1 Direct Differentiation

MP2 energy in spin-orbital formalism:

$$
\begin{aligned}
E^{(2)} =& \frac{1}{4}\sum_{ijab}\frac{\langle ab||ij\rangle\langle ij||ab\rangle}{f_{ii}+f_{jj}-f_{aa}-f_{bb}} \\
=& \frac{1}{4}\sum_{ijab} T_{ij}^{ab}\langle ij||ab\rangle
\end{aligned} \tag{1}
$$

in which we denote the MP2 amplitude:

$$
T_{ij}^{ab} = \frac{\langle ab||ij\rangle}{\Delta_{ab}^{ij}} = \frac{\langle ab||ij\rangle}{f_{ii}+f_{jj}-f_{aa}-f_{bb}} \tag{2}
$$

Directly differentiate the second-order energy w.r.t. perturbation parameter λ:

$$
\begin{aligned}
\frac{\partial E^{(2)}}{\partial\lambda} =& \frac{1}{4}\sum_{ijab}\frac{\partial}{\partial\lambda}\Big(T_{ij}^{ab}\langle ij||ab\rangle\Big) \\
=& \frac{1}{4}\sum_{ijab}\Big(\frac{\partial T_{ij}^{ab}}{\partial\lambda}\Big)\langle ij||ab\rangle + \frac{1}{4}\sum_{ijab} T_{ij}^{ab}\Big(\frac{\partial\langle ij||ab\rangle}{\partial\lambda}\Big)
\end{aligned} \tag{3}
$$

in which:

$$
\frac{\partial\langle ij||ab\rangle}{\partial\lambda} = \langle i^\lambda j||ab\rangle + \langle ij^\lambda||ab\rangle + \langle ij||a^\lambda b\rangle + \langle ij||ab^\lambda\rangle \tag{4}
$$

exploiting the permutational symmetry and equivalence of the dummy indices:

$$
\sum_{ijab}\langle ij^\lambda||ab\rangle = \sum_{ijab}\langle j^\lambda i||ba\rangle = \sum_{jiba}\langle i^\lambda j||ab\rangle \tag{5}
$$

Therefore:

$$
\sum_{ijab}\langle ij||ab\rangle^\lambda = 2\sum_{ijab}(\langle i^\lambda j||ab\rangle + \langle ij||a^\lambda b\rangle) \tag{6}
$$

Then:

$$
\begin{aligned}
\frac{\partial T_{ij}^{ab}}{\partial\lambda} =& \frac{\partial}{\partial\lambda}\left(\frac{\langle ab||ij\rangle}{\Delta_{ab}^{ij}}\right) \\
=& \frac{\langle ab||ij\rangle^\lambda}{\Delta_{ab}^{ij}} - \frac{\langle ab||ij\rangle}{(\Delta_{ab}^{ij})^2}\Big(\frac{\partial\Delta_{ab}^{ij}}{\partial\lambda}\Big) \\
=& \frac{\langle ab||ij\rangle^\lambda}{\Delta_{ab}^{ij}} - \frac{\langle ab||ij\rangle}{(\Delta_{ab}^{ij})^2}(\varepsilon_i^\lambda + \varepsilon_j^\lambda - \varepsilon_a^\lambda - \varepsilon_b^\lambda)
\end{aligned} \tag{7}
$$

Putting eqns (6) and (7) together:

$$
\begin{aligned}
\frac{\partial E^{(2)}}{\partial\lambda} =& \frac{1}{4}\sum_{ijab}\langle ij||ab\rangle(T_{ij}^{ab})^\lambda + \frac{1}{4}\sum_{ijab} T_{ij}^{ab}\langle ij||ab\rangle^\lambda \\
=& \frac{1}{4}\sum_{ijab}\langle ij||ab\rangle\Big(\frac{\langle ab||ij\rangle^\lambda}{\Delta_{ab}^{ij}} - \frac{\langle ab||ij\rangle}{(\Delta_{ab}^{ij})^2}(\varepsilon_i^\lambda + \varepsilon_j^\lambda - \varepsilon_a^\lambda - \varepsilon_b^\lambda)\Big) + \frac{1}{4}\sum_{ijab}\langle ij||ab\rangle^\lambda T_{ij}^{ab} \\
=& \frac{1}{4}\sum_{ijab}\frac{\langle ij||ab\rangle\langle ab||ij\rangle^\lambda}{\Delta_{ab}^{ij}} + \frac{1}{4}\sum_{ijab}\frac{\langle ij||ab\rangle^\lambda\langle ab||ij\rangle}{\Delta_{ab}^{ij}} - \frac{1}{4}\sum_{ijab}\frac{\langle ij||ab\rangle\langle ab||ij\rangle}{(\Delta_{ab}^{ij})^2}(2\varepsilon_i^\lambda - 2\varepsilon_a^\lambda)
\end{aligned}
$$

$$
\begin{aligned}
=&\frac{1}{2}\sum_{ijab}(T_{ij}^{ab})^*\langle a^\lambda b||ij\rangle + \frac{1}{2}\sum_{ijab}(T_{ij}^{ab})^*\langle ab||i^\lambda j\rangle + \frac{1}{2}\sum_{ijab}T_{ij}^{ab}\langle i^\lambda j||ab\rangle + \frac{1}{2}\sum_{ijab}T_{ij}^{ab}\langle ij||a^\lambda b\rangle \\
&-\frac{1}{2}\sum_{ijab}T_{ij}^{ab}(T_{ij}^{ab})^*(\varepsilon_i^\lambda - \varepsilon_a^\lambda)
\end{aligned}
\tag{8}
$$

Using the expression for $|i^\lambda\rangle$ and $|a^\lambda\rangle$:

$$
\begin{aligned}
\frac{\partial E^{(2)}}{\partial\lambda} =&\frac{1}{2}\sum_{ijab}(T_{ij}^{ab})^*\Big(\sum_{k}(U_{ka}^\lambda)^*\langle kb||ij\rangle + \sum_{f\neq a}(U_{fa}^\lambda)^*\langle fb||ij\rangle + \sum_{\mu}C_{\mu a}^*\langle\mu^\lambda b||ij\rangle\Big) \\
&+\frac{1}{2}\sum_{ijab}(T_{ij}^{ab})^*\Big(\sum_{k\neq i}U_{ki}^\lambda\langle ab||kj\rangle + \sum_{f}U_{fi}^\lambda\langle ab||fj\rangle + \sum_{\mu}C_{\mu i}\langle ab||\mu^\lambda j\rangle\Big) \\
&+\frac{1}{2}\sum_{ijab}T_{ij}^{ab}\Big(\sum_{k\neq i}(U_{ki}^\lambda)^*\langle kj||ab\rangle + \sum_{f}(U_{fi}^\lambda)^*\langle fj||ab\rangle + \sum_{\mu}C_{\mu i}^*\langle\mu^\lambda j||ab\rangle\Big) \\
&+\frac{1}{2}\sum_{ijab}T_{ij}^{ab}\Big(\sum_{k}U_{ka}^\lambda\langle ij||kb\rangle + \sum_{f\neq a}U_{fa}^\lambda\langle ij||fb\rangle + \sum_{\mu}C_{\mu a}\langle ij||\mu^\lambda b\rangle\Big) \\
&-\frac{1}{2}\sum_{ijab}T_{ij}^{ab}(T_{ij}^{ab})^*(\varepsilon_i^\lambda - \varepsilon_a^\lambda)
\end{aligned}
\tag{9}
$$

Using the orthonormality condition on $(U_{ka}^\lambda)^*$, $(U_{fa}^\lambda)^*$, $(U_{ki}^\lambda)^*$ and U_{ka}^λ, and omitting the AO terms (terms involving $|\phi_\mu\rangle$) for now:

$$
\begin{aligned}
\frac{\partial E^{(2)}}{\partial\lambda} =&\frac{1}{2}\sum_{ijab}\sum_{k}(T_{ij}^{ab})^*\langle kb||ij\rangle(-S_{ak}^\lambda - U_{ak}^\lambda) + \frac{1}{2}\sum_{ijab}\sum_{f\neq a}(T_{ij}^{ab})^*\langle fb||ij\rangle(-S_{af}^\lambda - U_{af}^\lambda) \\
&+\frac{1}{2}\sum_{ijab}\sum_{k\neq i}(T_{ij}^{ab})^*\langle ab||kj\rangle U_{ki}^\lambda + \frac{1}{2}\sum_{ijab}\sum_{f}(T_{ij}^{ab})^*\langle ab||fi\rangle U_{fi}^\lambda \\
&+\frac{1}{2}\sum_{ijab}\sum_{k\neq i}T_{ij}^{ab}\langle kj||ab\rangle(-S_{ik}^\lambda - U_{ik}^\lambda) + \frac{1}{2}\sum_{ijab}\sum_{f}T_{ij}^{ab}\langle fj||ab\rangle(U_{fi}^\lambda)^* \\
&+\frac{1}{2}\sum_{ijab}\sum_{k}T_{ij}^{ab}\langle ij||kb\rangle(-S_{ak}^\lambda - (U_{ak}^\lambda)^*) + \frac{1}{2}\sum_{ijab}\sum_{f\neq a}T_{ij}^{ab}\langle ij||fb\rangle U_{fa}^\lambda \\
&-\frac{1}{2}\sum_{ijab}T_{ij}^{ab}(T_{ij}^{ab})^*(\varepsilon_i^\lambda - \varepsilon_a^\lambda) + \text{AO terms}
\end{aligned}
\tag{10}
$$

collecting the U_{af}^λ and U_{fa}^λ terms and swapping some dummy indices:

$$
\begin{aligned}
A =& -\frac{1}{2}\sum_{ijab}\sum_{f\neq a}(T_{ij}^{ab})^*\langle fb||ij\rangle U_{af}^\lambda + \frac{1}{2}\sum_{ijab}\sum_{f\neq a}T_{ij}^{ab}\langle ij||fb\rangle U_{fa}^\lambda \\
=& -\frac{1}{2}\sum_{ijfb}\sum_{a\neq f}(T_{ij}^{fb})^*\langle ab||ij\rangle U_{fa}^\lambda + \frac{1}{2}\sum_{ijab}\sum_{f\neq a}T_{ij}^{ab}\langle ij||fb\rangle U_{fa}^\lambda \\
=&\frac{1}{2}\sum_{ijab}\sum_{f\neq a}\langle ij||fb\rangle\langle ab||ij\rangle U_{fa}^\lambda\Big(\frac{1}{\Delta_{ab}^{ij}} - \frac{1}{\Delta_{fb}^{ij}}\Big) \\
=&\frac{1}{2}\sum_{ijab}\sum_{f\neq a}\langle ij||fb\rangle\langle ab||ij\rangle U_{fa}^\lambda\frac{\epsilon_a - \epsilon_f}{\Delta_{ab}^{ij}\Delta_{fb}^{ij}}
\end{aligned}
\tag{11}
$$

using the expression for U_{fa}^λ:

$$
A =\frac{1}{2}\sum_{ijab}\sum_{f\neq a}\frac{\langle ij||fb\rangle\langle ab||ij\rangle(Q_{fa}^\lambda + \sum_{gm}[U_{gm}^\lambda\langle fm||ag\rangle + (U_{gm}^\lambda)^*\langle fg||am\rangle])}{\Delta_{ab}^{ij}\Delta_{fb}^{ij}}
$$

$$=\frac{1}{2}\sum_{ijab}\sum_{f\neq a}T_{ij}^{ab}(T_{ij}^{fb})^*\Big(Q_{fa}^{\lambda}+\sum_{gm}[U_{gm}^{\lambda}\langle fm||ag\rangle+(U_{gm}^{\lambda})^*\langle fg||am\rangle]\Big) \tag{12}$$

evaluating the ε_a^λ term in $\frac{\partial E^{(2)}}{\partial \lambda}$ expression:

$$\begin{aligned}\frac{1}{2}\sum_{ijab}T_{ij}^{ab}(T_{ij}^{ab})^*\varepsilon_a^{\lambda}=&\frac{1}{2}\sum_{ijab}T_{ij}^{ab}(T_{ij}^{ab})^*\Big(Q_{aa}^{\lambda}+\sum_{gm}[U_{gm}^{\lambda}\langle am||ag\rangle+(U_{gm}^{\lambda})^*\langle ag||am\rangle]\Big)\\=&\frac{1}{2}\sum_{ijab}\sum_{f=a}T_{ij}^{ab}(T_{ij}^{fb})^*(Q_{fa}^{\lambda}+\sum_{gm}[U_{gm}^{\lambda}\langle fm||ag\rangle+(U_{gm}^{\lambda})^*\langle fg||am\rangle])\end{aligned} \tag{13}$$

add this term into A:

$$A+\frac{1}{2}\sum_{ijab}T_{ij}^{ab}(T_{ij}^{ab})^*\varepsilon_a^{\lambda}=\frac{1}{2}\sum_{ijabf}T_{ij}^{ab}(T_{ij}^{fb})^*\Big(Q_{fa}^{\lambda}+\sum_{gm}[U_{gm}^{\lambda}\langle fm||ag\rangle+(U_{gm}^{\lambda})^*\langle fg||am\rangle]\Big) \tag{14}$$

Similarly, collecting the U_{ki}^λ and U_{ik}^λ terms, and add the ε_i^λ term into them we get:

$$-\frac{1}{2}\sum_{ijabk}(T_{ij}^{ab})^*T_{kj}^{ab}\Big(Q_{ki}^{\lambda}+\sum_{gm}[U_{gm}^{\lambda}\langle km||ig\rangle+(U_{gm}^{\lambda})^*\langle kg||im\rangle]\Big) \tag{15}$$

Now looking at the S_{ak}^λ terms:

$$\begin{aligned}&-\frac{1}{2}\sum_{ijab}\sum_{k}(T_{ij}^{ab})^*\langle kb||ij\rangle S_{ak}^{\lambda}-\frac{1}{2}\sum_{ijab}\sum_{k}T_{ij}^{ab}\langle ij||kb\rangle S_{ak}^{\lambda}\\&=-\frac{1}{2}\sum_{ijkab}S_{ak}^{\lambda}\Big(\frac{\langle ij||ab\rangle\langle kb||ij\rangle+\langle ab||ij\rangle\langle ij||kb\rangle}{\Delta_{ab}^{ij}}\Big)\end{aligned} \tag{16}$$

no further simplification for general (complex) orbitals, but could be further simplified if assumed real orbitals

Now putting these all back into eqn (10):

$$\begin{aligned}\frac{\partial E^{(2)}}{\partial\lambda}=&-\frac{1}{2}\sum_{ijkab}S_{ak}^{\lambda}\Big(T_{ij}^{ab}\langle ij||kb\rangle+(T_{ij}^{ab})^*\langle kb||ij\rangle\Big)\\&-\frac{1}{2}\sum_{ijab}\sum_{f\neq a}(T_{ij}^{ab})^*\langle fb||ij\rangle S_{af}^{\lambda}-\frac{1}{2}\sum_{ijab}\sum_{k\neq i}T_{ij}^{ab}\langle kj||ab\rangle S_{ik}^{\lambda}\\&+\frac{1}{2}\sum_{ijab}\sum_{f}(T_{ij}^{ab})^*\langle ab||fi\rangle U_{fi}^{\lambda}+\frac{1}{2}\sum_{ijab}\sum_{f}T_{ij}^{ab}\langle fj||ab\rangle(U_{fi}^{\lambda})^*\\&-\frac{1}{2}\sum_{ijab}\sum_{k}(T_{ij}^{ab})^*\langle kb||ij\rangle U_{ak}^{\lambda}-\frac{1}{2}\sum_{ijab}\sum_{k}T_{ij}^{ab}\langle ij||kb\rangle(U_{ak}^{\lambda})^*\\&+\frac{1}{2}\sum_{ijabf}T_{ij}^{ab}(T_{ij}^{fb})^*\Big(Q_{fa}^{\lambda}+\sum_{gm}[U_{gm}^{\lambda}\langle fm||ag\rangle+(U_{gm}^{\lambda})^*\langle fg||am\rangle]\Big)\\&-\frac{1}{2}\sum_{ijabk}(T_{ij}^{ab})^*T_{kj}^{ab}\Big(Q_{ki}^{\lambda}+\sum_{gm}[U_{gm}^{\lambda}\langle km||ig\rangle+(U_{gm}^{\lambda})^*\langle kg||im\rangle]\Big)\end{aligned} \tag{17}$$

By defining:

$$D_{ki}=-\frac{1}{2}\sum_{jab}(T_{ij}^{ab})^*T_{kj}^{ab} \tag{18}$$

$$D_{fa} = \frac{1}{2}\sum_{ijb}(T_{ij}^{fb})^* T_{ij}^{ab} \tag{19}$$

$$I_{ik} = -\frac{1}{2}\sum_{jab} T_{ij}^{ab}\langle kj||ab\rangle \tag{20}$$

$$I_{af} = -\frac{1}{2}\sum_{ijb}(T_{ij}^{ab})^*\langle fb||ij\rangle \tag{21}$$

$$I_{ak} = -\frac{1}{2}\sum_{ijb}(T_{ij}^{ab}\langle ij||kb\rangle + (T_{ij}^{ab})^*\langle kb||ij\rangle) \tag{22}$$

the derivative becomes:

$$\begin{aligned}
\frac{\partial E^{(2)}}{\partial \lambda} =& \sum_{ak} S_{ak}^{\lambda} I_{ak} + \sum_{a\neq f} S_{af}^{\lambda} I_{af} + \sum_{i\neq k} S_{ik}^{\lambda} I_{ik} \\
&+ \sum_{af} D_{fa} Q_{fa}^{\lambda} + \sum_{ik} D_{ki} Q_{ki}^{\lambda} \\
&+ \frac{1}{2}\sum_{ijabf}(T_{ij}^{fb})^*\langle fb||ai\rangle U_{ai}^{\lambda} + \frac{1}{2}\sum_{ijabf} T_{ij}^{fb}\langle aj||fb\rangle (U_{ai}^{\lambda})^* \\
&- \frac{1}{2}\sum_{ijkab}(T_{kj}^{ab})^*\langle ib||kj\rangle U_{ai}^{\lambda} - \frac{1}{2}\sum_{ijkab} T_{kj}^{ab}\langle kj||ib\rangle (U_{ai}^{\lambda})^* \\
&+ \frac{1}{2}\sum_{ijmabfg} T_{mj}^{gb}(T_{mj}^{fb})^* U_{ai}^{\lambda}\langle fi||ga\rangle + \frac{1}{2}\sum_{ijmabfg} T_{mj}^{gb}(T_{mj}^{fb})^*(U_{ai}^{\lambda})^*\langle fa||gi\rangle \\
&- \frac{1}{2}\sum_{ijkmabg}(T_{mj}^{gb})^* T_{kj}^{gb} U_{ai}^{\lambda}\langle ki||ma\rangle - \frac{1}{2}\sum_{ijkmabg}(T_{mj}^{gb})^* T_{kj}^{gb}(U_{ai}^{\lambda})^*\langle ka||mi\rangle \\
=& \sum_{ak} S_{ak}^{\lambda} I_{ak} + \sum_{a\neq f} S_{af}^{\lambda} I_{af} + \sum_{i\neq k} S_{ik}^{\lambda} I_{ik} \\
&+ \sum_{af} D_{fa} Q_{fa}^{\lambda} + \sum_{ik} D_{ki} Q_{ki}^{\lambda} \\
&+ \frac{1}{2}\sum_{ijabf}(T_{ij}^{fb})^*\langle fb||ai\rangle U_{ai}^{\lambda} + \frac{1}{2}\sum_{ijabf} T_{ij}^{fb}\langle aj||fb\rangle (U_{ai}^{\lambda})^* \\
&- \frac{1}{2}\sum_{ijkab}(T_{kj}^{ab})^*\langle ib||kj\rangle U_{ai}^{\lambda} - \frac{1}{2}\sum_{ijkab} T_{kj}^{ab}\langle kj||ib\rangle (U_{ai}^{\lambda})^* \\
&+ \sum_{fg}\sum_{ai} D_{fg}\langle fi||ga\rangle U_{ai}^{\lambda} + \sum_{fg}\sum_{ai} D_{fg}\langle fa||gi\rangle (U_{ai}^{\lambda})^* \\
&+ \sum_{km}\sum_{ai} D_{km}\langle ki||ma\rangle U_{ai}^{\lambda} + \sum_{km}\sum_{ai} D_{km}\langle ka||mi\rangle (U_{ai}^{\lambda})^* \\
=& \sum_{ai} S_{ai}^{\lambda} I_{ai} + \sum_{a\neq b} S_{a}^{\lambda} I_{ab} + \sum_{i\neq j} S_{ij}^{\lambda} I_{ij} + \sum_{ab} D_{ab} Q_{ab}^{\lambda} + \sum_{ij} D_{ij} Q_{ij}^{\lambda} \\
&+ \frac{1}{2}\sum_{ai}\sum_{jbc}(T_{ij}^{bc})^*\langle bc||ai\rangle U_{ai}^{\lambda} + \frac{1}{2}\sum_{ai}\sum_{jbc} T_{ij}^{bc}\langle aj||bc\rangle (U_{ai}^{\lambda})^* \\
&- \frac{1}{2}\sum_{ai}\sum_{jkb}(T_{kj}^{ab})^*\langle ib||kj\rangle U_{ai}^{\lambda} - \frac{1}{2}\sum_{ai}\sum_{jkb} T_{kj}^{ab}\langle kj||ib\rangle (U_{ai}^{\lambda})^* \\
&+ \sum_{ai}\sum_{bc} D_{bc}\langle bi||ca\rangle U_{ai}^{\lambda} + \sum_{ai}\sum_{bc} D_{bc}\langle ba||ci\rangle (U_{ai}^{\lambda})^*
\end{aligned}$$

$$
\begin{aligned}
&+\sum_{ai}\sum_{jk} D_{jk}\langle ji||ka\rangle U^{\lambda}_{ai} + \sum_{ai}\sum_{jk} D_{jk}\langle ja||ki\rangle (U^{\lambda}_{ai})^{*} \\
=&\sum_{ai} S^{\lambda}_{ai} I_{ai} + \sum_{ab} S^{\lambda}_{ab} I_{ab} + \sum_{ij} S^{\lambda}_{ij} I_{ij} + \sum_{ab} D_{ab} Q^{\lambda}_{ab} + \sum_{ij} D_{ij} Q^{\lambda}_{ij} \\
&+ \text{something like} \sum_{ai} X_{ai} U^{\lambda}_{ai}
\end{aligned}
\tag{23}
$$

$\sum_{a\neq b}$ and $\sum_{i\neq j}$ terms, what about the $a = b$ and $i = j$ terms?
Should I drop the complex conjugate? but still can't see how to merge $\langle bi||ca\rangle$ and $\langle ba||ci\rangle$ terms hence could not get the same X_{ai} intermediate as in the article.

2 Some Identities

From CPHF orthonormality condition:

$$U_{pq}^{\lambda} + (U_{qp}^{\lambda})^* + S_{pq}^{\lambda} = 0 \tag{24}$$

Consider the spin-orbital (and using $\mathbf{C}(\lambda) = \mathbf{C}(0)\mathbf{U}(\lambda)$):

$$\begin{aligned} |a\rangle = |\psi_a\rangle &= \sum_{\mu} C_{\mu a}(\lambda)|\phi_\mu\rangle \\ &= \sum_{\mu}\Big(\sum_{q} C_{\mu q}(0)U_{qa}(\lambda)\Big)|\phi_\mu\rangle \\ &= \sum_{\mu}\Big(\sum_{k} C_{\mu k}(0)U_{ka}(\lambda)\Big)|\phi_\mu\rangle + \sum_{\mu}\Big(\sum_{f\neq a} C_{\mu f}(0)U_{fa}(\lambda)\Big)|\phi_\mu\rangle \end{aligned} \tag{25}$$

Question: Why not include U_{aa} into this sum?

Taking derivative w.r.t. λ:

$$\begin{aligned} |a^{\lambda}\rangle = &\sum_{\mu}\Big(\sum_{k} C_{\mu k}(0)U_{ka}^{\lambda}\Big)|\phi_\mu\rangle + \sum_{\mu}\Big(\sum_{f\neq a} C_{\mu f}(0)U_{fa}^{\lambda}\Big)|\phi_\mu\rangle \\ &+ \sum_{\mu}\Big(\sum_{k} C_{\mu k}(0)U_{ka}\Big)|\phi_\mu^{\lambda}\rangle + \sum_{\mu}\Big(\sum_{f\neq a} C_{\mu f}(0)U_{fa}\Big)|\phi_\mu^{\lambda}\rangle \end{aligned} \tag{26}$$

Noticing that $\mathbf{U}(0) = \mathbf{I}$ hence $\sum_{\mu} C_{\mu k}(0)|\phi_\mu\rangle = |\psi_k\rangle$:

$$\begin{aligned} |a^{\lambda}\rangle &= \sum_{k} U_{ka}^{\lambda}|\psi_k\rangle + \sum_{f\neq a} U_{fa}^{\lambda}|\psi_f\rangle + \sum_{\mu q} C_{\mu_q}(0)U_{qa}|\phi_\mu^{\lambda}\rangle \\ &= \sum_{k} U_{ka}^{\lambda}|k\rangle + \sum_{f\neq a} U_{fa}^{\lambda}|f\rangle + \sum_{\mu} C_{\mu a}|\mu^{\lambda}\rangle \end{aligned} \tag{27}$$

Similarly:

$$|i^{\lambda}\rangle = \sum_{k\neq i} U_{ki}^{\lambda}|k\rangle + \sum_{f} U_{fi}^{\lambda}|f\rangle + \sum_{\mu} C_{\mu i}|\mu^{\lambda}\rangle \tag{28}$$

Expression for CPHF coefficients (c.f. Pople et al. 1979):

$$U_{fa}^{\lambda} = \frac{1}{\varepsilon_a - \varepsilon_f}(Q_{fa}^{\lambda} + \sum_{gm}[U_{gm}^{\lambda}\langle fm||ag\rangle + (U_{gm}^{\lambda})^*\langle fg||am\rangle]) \tag{29}$$

$$U_{ki}^{\lambda} = \frac{1}{\varepsilon_i - \varepsilon_k}(Q_{ki}^{\lambda} + \sum_{gm}[U_{gm}^{\lambda}\langle fm||ag\rangle + (U_{gm}^{\lambda})^*\langle kg||im\rangle]) \tag{30}$$

$$\varepsilon_a^{\lambda} = Q_{aa}^{\lambda} + \sum_{gm}[U_{gm}^{\lambda}\langle am||ag\rangle + (U_{gm}^{\lambda})^*\langle ag||am\rangle] \tag{31}$$

$$\varepsilon_i^{\lambda} = Q_{ii}^{\lambda} + \sum_{gm}[U_{gm}^{\lambda}\langle im||ig\rangle + (U_{gm}^{\lambda})^*\langle ig||im\rangle] \tag{32}$$

3 Lagrangian Method

The MP2 Lagrangian could be written as:

$$\begin{aligned}\mathcal{L}_{\text{MP2}} =& E_{\text{MP2}} + C_{\text{Bri}} \\ =& E_{\text{HF}} + E_{\text{H}} + C_{\text{Bri}}\end{aligned} \tag{33}$$

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.

3.1 Hartree Fock Energy

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

$$\begin{aligned}E_{\text{HF}} =& E^{(0)} + E^{(1)} \\ =& \sum_i h_{ii} + \sum_{ij} \langle ij||ij\rangle - \frac{1}{2}\sum_{ij}\langle ij||ij\rangle \\ =& \sum_i h_{ii} + \frac{1}{2}\sum_{ij}\langle ij||ij\rangle\end{aligned} \tag{34}$$

3.2 Hylleraas Functional

The Hylleraas functional is defined as:

$$\begin{aligned}E_{\text{H}} =& \langle \Psi^{(1)}|\hat{V} - E^{(1)}|\Phi_0\rangle + \langle \Phi_0|\hat{V} - E^{(1)}|\Psi^{(1)}\rangle + \langle \Psi^{(1)}|\hat{H}^{(0)} - E^{(0)}|\Psi^{(1)}\rangle \\ =& 2\,\text{Re}\langle \Psi^{(1)}|\hat{V} - E^{(1)}|\Phi_0\rangle + \langle \Psi^{(1)}|\hat{H}^{(0)} - E^{(0)}|\Psi^{(1)}\rangle\end{aligned} \tag{35}$$

in which the relevant operators and functions are:

$$\hat{V} - E^{(1)} = \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\} \tag{36}$$

$$\hat{H}^{(0)} - E^{(0)} = \sum_{pq} f_{pq}\{\hat{p}^\dagger\hat{q}\} = \sum_{pq} h_{pq}\{\hat{p}^\dagger\hat{q}\} + \sum_{pqi}\langle pi||qi\rangle\{\hat{p}^\dagger\hat{q}\} \tag{37}$$

$$|\Psi^{(1)}\rangle = \frac{1}{4}\sum_{ijab} T_{ij}^{ab}|\Phi_{ij}^{ab}\rangle \tag{38}$$

Therefore the Hylleraas functional could be written as:

$$\begin{aligned}E_{\text{H}} =& \frac{1}{8}\,\text{Re}\left\{\sum_{ijab}(T_{ij}^{ab})^* \sum_{pqrs}\langle pq||rs\rangle\langle\Phi_{ij}^{ab}|\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}|\Phi_0\rangle\right\} \\ &+ \frac{1}{16}\sum_{ijab}(T_{ij}^{ab})^*\sum_{klcd}T_{kl}^{cd}\sum_{pq}\langle\Phi_{ij}^{ab}|\{\hat{p}^\dagger\hat{q}\}|\Phi_{kl}^{cd}\rangle f_{pq}\end{aligned} \tag{39}$$

First, we need to work out the following expectations:

$$\langle\Phi_{ij}^{ab}|\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}|\Phi_0\rangle = \langle\Phi_0|\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\}\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}|\Phi_0\rangle \tag{40}$$

$$\langle\Phi_{ij}^{ab}|\{\hat{p}^\dagger\hat{q}\}|\Phi_{kl}^{cd}\rangle = \langle\Phi_0|\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\}\{\hat{p}^\dagger\hat{q}\}\{\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\}|\Phi_0\rangle \tag{41}$$

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

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

$$=\delta_{ir}\delta_{js}\delta_{bq}\delta_{ap}+\delta_{is}\delta_{jr}\delta_{bp}\delta_{aq}-\delta_{ir}\delta_{js}\delta_{bp}\delta_{aq}-\delta_{is}\delta_{jr}\delta_{bq}\delta_{ap}+\dots \tag{42}$$

$$\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{43}$$

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

$$\begin{aligned}
&\frac{1}{8}\,\mathrm{Re}\left\{\sum_{ijab}(T_{ij}^{ab})^*\sum_{pqrs}\langle pq||rs\rangle\langle\Phi_{ij}^{ab}|\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}|\Phi_0\rangle\right\}\\
=&\frac{1}{8}\,\mathrm{Re}\left\{\sum_{ijab}(T_{ij}^{ab})^*(\langle ab||ij\rangle+\langle ba||ji\rangle-\langle ba||ij\rangle-\langle ab||ji\rangle)\right\}\\
=&\frac{1}{2}\,\mathrm{Re}\left\{\sum_{ijab}(T_{ij}^{ab})^*\langle ab||ij\rangle\right\}
\end{aligned} \tag{44}$$

$$\begin{aligned}
&\frac{1}{16}\sum_{ijab}(T_{ij}^{ab})^*\sum_{klcd}T_{kl}^{cd}\sum_{pq}\langle\Phi_{ij}^{ab}|\{\hat{p}^\dagger\hat{q}\}|\Phi_{kl}^{cd}\rangle f_{pq}\\
=&\frac{1}{16}\Big(\sum_{ijlab}f_{li}(T_{ij}^{ab})^*T_{jl}^{ab}-\sum_{ijlab}f_{li}(T_{ij}^{ab})^*T_{jl}^{ba}-\sum_{ijkab}f_{ki}(T_{ij}^{ab})^*T_{kj}^{ab}+\sum_{ijkab}f_{ki}(T_{ij}^{ab})^*T_{kj}^{ba}\\
&-\sum_{ijlab}f_{lj}(T_{ij}^{ab})^*T_{il}^{ab}+\sum_{ijlab}f_{lj}(T_{ij}^{ab})^*T_{il}^{ba}+\sum_{ijkab}f_{kj}(T_{ij}^{ab})^*T_{ki}^{ab}-\sum_{ijkab}f_{kj}(T_{ij}^{ab})^*T_{ki}^{ba}\\
&+\sum_{ijabd}f_{bd}(T_{ij}^{ab})^*T_{ij}^{ad}-\sum_{ijabd}f_{bd}(T_{ij}^{ab})^*T_{ji}^{ad}-\sum_{ijabc}f_{bc}(T_{ij}^{ab})^*T_{ij}^{ca}+\sum_{ijabc}f_{bc}(T_{ij}^{ab})^*T_{ji}^{ca}\\
&+\sum_{ijabc}f_{ac}(T_{ij}^{ab})^*T_{ij}^{cb}-\sum_{ijabc}f_{ac}(T_{ij}^{ab})^*T_{ji}^{cb}-\sum_{ijabd}f_{ad}(T_{ij}^{ab})^*T_{ij}^{bd}+\sum_{ijabd}f_{ad}(T_{ij}^{ab})^*T_{ji}^{bd}\Big)\\
=&\frac{1}{4}\Big(\sum_{ijkab}f_{ki}(T_{ij}^{ab})^*T_{jk}^{ab}-\sum_{ijkab}f_{ki}(T_{ji}^{ab})^*T_{jk}^{ab}+\sum_{ijabc}f_{ac}(T_{ij}^{ba})^*T_{ij}^{bc}-\sum_{ijabc}f_{ac}(T_{ij}^{ab})^*T_{ij}^{bc}\Big)\\
=&\frac{1}{2}\Big(\sum_{ijkab}f_{ki}(T_{ij}^{ab})^*T_{jk}^{ab}-\sum_{ijabc}f_{ac}(T_{ij}^{ab})^*T_{ij}^{bc}\Big)
\end{aligned} \tag{45}$$

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

$$E_{\mathrm{H}} = \frac{1}{2}\,\mathrm{Re}\left\{\sum_{ijab}(T_{ij}^{ab})^*\langle ab||ij\rangle\right\} + \frac{1}{2}\Big(\sum_{ijkab} f_{ki}(T_{ij}^{ab})^* T_{jk}^{ab} - \sum_{ijabc} f_{ac}(T_{ij}^{ab})^* T_{ij}^{bc}\Big) \tag{46}$$

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.

$$\begin{aligned}
E_{\mathrm{H}} =& \frac{1}{2}\,\mathrm{Re}\left\{\sum_{ijab}(T_{ij}^{ab})^*\langle ab||ij\rangle\right\} + \frac{1}{2}\Big(\sum_{ijkab} h_{ki}(T_{ij}^{ab})^* T_{jk}^{ab} - \sum_{ijabc} h_{ac}(T_{ij}^{ab})^* T_{ij}^{bc}\Big) \\
&+ \frac{1}{2}\Big(\sum_{ijklab}\langle kl||il\rangle(T_{ij}^{ab})^* T_{jk}^{ab} - \sum_{ijkabc}\langle ak||ck\rangle(T_{ij}^{ab})^* T_{ij}^{bc}\Big) \\
=& \sum_{ij} h_{ij}\gamma_{ij} + \sum_{ab} h_{ab}\gamma_{ab} + \sum_{ijab}\mathrm{Re}\Big\{\langle ab||ij\rangle\Gamma_{ij}^{ab}\Big\} + \sum_{ijkl}\langle ij||kl\rangle\Gamma_{kl}^{ij} + \sum_{ijab}\langle ai||bj\rangle\Gamma_{bj}^{ai}
\end{aligned} \tag{47}$$

in which

$$\gamma_{ij} = \frac{1}{2}\sum_{kab}(T_{jk}^{ab})^* T_{ki}^{ab} \tag{48}$$

$$\gamma_{ab} = -\frac{1}{2}\sum_{ijc}(T_{ij}^{ac})^* T_{ij}^{cb} \tag{49}$$

$$\Gamma_{ij}^{ab} = \frac{1}{2}(T_{ij}^{ab})^* \tag{50}$$

$$\Gamma_{kl}^{ij} = \frac{1}{2}\sum_{mab}(T_{km}^{ab})^* T_{mi}^{ab}\delta_{jl} \tag{51}$$

$$\Gamma_{bj}^{ai} = -\frac{1}{2}\sum_{klc}(T_{kl}^{ac})^* T_{kl}^{cb}\delta_{ij} \tag{52}$$

3.3 Perturbed Orthonormality Condition

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

$$S_{pq} = \langle p|q\rangle = \delta_{pq} \tag{53}$$

$$\sum_{\mu\nu} C_{\mu p}^* S_{\mu\nu} C_{\nu q} = \delta_{pq} \tag{54}$$

Parameterization of the MO coefficients:

$$\mathbf{C}(\lambda) = \mathbf{C}(0)\mathbf{U}(\lambda) \tag{55}$$

$$C_{\mu p}(\lambda) = \sum_r C_{\mu r}(0) U_{rp}(\lambda) \tag{56}$$

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

Now the orthonormality condition using this parameterization:

$$\sum_{\mu\nu}\Big(\sum_r U_{rp}^*(\lambda) C_{\mu r}^*(0)\Big) S_{\mu\nu}(\lambda)\Big(\sum_s C_{\nu s}(0) U_{sq}(\lambda)\Big) = \delta_{pq} \tag{57}$$

Introducing the transformed overlap matrix:

$$\mathcal{S}_{pq}(\lambda) = \sum_{\mu\nu} C^*_{\mu p}(0) S_{\mu\nu}(\lambda) C_{\nu q}(0) \tag{58}$$

we have:

$$\sum_{rs} U^*_{rp}(\lambda)\mathcal{S}_{rs}(\lambda)U_{sq}(\lambda) = \delta_{pq} \tag{59}$$

differentiating both sides of the equation gives:

$$\sum_{rs} \frac{\mathrm{d}U^*_{rp}(\lambda)}{\mathrm{d}\lambda}\mathcal{S}_{rs}(\lambda)U_{sq}(\lambda) + \sum_{rs} U^*_{rp}(\lambda)\frac{\mathrm{d}\mathcal{S}_{rs}(\lambda)}{\mathrm{d}\lambda}U_{sq}(\lambda) + \sum_{rs} U^*_{rp}(\lambda)\mathcal{S}_{rs}(\lambda)\frac{\mathrm{d}U_{sq}(\lambda)}{\mathrm{d}\lambda} = 0 \tag{60}$$

Noting that $\boldsymbol{\mathcal{S}}(0) = \mathbf{I}$ because the unperturbed spin-orbitals are orthonormal, and it is trivial that $\mathbf{U}(0) = \mathbf{I}$.
Therefore evaluating the derivative at $\lambda = 0$, and denoting $A^\lambda = \left(\frac{\mathrm{d}A}{\mathrm{d}\lambda}\right)\big|_{\lambda=0}$ results in:

$$\sum_{rs}(U^\lambda_{rp})^*\delta_{rs}\delta_{sq} + \sum_{rs}\delta_{rp}\mathcal{S}^\lambda_{rs}\delta_{sq} + \sum_{rs}\delta_{rp}\delta_{rs}U^\lambda_{sq} = 0 \tag{61}$$

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

$$(U^\lambda_{qp})^* + \mathcal{S}^\lambda_{pq} + U^\lambda_{pq} = 0 \tag{62}$$

3.4 Perturbed Brillouin Condition

The SCF density matrix is defined as:

$$D^{\text{SCF}}_{\mu\nu} = \sum_i^N C^*_{\mu i}C_{\nu i} \tag{63}$$

in which the MO coefficients are parameterized as:

$$C_{\mu p}(\lambda) = \sum_q C_{\mu q}(0)U(\lambda)_{qp} \tag{64}$$

$$\mathbf{C}(\lambda) = \mathbf{C}(0)\mathbf{U}(\lambda) \tag{65}$$

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

$$\begin{aligned} h_{pq} &= \langle p|\hat{h}|q\rangle = \sum_{\mu\nu} C^*_{\mu p}h^{\text{AO}}_{\mu\nu}C_{\nu q} & g_{pq} &= \sum_i \langle pi||qi\rangle = \sum_i\sum_{\mu\nu} C^*_{\mu p}\langle \mu i||\nu i\rangle C_{\nu q} \\ h^{\text{AO}}_{\mu\nu} &= \langle \mu|\hat{h}|\nu\rangle & g^{\text{AO}}_{\mu\nu} &= \sum_i \langle \mu i||\nu i\rangle = \sum_{\rho\sigma} D_{\rho\sigma}\langle \mu\rho||\nu\sigma\rangle \\ \mathbf{h} &= \mathbf{C}^\dagger\mathbf{h}^{\text{AO}}\mathbf{C} & \mathbf{g} &= \mathbf{C}^\dagger\mathbf{g}^{\text{AO}}\mathbf{C} \end{aligned} \tag{66}$$

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

$$\begin{aligned} f_{pq} &= h_{pq} + \sum_i \langle pi||qi\rangle \\ &= \sum_{\mu\nu} C^*_{\mu p}h^{\text{AO}}_{\mu\nu}C_{\nu q} + \sum_{\mu\nu} C^*_{\mu p}g^{\text{AO}}_{\mu\nu}C_{\nu q} \\ &= \sum_{\mu\nu} C^*_{\mu p}\langle\mu|\hat{h}|\nu\rangle C_{\nu q} + \sum_{\mu\nu} C^*_{\mu p}\big(\sum_{\rho\sigma} D_{\rho\sigma}\langle\mu\rho||\nu\sigma\rangle\big)C_{\nu q} \end{aligned} \tag{67}$$

$$
\begin{aligned}
f_{\mu\nu}^{\mathrm{AO}} =& h_{\mu\nu}^{\mathrm{AO}} + g_{\mu\nu}^{\mathrm{AO}} = \langle\mu|\hat{h}|\nu\rangle + \sum_{\rho\sigma} D_{\rho\sigma}\langle\mu\rho||\nu\sigma\rangle && (68)\\
\mathbf{f} =& \mathbf{h} + \mathbf{g}[\mathbf{D}^{\mathrm{SCF}}]\\
=& \mathbf{C}^\dagger\mathbf{h}^{\mathrm{AO}}\mathbf{C} + \mathbf{C}^\dagger\mathbf{g}^{\mathrm{AO}}[\mathbf{D}^{\mathrm{SCF}}]\mathbf{C}\\
=& \mathbf{C}^\dagger\mathbf{F}^{\mathrm{AO}}[\mathbf{D}^{\mathrm{SCF}}]\mathbf{C} && (69)\\
\mathbf{f}^{\mathrm{AO}}[\mathbf{D}^{\mathrm{SCF}}] =& \mathbf{h}^{\mathrm{AO}} + \mathbf{g}^{\mathrm{AO}}[\mathbf{D}^{\mathrm{SCF}}] && (70)
\end{aligned}
$$

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

$$
\begin{aligned}
\mathbf{f}^\lambda =& \frac{\mathrm{d}\mathbf{f}(\lambda)}{\mathrm{d}\lambda}\Big|_{\lambda=0} = \Big(\mathbf{C}^\dagger(\lambda)\mathbf{f}^{\mathrm{AO}}[\mathbf{D}^{\mathrm{SCF}}(\lambda)](\lambda)\mathbf{C}(\lambda)\Big)^\lambda\\
=& \mathbf{C}^{\lambda\dagger}(\lambda)\mathbf{f}^{\mathrm{AO}}[\mathbf{D}^{\mathrm{SCF}}(\lambda)](\lambda)\mathbf{C}(\lambda) + \mathbf{C}^\dagger(\lambda)\mathbf{f}^{\mathrm{AO}}[\mathbf{D}^{\mathrm{SCF}}(\lambda)](\lambda)\mathbf{C}^\lambda(\lambda)\\
&+ \mathbf{C}^\dagger(\lambda)\Big(\mathbf{h}^{\mathrm{AO}}(\lambda) + \mathbf{g}^{\mathrm{AO}}[\mathbf{D}^{\mathrm{SCF}}(\lambda)](\lambda)\Big)^\lambda\mathbf{C}(\lambda)\\
=& \mathbf{U}^{\lambda\dagger}(\lambda)\underbrace{\mathbf{U}^\dagger(0)\mathbf{C}^\dagger(0)}_{\mathbf{C}^\dagger(\lambda=0)}\mathbf{f}^{\mathrm{AO}}[\mathbf{D}^{\mathrm{SCF}}(\lambda)](\lambda)\mathbf{C}(\lambda) + \mathbf{C}^\dagger(\lambda)\mathbf{f}^{\mathrm{AO}}[\mathbf{D}^{\mathrm{SCF}}(\lambda)](\lambda)\underbrace{\mathbf{C}(0)\mathbf{U}(0)}_{\mathbf{C}(\lambda=0)}\mathbf{U}^\lambda(\lambda)\\
&+ \mathbf{C}^\dagger(\lambda)\Big(\mathbf{h}^{\mathrm{AO},\lambda}(\lambda) + \mathbf{g}^{\mathrm{AO},\lambda}[\mathbf{D}^{\mathrm{SCF}}(\lambda)](\lambda) + \mathbf{g}^{\mathrm{AO}}[\mathbf{D}^{\mathrm{SCF},\lambda}(\lambda)](\lambda)\Big)\mathbf{C}(\lambda)\\
=& \mathbf{U}^{\lambda\dagger}\mathbf{f} + \mathbf{f}\mathbf{U}^\lambda + \mathbf{C}^\dagger\mathbf{h}^{\mathrm{AO},\lambda}\mathbf{C} + \mathbf{C}^\dagger\mathbf{g}^{\mathrm{AO},\lambda}[\mathbf{D}^{\mathrm{SCF}}]\mathbf{C} + \mathbf{C}^\dagger\mathbf{g}^{\mathrm{AO}}[\mathbf{D}^{\mathrm{SCF},\lambda}]\mathbf{C} && (71)
\end{aligned}
$$

The perturbed Brillouin condition is:

$$f_{ai}^\lambda = 0 \tag{72}$$

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

$$
\begin{aligned}
(\mathbf{U}^{\lambda\dagger}\mathbf{f})_{ai} =& U_{ia}^{\lambda *}\varepsilon_i = \frac{\mathrm{d}U_{ia}^*}{\mathrm{d}\lambda}\Big|_{\lambda=0}\varepsilon_i && (73)\\
(\mathbf{f}\mathbf{U}^\lambda)_{ai} =& \varepsilon_a U_{ai}^\lambda = \varepsilon_a\frac{\mathrm{d}U_{ai}}{\mathrm{d}\lambda}\Big|_{\lambda=0} && (74)\\
(\mathbf{C}^\dagger\mathbf{h}^{\mathrm{AO},\lambda}\mathbf{C})_{ai} =& \sum_{\mu\nu} C_{\mu a}^* h_{\mu\nu}^\lambda C_{\nu i} = \sum_{\mu\nu} C_{\nu a}^*\frac{\mathrm{d}h_{\mu\nu}}{\mathrm{d}\lambda}\Big|_{\lambda=0} C_{\nu i} && (75)\\
(\mathbf{C}^\dagger\mathbf{g}^{\mathrm{AO},\lambda}[\mathbf{D}^{\mathrm{SCF}}]\mathbf{C})_{ai} =& \sum_{\mu\nu} C_{\mu a}^*(\sum_{\rho\sigma} D_{\rho\sigma}\langle\mu\rho||\nu\sigma\rangle^\lambda)C_{\nu i}\\
=& \sum_{\mu\nu} C_{\mu a}^*(\sum_{\rho\sigma} D_{\rho\sigma}\frac{\mathrm{d}\langle\mu\rho||\nu\sigma\rangle}{\mathrm{d}\lambda}\Big|_{\lambda=0})C_{\nu i} && (76)\\
(\mathbf{C}^\dagger\mathbf{g}^{\mathrm{AO}}[\mathbf{D}^{\mathrm{SCF},\lambda}]\mathbf{C})_{ai} =& \sum_{\mu\nu} C_{\mu a}^*(\sum_{\rho\sigma} D_{\rho\sigma}^\lambda\langle\mu\rho||\nu\sigma\rangle)C_{\nu i}\\
=& \sum_{\mu\nu} C_{\mu a}^*(\sum_{\rho\sigma}\frac{\mathrm{d}D_{\rho\sigma}}{\mathrm{d}\lambda}\Big|_{\lambda=0}\langle\mu\rho||\nu\sigma\rangle)C_{\nu i} && (77)
\end{aligned}
$$

3.5 Z-Vector Equation (Matrix Parameterization)

Imposing the stationary condition on the Lagrangian w.r.t. the orbital rotation parameter: (Usually take the linear combination of f_{ai} and f^*_{ia} to make the Lagrangian real, and remember that the fock matrix is Hermitian.)
In Matrix Parameterization, C_{ON} is required!

$$\begin{aligned}\mathcal{L}_{\mathrm{MP2}} =& E_{\mathrm{HF}} + E_{\mathrm{H}} + \sum_{ai} z_{ai} f_{ai} \\ =& \sum_{pq} h_{pq}\gamma_{pq} + \sum_{pqrs} \Gamma^{pq}_{rs}\langle pq||rs\rangle + \sum_{ai} z_{ai} f_{ai} \\ =& \sum_{pq} h_{pq}\gamma^{\mathrm{HF}}_{pq} + \sum_{pqrs} (\Gamma^{pq}_{rs})^{\mathrm{HF}}\langle pq||rs\rangle \\ &+ \sum_{pq} h_{pq}\gamma^{\mathrm{H}}_{pq} + \sum_{pqrs} (\Gamma^{pq}_{rs})^{\mathrm{H}}\langle pq||rs\rangle + \sum_{ai} z_{ai} f_{ai}\end{aligned} \tag{78}$$

$$\frac{\partial \mathcal{L}_{\mathrm{MP2}}}{\partial \mathbf{U}} = \frac{\partial E_{\mathrm{HF}}}{\partial \mathbf{U}} + \frac{\partial E_{\mathrm{H}}}{\partial \mathbf{U}} + \sum_{ai} z_{ai}\frac{\partial f_{ai}}{\partial \mathbf{U}} = 0 \tag{79}$$

The Hylleraas part (assuming real):

$$E_{\mathrm{H}} = \sum_{ij} h_{ij}\gamma_{ij} + \sum_{ab} h_{ab}\gamma_{ab} + \sum_{ijab}\langle ab||ij\rangle\Gamma^{ab}_{ij} + \sum_{ijkl}\langle ij||kl\rangle\Gamma^{ij}_{kl} + \sum_{ijab}\langle ai||bj\rangle\Gamma^{ai}_{bj} \tag{80}$$

Which blocks of $\mathbf{U}$ should be considered?
In general, all of them! But some will come out to be redundant and the ones contribute are the virtual-occupied blocks.
Also, need to take linear combination of $\frac{\partial}{\partial U_{pq}}$ and $\frac{\partial}{\partial U^*_{qp}}$ to get rid of the Lagrange multilpier in C_{ON} condition.
Could treat $\mathbf{U}$ and $\mathbf{U}^*$ as independent variables, i.e.:

$$\frac{\partial U_{pq}}{\partial U^*_{rs}} = 0 \tag{81}$$

Or just treat real and imaginary parts separately.

$$\begin{aligned}\frac{\partial h_{ij}}{\partial U_{pq}} =& \frac{\partial}{\partial U_{pq}}\sum_{\mu\nu} C^*_{\mu i} h_{\mu\nu} C_{\nu j} \\ =& \frac{\partial}{\partial U_{pq}}\sum_{\mu\nu rs} C^*_{\mu r}(0)U^*_{ri} h_{\mu\nu} C_{\nu s}(0)U_{sj} \\ =& \sum_{\mu\nu r} C^*_{\mu r}(0)\frac{\partial U^*_{ri}}{\partial U_{pq}} h_{\mu\nu} C_{\nu j} + \sum_{\mu\nu r} C^*_{\mu i} h_{\mu\nu} C_{\nu r}(0)\frac{\partial U_{rj}}{\partial U_{pq}} \\ =& 0 + \sum_{\mu\nu r} C^*_{\mu i} h_{\mu\nu} C_{\nu r}(0)\delta_{pr}\delta_{qj} \\ =& \sum_{\mu\nu} C^*_{\mu i} h_{\mu\nu} C_{\nu p}(0)\delta_{qj}\end{aligned} \tag{82}$$

Similarly:

$$\frac{\partial h_{ab}}{\partial U_{pq}} = \sum_{\mu\nu r} C^*_{\mu r}(0)\left(\frac{\partial U_{ra}}{\partial U_{pq}}\right)^* h_{\mu\nu} C_{\nu b} + \sum_{\mu\nu r} C^*_{\mu a} h_{\mu\nu} C_{\nu r}(0)\frac{\partial U_{rb}}{\partial U_{pq}} \tag{83}$$

$$\frac{\partial\langle ab||ij\rangle}{\partial U_{pq}} = \frac{\partial}{\partial U_{pq}}\sum_{\mu\nu\sigma\tau} C^*_{\mu a} C^*_{\nu b}\langle \mu\nu||\sigma\tau\rangle C_{\sigma i} C_{\tau j}$$

$$\begin{aligned} &= \sum_{\mu\nu\sigma\tau r} C^*_{\mu r}(0)(\frac{\partial U_{ra}}{\partial U_{pq}})^* C^*_{\nu b}\langle\mu\nu||\sigma\tau\rangle C_{\sigma i}C_{\tau j} \\ &\quad + \sum_{\mu\nu\sigma\tau r} C^*_{\mu a}C^*_{\nu r}(0)(\frac{\partial U_{rb}}{\partial U_{pq}})^*\langle\mu\nu||\sigma\tau\rangle C_{\sigma i}C_{\tau j} \\ &\quad + \sum_{\mu\nu\sigma\tau r} C^*_{\mu a}C^*_{\nu b}\langle\mu\nu||\sigma\tau\rangle C_{\sigma r}(0)\frac{\partial U_{ri}}{\partial U_{pq}}C_{\tau j} \\ &\quad + \sum_{\mu\nu\sigma\tau r} C^*_{\mu a}C^*_{\nu b}\langle\mu\nu||\sigma\tau\rangle C_{\sigma i}C_{\tau r}(0)\frac{\partial U_{rj}}{\partial U_{pq}} \end{aligned} \tag{84}$$

Other blocks of the 2e-integrals are similar.
note:

$$\frac{\mathrm{d}U_{pq}}{\mathrm{d}U_{rs}} = \delta_{pr}\delta_{qs} \tag{85}$$

Now the Brillouin part:

$$\frac{\partial f_{ai}}{\partial U_{pq}} = \frac{\partial}{\partial U_{pq}}\left(h_{ai} + \sum_j \langle aj||ij\rangle\right) \tag{86}$$

The constituent parts have been worked out from above.

3.6 Z-Vector Equation (Exponential Parameterization)

$$\begin{aligned} \mathbf{U} &= \exp(-\boldsymbol{\kappa}) \\ &= \sum_{n=0}^{\infty}(-1)^n\frac{\boldsymbol{\kappa}^n}{n!} \end{aligned} \tag{87}$$

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

$$\boldsymbol{\kappa}^\dagger = (\boldsymbol{\kappa}^*)^T = -\boldsymbol{\kappa} \tag{88}$$

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

$$\mathbf{U}^\dagger\mathbf{U} = \exp\left(-\boldsymbol{\kappa}^\dagger\right)\exp(-\boldsymbol{\kappa}) = \exp(\boldsymbol{\kappa})\exp(-\boldsymbol{\kappa}) = \mathbf{I} \tag{89}$$

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

$$\mathbf{C}(\lambda) = \mathbf{C}(0)\mathbf{U}(\lambda) = \mathbf{C}(0)\exp[-\boldsymbol{\kappa}(\lambda)] \tag{90}$$

$$C_{\mu p}(\lambda) = \sum_r C_{\mu r}(0)U_{rp}(\lambda) = \sum_r C_{\mu r}(0)(\exp[-\boldsymbol{\kappa}(\lambda)])_{rp} \tag{91}$$

$$\begin{aligned} [\exp(-\boldsymbol{\kappa})]_{rp} &= (\mathbf{I} - \boldsymbol{\kappa} + \frac{1}{2!}\boldsymbol{\kappa}^2 - \frac{1}{3!}\boldsymbol{\kappa}^3 + \dots)_{rp} \\ &= \delta_{rp} - \kappa_{rp} + \frac{1}{2!}\sum_x k_{rx}k_{xp} - \frac{1}{3!}\sum_{xy} k_{rx}k_{xy}k_{yp} + \dots \end{aligned} \tag{92}$$

The orthonormality condition is enforced explicitly in matrix parameterization, while in exponential parameterization it comes naturally from the anti-Hermitian property of $\boldsymbol{\kappa}$:

$$\begin{aligned} \mathbf{C}^\dagger(\lambda)\mathbf{S}^{\mathrm{AO}}(\lambda)\mathbf{C}(\lambda) &= (\mathbf{C}(0)\exp[-\boldsymbol{\kappa}(\lambda)])^\dagger\mathbf{S}^{\mathrm{AO}}(\lambda)\mathbf{C}(0)\exp[-\boldsymbol{\kappa}(\lambda)] \\ &= \exp\left[-\boldsymbol{\kappa}^\dagger(\lambda)\right]\underbrace{\mathbf{C}^\dagger(0)\mathbf{S}^{\mathrm{AO}}(\lambda)\mathbf{C}(0)}_{=\mathbf{I}}\exp[-\boldsymbol{\kappa}(\lambda)] \end{aligned}$$

$$\begin{aligned} &= \exp[\boldsymbol{\kappa}(\lambda)] \exp[-\boldsymbol{\kappa}(\lambda)] \\ &= \mathbf{I} \end{aligned} \tag{93}$$

NO! Take derivatives!:

$$\begin{aligned} \mathbf{I} =& \mathbf{S}(\lambda) \\ =& \mathbf{C}^\dagger(\lambda)\mathbf{S}^{\mathrm{AO}}(\lambda)\mathbf{C}(\lambda) \\ =& (\mathbf{C}(0)\exp[-\boldsymbol{\kappa}(\lambda)])^\dagger \mathbf{S}^{\mathrm{AO}}(\lambda)\mathbf{C}(0)\exp[-\boldsymbol{\kappa}(\lambda)] \\ =& \exp\left[-\boldsymbol{\kappa}^\dagger(\lambda)\right]\mathbf{C}^\dagger(0)\mathbf{S}^{\mathrm{AO}}(\lambda)\mathbf{C}(0)\exp[-\boldsymbol{\kappa}(\lambda)] \\ =& \exp[\boldsymbol{\kappa}(\lambda)]\boldsymbol{\mathcal{S}}(\lambda)\exp[-\boldsymbol{\kappa}(\lambda)] \\ =& \left[\mathbf{I} + \boldsymbol{\kappa}(\lambda) + \frac{1}{2}\boldsymbol{\kappa}^2(\lambda) + \dots\right]\boldsymbol{\mathcal{S}}(\lambda)\left[\mathbf{I} - \boldsymbol{\kappa}(\lambda) + \frac{1}{2}\boldsymbol{\kappa}^2(\lambda) + \dots\right] \end{aligned} \tag{94}$$

$$\begin{aligned} \Leftrightarrow \delta_{pq} =& \sum_{\mu\nu} C^*_{\mu p}(\lambda) S^{\mathrm{AO}}_{\mu\nu}(\lambda) C_{\nu q}(\lambda) \\ =& \sum_{\mu\nu}\Big(\sum_r C^*_{\mu r}(0)\exp[-\boldsymbol{\kappa}(\lambda)]^*_{rp}\Big) S^{\mathrm{AO}}_{\mu\nu}(\lambda)\Big(\sum_s C_{\nu s}\exp[-\boldsymbol{\kappa}(\lambda)]_{sq}\Big) \\ =& \sum_{\mu\nu rs}\exp[\boldsymbol{\kappa}(\lambda)]_{pr}\big(C^*_{\mu r}(0)S^{\mathrm{AO}}_{\mu\nu}(\lambda)C_{\nu s}(0)\big)\exp[-\boldsymbol{\kappa}(\lambda)]_{sq} \\ =& \sum_{rs}\exp[\boldsymbol{\kappa}(\lambda)]_{pr}\mathcal{S}_{rs}(\lambda)\exp[-\boldsymbol{\kappa}(\lambda)]_{sq} \\ =& \sum_{rs}\left[\delta_{pr} + \kappa_{pr}(\lambda) + \frac{1}{2}\sum_x \kappa_{px}(\lambda)\kappa_{xr}(\lambda)\right]\mathcal{S}_{rs}(\lambda)\left[\delta_{sq} + \kappa_{sq}(\lambda) + \frac{1}{2}\sum_y \kappa_{sy}(\lambda)\kappa_{yq}(\lambda)\right] \end{aligned} \tag{95}$$

index x & y look weird, find other appropriate indices.
For derivative of ON condition, only first order expansion is needed.

$$\begin{aligned} \delta_{pq} =& \sum_{rs}\left[\delta_{pr} + \kappa_{pr}(\lambda)\right]\mathcal{S}_{rs}(\lambda)\left[\delta_{sq} + \kappa_{sq}(\lambda)\right] \\ =& \sum_{rs}\delta_{pr}\mathcal{S}_{rs}(\lambda)\delta_{sq} + \sum_{rs}\kappa_{pr}(\lambda)\mathcal{S}_{rs}(\lambda)\kappa_{sq}(\lambda) \\ =& \mathcal{S}_{pq}(\lambda) + \sum_{rs}\kappa_{pr}(\lambda)\mathcal{S}_{rs}(\lambda)\kappa_{sq}(\lambda) \end{aligned} \tag{96}$$

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

$$\begin{aligned} 0 =& \frac{\partial\mathcal{S}_{pq}(\lambda)}{\partial\lambda}\Big|_{\lambda=0} + \sum_{rs}\frac{\partial\kappa_{pr}(\lambda)}{\partial\lambda}\Big|_{\lambda=0}\mathcal{S}_{sr}(\lambda)\kappa_{sq}(\lambda) + \sum_{rs}\kappa_{pr}(\lambda)\mathcal{S}_{rs}\frac{\partial\kappa_{sq}(\lambda)}{\partial\lambda}\Big|_{\lambda=0} \\ =& \mathcal{S}^\lambda_{pq} + \sum_{rs}\kappa^\lambda_{pr}\delta_{sr}\kappa_{sq} + \sum_{rs}\kappa_{pr}\delta_{rs}\kappa^\lambda_{sq} \\ =& \mathcal{S}^\lambda_{pq} + \sum_r \kappa^\lambda_{pr}\kappa_{rq} + \sum_r \kappa_{pr}\kappa^\lambda_{rq} \\ =& \mathcal{S}^\lambda_{pq} + \sum_r(-\kappa^{\lambda*}_{rp})(-\kappa^*_{qr}) + \sum_r \kappa_{pr}\kappa^\lambda_{rq} \\ =& \mathcal{S}^\lambda_{pq} + \sum_r \kappa^*_{qr}\kappa^{\lambda*}_{rp} + \sum_r \kappa_{pr}\kappa^\lambda_{rq} \end{aligned} \tag{97}$$

Now to impose the stationary condition: (only taking up to second derivative, so could truncate κ series up to quadratic term. Could also just use BCH, if that's better for the code generator)

$$\frac{\partial\mathcal{L}_{\mathrm{MP2}}}{\partial\boldsymbol{\kappa}} = \frac{\partial E_{\mathrm{HF}}}{\partial\boldsymbol{\kappa}} + \frac{\partial E_{\mathrm{H}}}{\partial\boldsymbol{\kappa}} + \sum_{ai} z_{ai}\frac{\partial f_{ai}}{\partial\boldsymbol{\kappa}} = 0 \tag{98}$$

$$\frac{\partial E_{\mathrm{HF}}}{\partial \boldsymbol{\kappa}} = \tag{99}$$

$$\frac{\partial E_{\mathrm{H}}}{\partial \boldsymbol{\kappa}} = \tag{100}$$

$$\frac{\partial f_{ai}}{\partial \boldsymbol{\kappa}} = \tag{101}$$

The specific blocks:

$$\begin{aligned}\frac{\partial h_{pq}}{\partial \kappa_{rs}} =& \frac{\partial}{\partial \kappa_{rs}} \sum_{\mu\nu} C^*_{\mu p} h_{\mu\nu} C_{\nu q} \\ =& \frac{\partial}{\partial \kappa_{rs}} \sum_{\mu\nu}\end{aligned} \tag{102}$$

3.7 Z-Vector Equation (Improved Exponential Parameterization)

$$\mathbf{C}(\lambda) = \mathbf{C}(0)\mathbf{U}(\lambda) \tag{103}$$

$$\mathbf{U}(\lambda) = \boldsymbol{\mathcal{S}}^{-\frac{1}{2}}(\lambda)\exp[-\boldsymbol{\kappa}(\lambda)] \tag{104}$$

$$\boldsymbol{\mathcal{S}} = \mathbf{C}^\dagger(0)\mathbf{S}^{\mathrm{AO}}(\lambda)\mathbf{C}(0) \tag{105}$$

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).

In this way:

$$\begin{aligned}\mathbf{S}(\lambda) =& \mathbf{C}^\dagger(\lambda)\mathbf{S}^{\mathrm{AO}}(\lambda)\mathbf{C}(\lambda) \\ =& \mathbf{U}^\dagger(\lambda)\mathbf{C}^\dagger(0)\mathbf{S}^{\mathrm{AO}}(\lambda)\mathbf{C}(0)\mathbf{U}(\lambda) \\ =& \mathbf{U}^\dagger(\lambda)\boldsymbol{\mathcal{S}}(\lambda)\mathbf{U}(\lambda) \\ =& \exp[-\boldsymbol{\kappa}(\lambda)]^\dagger \boldsymbol{\mathcal{S}}^{-\frac{1}{2}\dagger}(\lambda)\boldsymbol{\mathcal{S}}(\lambda)\boldsymbol{\mathcal{S}}^{-\frac{1}{2}}(\lambda)\exp[-\boldsymbol{\kappa}(\lambda)] \\ =& \exp[\boldsymbol{\kappa}(\lambda)]\exp[-\boldsymbol{\kappa}(\lambda)] \\ =& \mathbf{I}\end{aligned} \tag{106}$$

the orthonormality is ensured (only when $\boldsymbol{\mathcal{S}}^{-\frac{1}{2}\dagger}\boldsymbol{\mathcal{S}}\boldsymbol{\mathcal{S}}^{-\frac{1}{2}} = \mathbf{I}$ holds), and the perturbed orthonormality condition is trivial:

$$\mathbf{S}^\lambda = \frac{\partial \mathbf{S}(\lambda)}{\partial \lambda}\bigg|_{\lambda=0} = \mathbf{0} \tag{107}$$

The derivative of $\mathbf{U}(\lambda)$ is no longer needed here but if required, the derivative of $\boldsymbol{\mathcal{S}}^{-\frac{1}{2}}(\lambda)$ could be solved by taking derivative on this equation (How to demonstrate this?):

$$\boldsymbol{\mathcal{S}}^{-\frac{1}{2}\dagger}\boldsymbol{\mathcal{S}}\boldsymbol{\mathcal{S}}^{-\frac{1}{2}} = \mathbf{I} \tag{108}$$

Does this come naturally? Or do we need to enforce it as the orthonormality condition? require the AO overlap matrix to be Hermitian

$$\boldsymbol{\mathcal{S}}^{-\frac{1}{2}\dagger}\boldsymbol{\mathcal{S}}\boldsymbol{\mathcal{S}}^{-\frac{1}{2}} = \mathbf{C}^{-\frac{1}{2}\dagger}(0)\mathbf{S}_{\mathrm{AO}}^{-\frac{1}{2}\dagger}\mathbf{C}^{-\frac{1}{2}}(0)\mathbf{C}^\dagger(0)\mathbf{S}^{\mathrm{AO}}\mathbf{C}(0)\mathbf{C}^{-\frac{1}{2}\dagger}(0)\mathbf{S}_{\mathrm{AO}}^{-\frac{1}{2}}\mathbf{C}^{-\frac{1}{2}}(0) \tag{109}$$

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

$$\exp(-\boldsymbol{\kappa}) = \mathbf{I} - \boldsymbol{\kappa} + \frac{1}{2}\boldsymbol{\kappa}^2 \tag{110}$$

Then the relevant integrals could be expressed as:

$$\begin{aligned}\mathbf{h} =&\mathbf{C}^\dagger(\lambda)\mathbf{h}^{\text{AO}}(\lambda)\mathbf{C}(\lambda)\\ =&\exp[\boldsymbol{\kappa}(\lambda)]\boldsymbol{\mathcal{S}}^{-\frac{1}{2}\dagger}(\lambda)\mathbf{C}^\dagger(0)\mathbf{h}^{\text{AO}}(\lambda)\mathbf{C}(0)\boldsymbol{\mathcal{S}}^{-\frac{1}{2}}(\lambda)\exp[-\boldsymbol{\kappa}(\lambda)]\\ =&\big(\mathbf{I}+\boldsymbol{\kappa}+\frac{1}{2}\boldsymbol{\kappa}^2\big)\boldsymbol{\mathcal{S}}^{-\frac{1}{2}\dagger}(\lambda)\mathbf{C}^\dagger(0)\mathbf{h}^{\text{AO}}(\lambda)\mathbf{C}(0)\boldsymbol{\mathcal{S}}^{-\frac{1}{2}}(\lambda)\big(\mathbf{I}-\boldsymbol{\kappa}+\frac{1}{2}\boldsymbol{\kappa}^2\big)\end{aligned}\tag{111}$$

$$\big(\mathbf{I}+\boldsymbol{\kappa}+\frac{1}{2}\boldsymbol{\kappa}^2\big)_{pq}=\delta_{pq}+\kappa_{pq}+\frac{1}{2}\sum_x\kappa_{px}\kappa_{xq}\tag{112}$$

$$\frac{\partial\delta_{pq}}{\partial\kappa_{rs}}=0\tag{113}$$

$$\frac{\partial\kappa_{pq}}{\partial\kappa_{rs}}=\delta_{pr}\delta_{qs}\tag{114}$$

$$\begin{aligned}h_{pq}=&\sum_{\mu\nu}C^*_{\mu p}(\lambda)h^{\text{AO}}_{\mu\nu}(\lambda)C_{\nu q}(\lambda)\\ =&\sum_{\mu\nu rs}C^*_{\mu r}(0)U^*_{rp}(\lambda)h^{\text{AO}}_{\mu\nu}(\lambda)C_{vs}(0)U_{sq}(\lambda)\\ =&\sum_{\mu\nu rstu}C^*_{\mu r}\mathcal{S}^{-\frac{1}{2}*}_{rt}\exp[-\boldsymbol{\kappa}]^*_{tp}h^{\text{AO}}_{\mu\nu}C_{\nu s}\mathcal{S}^{-\frac{1}{2}}_{su}\exp[-\boldsymbol{\kappa}]_{uq}\end{aligned}\tag{115}$$

$$\begin{aligned}=&\sum_{\mu\nu rstu}C^*_{\mu r}\mathcal{S}^{-\frac{1}{2}*}_{rt}\exp[\boldsymbol{\kappa}]_{pt}h^{\text{AO}}_{\mu\nu}C_{\nu s}\mathcal{S}^{-\frac{1}{2}}_{su}\exp[-\boldsymbol{\kappa}]_{uq}\\ =&\sum_{\mu\nu rstu}C^*_{\mu r}\mathcal{S}^{-\frac{1}{2}*}_{rt}\left[\delta_{pt}+\kappa_{pt}+\dots\right]h^{\text{AO}}_{\mu\nu}C_{\nu s}\mathcal{S}^{-\frac{1}{2}}_{su}\left[\delta_{uq}-\kappa_{uq}+\dots\right]\\ =&\sum_{\mu\nu rstu}C^*_{\mu r}\mathcal{S}^{-\frac{1}{2}*}_{rt}h^{\text{AO}}_{\mu\nu}C_{\nu s}\mathcal{S}^{-\frac{1}{2}}_{su}\left[\delta_{pt}\delta_{uq}-\delta_{pt}\kappa_{uq}+\delta_{uq}\kappa_{pt}-\kappa_{pt}\kappa_{uq}\right]\end{aligned}\tag{116}$$

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

$$\begin{aligned}\frac{\partial h_{pq}}{\partial\kappa_{vw}}\Big|_{\lambda=0}=&\sum_{\mu\nu rstu}C^*_{\mu r}\mathcal{S}^{-\frac{1}{2}*}_{rt}h^{\text{AO}}_{\mu\nu}C_{\nu s}\mathcal{S}^{-\frac{1}{2}}_{su}\left(0-\delta_{pt}\frac{\partial\kappa_{uq}}{\partial\kappa_{vw}}\Big|_{\lambda=0}+\delta_{uq}\frac{\partial\kappa_{pt}}{\partial\kappa_{vw}}\Big|_{\lambda=0}\right)\\ =&\sum_{\mu\nu rstu}C^*_{\mu r}\mathcal{S}^{-\frac{1}{2}*}_{rt}h^{\text{AO}}_{\mu\nu}C_{\nu s}\mathcal{S}^{-\frac{1}{2}}_{su}\left(-\delta_{pt}\delta_{uv}\delta_{qw}+\delta_{uq}\delta_{pv}\delta_{tw}\right)\end{aligned}\tag{117}$$

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

$$\begin{aligned}\frac{\partial h_{pq}}{\partial\kappa_{vw}}\Big|_{\lambda=0}=&\sum_{\mu\nu rstu}C^*_{\mu r}\delta_{rt}h^{\text{AO}}_{\mu\nu}C_{vs}\delta_{su}\delta_{uq}\delta_{pv}\delta_{tw}-\sum_{\mu\nu rstu}C^*_{\mu r}\delta_{rt}h^{\text{AO}}_{\mu\nu}C_{\nu s}\delta_{su}\delta_{pt}\delta_{uv}\delta_{qw}\\ =&\sum_{\mu\nu}C^*_{\mu w}h^{\text{AO}}_{\mu\nu}C_{\nu q}\delta_{pv}-\sum_{\mu\nu}C^*_{\mu p}h^{\text{AO}}_{\mu\nu}C_{\nu v}\delta_{qw}\\ =&h_{wq}\delta_{pv}-h_{pv}\delta_{qw}\end{aligned}\tag{118}$$

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

$$\frac{\partial h_{pq}}{\partial\kappa_{rs}}\Big|_{\lambda=0}=h_{qs}\delta_{pr}-h_{pr}\delta_{qs}\tag{119}$$

hence:

$$\sum_{pq} \frac{\partial h_{pq}}{\partial \kappa_{rs}}\Big|_{\lambda=0} = \sum_{pq} h_{qs}\delta_{pr} - h_{pr}\delta_{qs} \tag{120}$$

Now the two-electron integral:

$$\begin{aligned}
\langle pq||rs\rangle &= \sum_{\mu\nu\sigma\tau} C^*_{\mu p} C^*_{\nu q} \langle\mu\nu||\sigma\tau\rangle C_{\sigma r} C_{\tau s} \\
&= \sum_{\mu\nu\sigma\tau}\sum_{tuvw} C^*_{\mu t} U^*_{tp} C^*_{\nu u} U^*_{uq} \langle\mu\nu||\sigma\tau\rangle C_{\sigma v} U_{vr} C_{\tau w} U_{ws} \\
&= \sum_{\mu\nu\sigma\tau}\sum_{tuvw}\sum_{ghmn} C^*_{\mu t} \mathcal{S}^{-\frac{1}{2}*}_{tg} \exp[-\boldsymbol{\kappa}]^*_{gp} C^*_{\nu u} \mathcal{S}^{-\frac{1}{2}*}_{uh} \exp[-\boldsymbol{\kappa}]^*_{hq} \\
&\quad \langle\mu\nu||\sigma\tau\rangle C_{\sigma v} \mathcal{S}^{-\frac{1}{2}}_{vm} \exp[-\boldsymbol{\kappa}]_{mr} C_{\tau w} \mathcal{S}^{-\frac{1}{2}}_{wn} \exp[-\boldsymbol{\kappa}]_{ns} \\
&= \sum_{\mu\nu\sigma\tau}\sum_{tuvw}\sum_{ghmn} C^*_{\mu t} \mathcal{S}^{-\frac{1}{2}*}_{tg} \left(\delta_{pg} + \kappa_{pg}\right) C^*_{\nu u} \mathcal{S}^{-\frac{1}{2}*}_{uh} \left(\delta_{qh} + \kappa_{qh}\right) \\
&\quad \langle\mu\nu||\sigma\tau\rangle C_{\sigma v} \mathcal{S}^{-\frac{1}{2}}_{vm} \left(\delta_{mr} - \kappa_{mr}\right) C_{\tau w} \mathcal{S}^{-\frac{1}{2}}_{wn} \left(\delta_{ns} - \kappa_{ns}\right) \\
&= \sum_{\mu\nu\sigma\tau}\sum_{tuvw}\sum_{ghmn} C^*_{\mu t} \mathcal{S}^{-\frac{1}{2}*}_{tg} C^*_{\nu u} \mathcal{S}^{-\frac{1}{2}*}_{uh} \langle\mu\nu||\sigma\tau\rangle C_{\sigma v} \mathcal{S}^{-\frac{1}{2}}_{vm} C_{\tau w} \mathcal{S}^{-\frac{1}{2}}_{wn} (\kappa_{pg}\delta_{qh}\delta_{mr}\delta_{ns} \\
&\quad + \kappa_{qh}\delta_{pg}\delta_{mr}\delta_{ns} - \kappa_{mr}\delta_{pg}\delta_{qh}\delta_{ns} - \kappa_{ns}\delta_{pg}\delta_{qh}\delta_{mr} + \dots)
\end{aligned} \tag{121}$$

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} \\
&\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_{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} \\
&\quad - \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{122}$$

Therefore, the orbital response for fock matrix is:

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

$$\begin{aligned}
&-\sum_k \langle ak||pk\rangle \delta_{iq} - \sum_k \langle ak||ip\rangle \delta_{kq} \\
=&\delta_{ap}\Big(h_{iq} + \sum_k \langle qk||ik\rangle\Big) - \delta_{iq}\Big(h_{ap} + \sum_k \langle ak||pk\rangle\Big) \\
&+ \sum_k \langle aq||ik\rangle \delta_{pk} - \sum_k \langle ak||ip\rangle \delta_{qk} \\
=&\delta_{ap} f_{iq} - \delta_{iq} f_{ap} + \langle aq||ip\rangle - \langle aq||ip\rangle \\
=&\delta_{ap}\delta_{iq}\varepsilon_i - \delta_{iq}\delta_{ap}\varepsilon_a \\
=&(\varepsilon_i - \varepsilon_a)\delta_{ap}\delta_{iq}
\end{aligned} \tag{123}$$

thus the only non-redundant orbital response is:

$$\frac{\partial f_{ai}}{\partial \kappa_{bj}}\Big|_{\lambda=0} = (\varepsilon_i - \varepsilon_a)\delta_{ab}\delta_{ij} \tag{124}$$

Then, the orbital response for the Hylleraas functional:

$$E_{\mathrm{H}} = \sum_{ij} h_{ij}\gamma_{ij} + \sum_{ab} h_{ab}\gamma_{ab} + \sum_{ijab} \langle ab||ij\rangle \Gamma_{ij}^{ab} + \sum_{ijkl} \langle ij||kl\rangle \Gamma_{kl}^{ij} + \sum_{ijab} \langle ai||bj\rangle \Gamma_{bj}^{ai} \tag{125}$$

$$\frac{\partial h_{ij}}{\partial \kappa_{pq}}\Big|_{\lambda=0} = h_{jq}\delta_{ip} - h_{ip}\delta_{jq} \tag{126}$$

$$\frac{\partial h_{ab}}{\partial \kappa_{pq}}\Big|_{\lambda=0} = h_{bq}\delta_{ap} - h_{ap}\delta_{bq} \tag{127}$$

$$\frac{\partial \langle ab||ij\rangle}{\partial \kappa_{pq}}\Big|_{\lambda=0} = \langle qb||ij\rangle \delta_{ap} + \langle aq||ij\rangle \delta_{bp} - \langle ab||pj\rangle \delta_{iq} - \langle ab||ip\rangle \delta_{jq} \tag{128}$$

$$\frac{\partial \langle ij||kl\rangle}{\partial \kappa_{pq}}\Big|_{\lambda=0} = \langle qj||kl\rangle \delta_{ip} + \langle iq||kl\rangle \delta_{jp} - \langle ij||pl\rangle \delta_{kq} - \langle ij||kp\rangle \delta_{lq} \tag{129}$$

$$\frac{\partial \langle ai||bj\rangle}{\partial \kappa_{pq}}\Big|_{\lambda=0} = \langle qi||bj\rangle \delta_{ap} + \langle aq||bj\rangle \delta_{ip} - \langle ai||pj\rangle \delta_{bq} - \langle ai||bp\rangle \delta_{jq} \tag{130}$$