_{am}}-\cancel{\langle ij||ae\rangle\delta_{bm}}\Big)(\Gamma^{\mathrm{H}})^{ij}_{ab}\\
=&0 \qquad (99)
\end{aligned}
$$

$$
\begin{aligned}
&\sum_{ijab}\frac{\partial\langle ij||ab\rangle}{\partial\kappa^*_{em}}\left(\Gamma^{\mathrm{H}}\right)^{ij}_{ab}\Big|_{\lambda=0}=-\sum_{ijab}\frac{\partial\langle ij||ab\rangle}{\partial\kappa_{me}}\left(\Gamma^{\mathrm{H}}\right)^{ij}_{ab}\Big|_{\lambda=0}\\
=&-\sum_{ijab}\Big(\langle ej||ab\rangle\delta_{im}+\langle ie||ab\rangle\delta_{jm}-\langle ij||mb\rangle\delta_{ae}-\langle ij||am\rangle\delta_{be}\Big)(\Gamma^{\mathrm{H}})^{ij}_{ab}\\
=&-\sum_{jab}\langle ej||ab\rangle(\Gamma^{\mathrm{H}})^{mj}_{ab}-\sum_{iab}\langle ie||ab\rangle(\Gamma^{\mathrm{H}})^{im}_{ab}+\sum_{ijb}\langle ij||mb\rangle(\Gamma^{\mathrm{H}})^{ij}_{eb}+\sum_{ija}\langle ij||am\rangle(\Gamma^{\mathrm{H}})^{ij}_{ae}\\
=&-\sum_{iab}\langle ie||ab\rangle(\Gamma^{\mathrm{H}})^{mi}_{ba}-\sum_{iab}\langle ie||ab\rangle(\Gamma^{\mathrm{H}})^{im}_{ab}+\sum_{ija}\langle ij||am\rangle(\Gamma^{\mathrm{H}})^{ji}_{ea}+\sum_{ija}\langle ij||am\rangle(\Gamma^{\mathrm{H}})^{ij}_{ae}\\
=&-\sum_{iab}\langle ie||ab\rangle\left((\Gamma^{\mathrm{H}})^{mi}_{ba}+(\Gamma^{\mathrm{H}})^{im}_{ab}\right)+\sum_{ija}\langle ij||am\rangle\left((\Gamma^{\mathrm{H}})^{ji}_{ea}+(\Gamma^{\mathrm{H}})^{ij}_{ae}\right)\\
=&-2\sum_{iab}\langle ie||ab\rangle(\Gamma^{\mathrm{H}})^{im}_{ab}+2\sum_{ija}\langle ij||am\rangle(\Gamma^{\mathrm{H}})^{ij}_{ae} \qquad (100)
\end{aligned}
$$

Then:

$$
\begin{aligned}
&\sum_{ijkl}\frac{\partial\langle ij||kl\rangle}{\partial\kappa_{em}}\left(\Gamma^{\mathrm{H}}\right)^{ij}_{kl}\Big|_{\lambda=0}\\
=&\sum_{ijkl}\Big(\cancel{\langle mj||kl\rangle\delta_{ie}}+\cancel{\langle im||kl\rangle\delta_{je}}-\langle ij||el\rangle\delta_{km}-\langle ij||ke\rangle\delta_{lm}\Big)(\Gamma^{\mathrm{H}})^{ij}_{kl}\\
=&-\sum_{ijl}\langle ij||el\rangle(\Gamma^{\mathrm{H}})^{ij}_{ml}-\sum_{ijk}\langle ij||ke\rangle(\Gamma^{\mathrm{H}})^{ij}_{km}\\
=&-\sum_{ijk}\langle ij||ek\rangle(\Gamma^{\mathrm{H}})^{ij}_{mk}-\sum_{ijk}\langle ij||ek\rangle(\Gamma^{\mathrm{H}})^{ji}_{km} \qquad (101)
\end{aligned}
$$

$$
\begin{aligned}
&\sum_{ijkl} \frac{\partial \langle ij||kl\rangle}{\partial \kappa_{em}^*} \left(\Gamma^{\mathrm{H}}\right)_{kl}^{ij}\Big|_{\lambda=0} = -\sum_{ijkl} \frac{\partial \langle ij||kl\rangle}{\partial \kappa_{me}} \left(\Gamma^{\mathrm{H}}\right)_{kl}^{ij}\Big|_{\lambda=0} \\
&= -\sum_{ijkl} \Big( \langle ej||kl\rangle \delta_{im} + \langle ie||kl\rangle \delta_{jm} - \cancel{\langle ij||ml\rangle \delta_{ke}} - \cancel{\langle ij||km\rangle \delta_{le}} \Big) (\Gamma^{\mathrm{H}})_{kl}^{ij} \\
&= -\sum_{jkl} \langle ej||kl\rangle (\Gamma^{\mathrm{H}})_{kl}^{mj} - \sum_{ikl} \langle ie||kl\rangle (\Gamma^{\mathrm{H}})_{kl}^{im} \\
&= -\sum_{ikl} \langle ie||kl\rangle (\Gamma^{\mathrm{H}})_{lk}^{mi} - \sum_{ikl} \langle ie||kl\rangle (\Gamma^{\mathrm{H}})_{kl}^{im}
\end{aligned}
\tag{102}
$$

No symmetry for $(\Gamma^{\mathrm{H}})_{kl}^{ij}$ could be used to simplify the expression.

$$
\begin{aligned}
&\sum_{ijab} \frac{\partial \langle ai||bj\rangle}{\partial \kappa_{em}} \left(\Gamma^{\mathrm{H}}\right)_{bj}^{ai}\Big|_{\lambda=0} \\
&= \sum_{ijab} \Big( \langle mi||bj\rangle \delta_{ae} + \cancel{\langle am||bj\rangle \delta_{ie}} - \cancel{\langle ai||ej\rangle \delta_{bm}} - \langle ai||be\rangle \delta_{jm} \Big) (\Gamma^{\mathrm{H}})_{bj}^{ai} \\
&= \sum_{ijb} \langle mi||bj\rangle (\Gamma^{\mathrm{H}})_{bj}^{ei} - \sum_{iab} \langle ai||be\rangle (\Gamma^{\mathrm{H}})_{bm}^{ai}
\end{aligned}
\tag{103}
$$

$$
\begin{aligned}
&\sum_{ijab} \frac{\partial \langle ai||bj\rangle}{\partial \kappa_{em}^*} \left(\Gamma^{\mathrm{H}}\right)_{bj}^{ai}\Big|_{\lambda=0} = -\sum_{ijab} \frac{\partial \langle ai||bj\rangle}{\partial \kappa_{me}} \left(\Gamma^{\mathrm{H}}\right)_{bj}^{ai}\Big|_{\lambda=0} \\
&= -\sum_{ijab} \Big( \cancel{\langle ei||bj\rangle \delta_{am}} + \langle ae||bj\rangle \delta_{im} - \langle ai||mj\rangle \delta_{be} - \cancel{\langle ai||bm\rangle \delta_{je}} \Big) (\Gamma^{\mathrm{H}})_{bj}^{ai} \\
&= -\sum_{jab} \langle ae||bj\rangle (\Gamma^{\mathrm{H}})_{bj}^{am} + \sum_{ija} \langle ai||mj\rangle (\Gamma^{\mathrm{H}})_{ej}^{ai}
\end{aligned}
\tag{104}
$$

Therefore, the overall Hylleraas response is:

$$
\begin{aligned}
\frac{\partial E_{\mathrm{H}}}{\partial \kappa_{bj}}\Big|_{\lambda=0} =& \sum_a h_{ja} \gamma_{ba}^{\mathrm{H}} - \sum_i h_{ib} \gamma_{ij}^{\mathrm{H}} \\
&+ 2\sum_{ika} \langle aj||ki\rangle (\Gamma^{\mathrm{H}})_{ik}^{ba} - 2\sum_{iac} \langle ac||bi\rangle (\Gamma^{\mathrm{H}})_{ji}^{ac} \\
&- \sum_{ikl} \langle ik||bl\rangle (\Gamma^{\mathrm{H}})_{jl}^{ik} - \sum_{ikl} \langle ik||bl\rangle (\Gamma^{\mathrm{H}})_{lj}^{ki} \\
&+ \sum_{ika} \langle ji||ak\rangle (\Gamma^{\mathrm{H}})_{ak}^{bi} - \sum_{iac} \langle ai||cb\rangle (\Gamma^{\mathrm{H}})_{cj}^{ai} \\
=& \sum_a h_{ja} \gamma_{ba}^{\mathrm{H}} - \sum_i h_{ib} \gamma_{ij}^{\mathrm{H}} + \frac{1}{2} \sum_{ika} \langle aj||ki\rangle (T_{ik}^{ba})^* - \frac{1}{2} \sum_{iac} \langle ac||bi\rangle (T_{ji}^{ac})^* \\
&- \sum_{ikl} \langle ik||bl\rangle \gamma_{ij}^{\mathrm{H}} \delta_{kl} - \sum_{ikl} \langle ik||bl\rangle \gamma_{kl}^{\mathrm{H}} \delta_{ij} + \sum_{ika} \langle ji||ak\rangle \gamma_{ba}^{\mathrm{H}} \delta_{ik} - \sum_{iac} \langle ai||cb\rangle \gamma_{ac}^{\mathrm{H}} \delta_{ij} \\
=& \sum_a h_{ja} \gamma_{ba}^{\mathrm{H}} - \sum_i h_{ib} \gamma_{ij}^{\mathrm{H}} + \frac{1}{2} \sum_{ika} \langle aj||ki\rangle (T_{ik}^{ba})^* - \frac{1}{2} \sum_{iac} \langle ac||bi\rangle (T_{ji}^{ac})^* \\
&- \sum_{ik} \langle ik||bk\rangle \gamma_{ij}^{\mathrm{H}} - \sum_{kl} \langle jk||bl\rangle \gamma_{kl}^{\mathrm{H}} + \sum_{ia} \langle ji||ai\rangle \gamma_{ba}^{\mathrm{H}} - \sum_{ac} \langle aj||cb\rangle \gamma_{ac}^{\mathrm{H}} \\
=& \sum_a \cancel{f_{ja}} \gamma_{ba}^{\mathrm{H}} - \sum_i \cancel{f_{ib}} \gamma_{ij}^{\mathrm{H}} + \frac{1}{2} \sum_{ika} \langle ja||ik\rangle (T_{ik}^{ba})^* - \frac{1}{2} \sum_{iac} \langle ac||bi\rangle (T_{ji}^{ac})^*
\end{aligned}
$$

$$
\begin{aligned}
&- \sum_{kl} \langle jk||bl\rangle \gamma^{\mathrm{H}}_{kl} - \sum_{ac} \langle aj||cb\rangle \gamma^{\mathrm{H}}_{ac} \\
=& - X_{bj}
\end{aligned}
\tag{105}
$$

$$
X_{bj} = \frac{1}{2}\sum_{iac} \langle ac||bi\rangle (T^{ac}_{ji})^* - \frac{1}{2}\sum_{ika} \langle ja||ik\rangle (T^{ba}_{ik})^* + \sum_{ac} \langle aj||cb\rangle \gamma^{\mathrm{H}}_{ac} + \sum_{kl} \langle jk||bl\rangle \gamma^{\mathrm{H}}_{kl}
\tag{106}
$$

$$
\begin{aligned}
\frac{\partial E_{\mathrm{H}}}{\partial \kappa^*_{bj}}\Big|_{\lambda=0} =& \sum_a h_{aj} \gamma^{\mathrm{H}}_{ab} - \sum_i h_{bi} \gamma^{\mathrm{H}}_{ji} \\
&+ 2\sum_{ika} \langle ik||aj\rangle (\Gamma^{\mathrm{H}})^{ik}_{ab} - 2\sum_{iac} \langle ib||ac\rangle (\Gamma^{\mathrm{H}})^{ij}_{ac} \\
&- \sum_{ikl} \langle ib||kl\rangle (\Gamma^{\mathrm{H}})^{ij}_{kl} - \sum_{ikl} \langle ib||kl\rangle (\Gamma^{\mathrm{H}})^{ji}_{lk} \\
&+ \sum_{ika} \langle ai||jk\rangle (\Gamma^{\mathrm{H}})^{ai}_{bk} - \sum_{iac} \langle ab||ci\rangle (\Gamma^{\mathrm{H}})^{aj}_{ci} \\
=& \sum_a h_{aj} \gamma^{\mathrm{H}}_{ab} - \sum_i h_{bi} \gamma^{\mathrm{H}}_{ji} + \frac{1}{2}\sum_{ika} \langle ik||aj\rangle T^{ab}_{ik} - \frac{1}{2}\sum_{iac} \langle ib||ac\rangle T^{ac}_{ij} \\
&- \sum_{ikl} \langle ib||kl\rangle \gamma^{\mathrm{H}}_{ik} \delta_{jl} - \sum_{ikl} \langle lb||ki\rangle \gamma^{\mathrm{H}}_{ji} \delta_{lk} + \sum_{ika} \langle ai||jk\rangle \gamma^{\mathrm{H}}_{ab} \delta_{ik} - \sum_{iac} \langle ab||ci\rangle \gamma^{\mathrm{H}}_{ac} \delta_{ij} \\
=& \sum_a f_{aj} \gamma^{\mathrm{H}}_{ab} - \sum_i f_{bi} \gamma^{\mathrm{H}}_{ji} + \frac{1}{2}\sum_{ika} \langle ik||aj\rangle T^{ab}_{ik} - \frac{1}{2}\sum_{iac} \langle ib||ac\rangle T^{ac}_{ij} \\
&- \sum_{ik} \langle ib||kj\rangle \gamma^{\mathrm{H}}_{ik} - \sum_{ac} \langle ab||cj\rangle \gamma^{\mathrm{H}}_{ac} \\
=& - X^*_{bj}
\end{aligned}
\tag{107}
$$

which are consistent with the Gauss-1993 paper.

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

$$
E_{\mathrm{HF}} = \sum_i h_{ii} + \frac{1}{2}\sum_{ik} \langle ik||ik\rangle
\tag{108}
$$

$$
\begin{aligned}
\frac{\partial E_{\mathrm{HF}}}{\partial \kappa_{bj}}\Big|_{\lambda=0} =& \sum_i \frac{\partial h_{ii}}{\partial \kappa_{bj}}\Big|_{\lambda=0} + \frac{1}{2}\sum_{ik} \frac{\partial \langle ik||ik\rangle}{\partial \kappa_{bj}}\Big|_{\lambda=0} \\
=& \sum_i (\cancel{h_{ji}\delta_{ib}} - h_{ib}\delta_{ij}) \\
&+ \frac{1}{2}\sum_{ik} \Big( \cancel{\langle jk||ik\rangle \delta_{ib}} + \cancel{\langle ij||ik\rangle \delta_{kb}} - \langle ik||bk\rangle \delta_{ij} - \langle ik||ib\rangle \delta_{kj} \Big) \\
=& - h_{jb} - \frac{1}{2}\sum_k \langle jk||bk\rangle - \frac{1}{2}\sum_i \langle ij||ib\rangle \\
=& - h_{jb} - \sum_i \langle ji||bi\rangle \\
=& - f_{jb} \\
=& 0
\end{aligned}
\tag{109}
$$

$$
\frac{\partial E_{\mathrm{HF}}}{\partial \kappa^*_{bj}}\Big|_{\lambda=0} = - \sum_i \frac{\partial h_{ii}}{\partial \kappa_{jb}}\Big|_{\lambda=0} - \frac{1}{2}\sum_{ik} \frac{\partial \langle ik||ik\rangle}{\partial \kappa_{jb}}\Big|_{\lambda=0}
$$

$$\begin{aligned}
&= -\sum_i (h_{bi}\delta_{ij} - \cancel{h_{ij}\delta_{ib}}) \\
&\quad - \frac{1}{2}\sum_{ik}\left(\langle bk||ik\rangle\delta_{ij} + \langle ib||ik\rangle\delta_{jk} - \cancel{\langle ik||jk\rangle\delta_{ib}} - \cancel{\langle ik||ij\rangle\delta_{bk}}\right) \\
&= -h_{bj} - \frac{1}{2}\sum_k \langle bk||jk\rangle - \frac{1}{2}\sum_i \langle ib||ij\rangle \\
&= -h_{bj} - \sum_i \langle bi||ji\rangle \\
&= -f_{bj} \\
&= 0
\end{aligned} \tag{110}$$

The Lagrangian constraints on orbital rotation:

$$\frac{\partial \mathcal{L}_{\mathrm{MP2}}}{\partial \kappa_{bj}}\Big|_{\lambda=0} = \frac{\partial E_{\mathrm{HF}}}{\partial \kappa_{bj}}\Big|_{\lambda=0} + \frac{\partial E_{\mathrm{H}}}{\partial \kappa_{bj}}\Big|_{\lambda=0} + \frac{1}{2}\sum_{ai} z_{ai}\frac{\partial f_{ai}}{\partial \kappa_{bj}}\Big|_{\lambda=0} + \frac{1}{2}\sum_{ai} z^*_{ai}\frac{\partial f^*_{ai}}{\partial \kappa_{bj}}\Big|_{\lambda=0} = 0 \tag{111}$$

$$\frac{\partial \mathcal{L}_{\mathrm{MP2}}}{\partial \kappa^*_{bj}}\Big|_{\lambda=0} = \frac{\partial E_{\mathrm{HF}}}{\partial \kappa^*_{bj}}\Big|_{\lambda=0} + \frac{\partial E_{\mathrm{H}}}{\partial \kappa^*_{bj}}\Big|_{\lambda=0} + \frac{1}{2}\sum_{ai} z_{ai}\frac{\partial f_{ai}}{\partial \kappa^*_{bj}}\Big|_{\lambda=0} + \frac{1}{2}\sum_{ai} z^*_{ai}\frac{\partial f^*_{ai}}{\partial \kappa^*_{bj}}\Big|_{\lambda=0} = 0 \tag{112}$$

The fock matrix derivatives:

$$\begin{aligned}
\sum_{ai} z_{ai}\frac{\partial f_{ai}}{\partial \kappa_{bj}}\Big|_{\lambda=0} &= \sum_{ai} z_{ai}(\varepsilon_i - \varepsilon_a)\delta_{ab}\delta_{ij} \\
&= z_{bj}(\varepsilon_j - \varepsilon_b)
\end{aligned} \tag{113}$$

$$\begin{aligned}
\sum_{ai} z^*_{ai}\frac{\partial f^*_{ai}}{\partial \kappa_{bj}}\Big|_{\lambda=0} &= \sum_{ai} z_{ia}\frac{\partial f_{ia}}{\partial \kappa_{bj}}\Big|_{\lambda=0} \\
&= \sum_{ai} z_{ia}(\varepsilon_a - \varepsilon_i)\delta_{ib}\delta_{ja} \\
&= 0
\end{aligned} \tag{114}$$

$$\begin{aligned}
\sum_{ai} z_{ai}\frac{\partial f_{ai}}{\partial \kappa^*_{bj}}\Big|_{\lambda=0} &= -\sum_{ai} z_{ai}\frac{\partial f_{ai}}{\partial k_{jb}}\Big|_{\lambda=0} \\
&= -\sum_{ai} z_{ai}(\varepsilon_i - \varepsilon_a)\delta_{aj}\delta_{bi} \\
&= 0
\end{aligned} \tag{115}$$

$$\begin{aligned}
\sum_{ai} z^*_{ai}\frac{\partial f^*_{ai}}{\partial \kappa^*_{bj}}\Big|_{\lambda=0} &= -\sum_{ai} z^*_{ai}\frac{\partial f_{ia}}{\partial \kappa_{jb}}\Big|_{\lambda=0} \\
&= -\sum_{ai} z^*_{ai}(\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ba} \\
&= z^*_{bj}(\varepsilon_j - \varepsilon_b)
\end{aligned} \tag{116}$$

Now the Z-Vector equations becomes:

$$\frac{1}{2}\sum_{ai} z_{ai}\frac{\partial f_{ai}}{\partial \kappa_{bj}}\Big|_{\lambda=0} = -\frac{\partial E_{\mathrm{H}}}{\partial \kappa_{bj}}\Big|_{\lambda=0} \tag{117}$$

$$\frac{1}{2}\sum_{ai} z^*_{ai} \frac{\partial f^*_{ai}}{\partial \kappa^*_{bj}}\Big|_{\lambda=0} = -\frac{\partial E_{\mathrm{H}}}{\partial \kappa^*_{bj}}\Big|_{\lambda=0} \tag{118}$$

in which the RHS are the orbital gradients for MP2. The RHS (Hylleraas response) has been worked out previously. Moving the negative sign to the left, we obtain the Z-Vector equations as:

$$\frac{1}{2}(\varepsilon_b - \varepsilon_j) z_{bj} = -X_{bj} \tag{119}$$

$$\frac{1}{2}(\varepsilon_b - \varepsilon_j) z^*_{bj} = -X^*_{bj} \tag{120}$$

in which

$$X_{bj} = \frac{1}{2}\sum_{iac}\langle ac||bi\rangle (T^{ac}_{ji})^* - \frac{1}{2}\sum_{ika}\langle ja||ik\rangle (T^{ba}_{ik})^* + \sum_{ac}\langle aj||cb\rangle \gamma^{\mathrm{H}}_{ac} + \sum_{kl}\langle jk||bl\rangle \gamma^{\mathrm{H}}_{kl} \tag{121}$$

## 2 Summary of MP2 Gradient

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

$$\begin{aligned}\mathcal{L}_{\text{MP2}} =& E_{\text{HF}} + E_{\text{H}} + \frac{1}{2}\sum_{ai}\left(z_{ai}f_{ai} + z_{ai}^* f_{ai}^*\right) \\ =& \sum_{pq} h_{pq}\gamma_{pq} + \sum_{pqrs}\Gamma_{rs}^{pq}\langle pq||rs\rangle + \frac{1}{2}\sum_{ai}\left(z_{ai}f_{ai} + z_{ai}^* f_{ai}^*\right)\end{aligned} \tag{122}$$

Constraints:

$$\frac{\partial\mathcal{L}_{\text{MP2}}}{\partial z_{bj}} = \frac{1}{2}f_{bj} = 0 \qquad \text{Hatree-Fock Condition} \tag{123}$$

$$\frac{\partial\mathcal{L}_{\text{MP2}}}{\partial z_{bj}^*} = \frac{1}{2}f_{bj}^* = 0 \qquad \text{Hatree-Fock Condition} \tag{124}$$

$$\frac{\partial\mathcal{L}_{\text{MP2}}}{\partial T_{ij}^{ab}} = \frac{\partial E_{\text{H}}}{\partial T_{ij}^{ab}} = 0 \qquad \text{MP2 Condition} \tag{125}$$

$$\frac{\partial\mathcal{L}_{\text{MP2}}}{\partial (T_{ij}^{ab})^*} = \frac{\partial E_{\text{H}}}{\partial (T_{ij}^{ab})^*} = 0 \qquad \text{MP2 Condition} \tag{126}$$

$$\frac{\partial\mathcal{L}_{\text{MP2}}}{\partial \kappa_{bj}} = \frac{\partial E_{\text{H}}}{\partial \kappa_{bj}} + \frac{1}{2}\sum_{ai}\left(z_{ai}\frac{\partial f_{ai}}{\partial\kappa_{bj}} + z_{ai}^*\frac{\partial f_{ai}^*}{\partial\kappa_{bj}}\right) = 0 \qquad \text{Z-Vector Equation} \tag{127}$$

$$\frac{\partial\mathcal{L}_{\text{MP2}}}{\partial \kappa_{bj}^*} = \frac{\partial E_{\text{H}}}{\partial \kappa_{bj}^*} + \frac{1}{2}\sum_{ai}\left(z_{ai}\frac{\partial f_{ai}}{\partial\kappa_{bj}^*} + z_{ai}^*\frac{\partial f_{ai}^*}{\partial\kappa_{bj}^*}\right) = 0 \qquad \text{Z-Vector Equation} \tag{128}$$

The orthonormality condition is already fulfilled through the parameterization of orbital rotation:

$$\begin{aligned}\mathbf{S}(\lambda) =& \mathbf{C}^\dagger(\lambda)\mathbf{S}^{\text{AO}}(\lambda)\mathbf{C}(\lambda) \\ =& \mathbf{U}^\dagger(\lambda)\mathbf{C}^\dagger(0)\mathbf{S}^{\text{AO}}(\lambda)\mathbf{C}(0)\mathbf{U}(\lambda) \\ =& \mathbf{U}^\dagger(\lambda)\boldsymbol{\mathcal{S}}(\lambda)\mathbf{U}(\lambda) \\ =& \exp[-\boldsymbol{\kappa}(\lambda)]^\dagger\boldsymbol{\mathcal{S}}^{-\frac{1}{2}\dagger}(\lambda)\boldsymbol{\mathcal{S}}(\lambda)\boldsymbol{\mathcal{S}}^{-\frac{1}{2}}(\lambda)\exp[-\boldsymbol{\kappa}(\lambda)] \\ =& \exp[\boldsymbol{\kappa}(\lambda)]\exp[-\boldsymbol{\kappa}(\lambda)] \\ =& \mathbf{I}\end{aligned} \tag{129}$$

Unrelaxed reduced density matrices (RDMs):

$$\gamma_{pq} = \gamma_{pq}^{\text{HF}} + \gamma_{pq}^{\text{H}} \tag{130}$$

$$\Gamma_{rs}^{pq} = (\Gamma^{\text{HF}})_{rs}^{pq} + (\Gamma^{\text{H}})_{rs}^{pq} \tag{131}$$

$$\gamma_{ij}^{\text{H}} = \frac{1}{2}\sum_{kab}(T_{jk}^{ab})^* T_{ki}^{ab} \qquad \gamma_{ij}^{\text{HF}} = \delta_{ij} \tag{132}$$

$$\gamma_{ab}^{\text{H}} = -\frac{1}{2}\sum_{ijc}(T_{ij}^{ac})^* T_{ij}^{cb} \tag{133}$$

$$(\Gamma^{\text{H}})_{ij}^{ab} = \frac{1}{4}(T_{ij}^{ab})^* \tag{134}$$

$$(\Gamma^{\text{H}})_{ab}^{ij} = \frac{1}{4}T_{ij}^{ab} \tag{135}$$

$$(\Gamma^{\text{H}})_{kl}^{ij} = \frac{1}{2}\sum_{mab}(T_{km}^{ab})^* T_{mi}^{ab}\delta_{jl} = \gamma_{ik}^{\text{H}}\delta_{jl} \qquad (\Gamma^{\text{HF}})_{kl}^{ij} = \frac{1}{2}\delta_{ik}\delta_{jl} \tag{136}$$

$$(\Gamma^{\text{H}})_{bj}^{ai} = -\frac{1}{2}\sum_{klc}(T_{kl}^{ac})^* T_{kl}^{cb}\delta_{ij} = \gamma_{ab}^{\text{H}}\delta_{ij} \tag{137}$$