

# 1 Direct Differentiation

MP2 energy in spin-orbital formalism:

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

in which we denote the MP2 amplitude:

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

Directly differentiate the second-order energy w.r.t. perturbation parameter  $\lambda$ :

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

in which:

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

exploiting the permutational symmetry and equivalence of the dummy indices:

$$\sum_{ijab} \langle i^\lambda j||ab\rangle = \sum_{ijab} \langle j^\lambda i||ba\rangle = \sum_{jiba} \langle i^\lambda j||ab\rangle \quad (5)$$

Therefore:

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

Then:

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

Putting eqns (6) and (7) together:

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

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

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

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

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

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

collecting the  $U_{af}^\lambda$  and  $U_{fa}^\lambda$  terms and swapping some dummy indices:

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

using the expression for  $U_{fa}^\lambda$ :

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

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

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

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

add this term into  $A$ :

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

Similarly, collecting the  $U_{ki}^\lambda$  and  $U_{ik}^\lambda$  terms, and add the  $\varepsilon_i^\lambda$  term into them we get:

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

Now looking at the  $S_{ak}^\lambda$  terms:

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

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

Now putting these all back into eqn (10):

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

By defining:

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

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

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

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

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

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}$$

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

$\sum_{a \neq b}$  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:

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

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

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

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

Taking derivative w.r.t.  $\lambda$ :

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

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

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

Similarly:

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

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

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

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

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

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

### 3 Lagrangian Method

The MP2 Lagrangian could be written as:

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

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.

#### 3.1 Hartree Fock Energy

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

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

#### 3.2 Hylleraas Functional

The Hylleraas functional is defined as:

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

in which the relevant operators and functions are:

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

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

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

Therefore the Hylleraas functional could be written as:

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

First, we need to work out the following expectations:

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

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

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

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

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

$$\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} \quad (43)$$

the terms not fully contrated are ommitted.

Therefore, the two parts of Hylleraas functional could be simplified as:

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

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



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

$$E_H = \frac{1}{2} \text{Re} \left\{ \sum_{ijab} (T_{ij}^{ab})^* \langle ab || ij \rangle \right\} + \frac{1}{2} \left( \sum_{ijkab} f_{ki} (T_{ij}^{ab})^* T_{jk}^{ab} - \sum_{ijabc} f_{ac} (T_{ij}^{ab})^* T_{ij}^{bc} \right) \quad (46)$$

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.

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

in which

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

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

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

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

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

### 3.3 Perturbed Orthonormality Condition

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

$$S_{pq} = \langle p | q \rangle = \delta_{pq} \quad (53)$$

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

Parameterization of the MO coefficients:

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

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

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

Now the orthonormality condition using this parameterization:

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

Introducing the transformed overlap matrix:

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

we have:

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

differentiating both sides of the equation gives:

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

Noting that  $\mathcal{S}(0) = \mathbf{I}$  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  $A^\lambda = \left(\frac{dA}{d\lambda}\right)\big|_{\lambda=0}$  results in:

$$\sum_{rs} (U_{rp}^\lambda)^* \delta_{rs} \delta_{sq} + \sum_{rs} \delta_{rp} \mathcal{S}_{rs}^\lambda \delta_{sq} + \sum_{rs} \delta_{rp} \delta_{rs} U_{sq}^\lambda = 0 \quad (61)$$

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

$$(U_{qp}^\lambda)^* + \mathcal{S}_{pq}^\lambda + U_{pq}^\lambda = 0 \quad (62)$$

### 3.4 Perturbed Brillouin Condition

The SCF density matrix is defined as:

$$D_{\mu\nu}^{\text{SCF}} = \sum_i^N C_{\mu i}^* C_{\nu i} \quad (63)$$

in which the MO coefficients are parameterized as:

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

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

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

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

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

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

$$f_{\mu\nu}^{\text{AO}} = h_{\mu\nu}^{\text{AO}} + g_{\mu\nu}^{\text{AO}} = \langle \mu | \hat{h} | \nu \rangle + \sum_{\rho\sigma} D_{\rho\sigma} \langle \mu\rho || \nu\sigma \rangle \quad (68)$$

$$\begin{aligned} \mathbf{f} &= \mathbf{h} + \mathbf{g}[\mathbf{D}^{\text{SCF}}] \\ &= \mathbf{C}^\dagger \mathbf{h}^{\text{AO}} \mathbf{C} + \mathbf{C}^\dagger \mathbf{g}^{\text{AO}} [\mathbf{D}^{\text{SCF}}] \mathbf{C} \\ &= \mathbf{C}^\dagger \mathbf{F}^{\text{AO}} [\mathbf{D}^{\text{SCF}}] \mathbf{C} \end{aligned} \quad (69)$$

$$\mathbf{f}^{\text{AO}} [\mathbf{D}^{\text{SCF}}] = \mathbf{h}^{\text{AO}} + \mathbf{g}^{\text{AO}} [\mathbf{D}^{\text{SCF}}] \quad (70)$$

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

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

The perturbed Brillouin condition is:

$$f_{ai}^\lambda = 0 \quad (72)$$

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

$$(\mathbf{U}^{\lambda\dagger} \mathbf{f})_{ai} = U_{ia}^{\lambda*} \varepsilon_i = \left. \frac{dU_{ia}^*}{d\lambda} \right|_{\lambda=0} \varepsilon_i \quad (73)$$

$$(\mathbf{f} \mathbf{U}^\lambda)_{ai} = \varepsilon_a U_{ai}^\lambda = \varepsilon_a \left. \frac{dU_{ai}}{d\lambda} \right|_{\lambda=0} \quad (74)$$

$$(\mathbf{C}^\dagger \mathbf{h}^{\text{AO},\lambda} \mathbf{C})_{ai} = \sum_{\mu\nu} C_{\mu a}^* h_{\mu\nu}^\lambda C_{\nu i} = \sum_{\mu\nu} C_{\nu a}^* \left. \frac{dh_{\mu\nu}}{d\lambda} \right|_{\lambda=0} C_{\nu i} \quad (75)$$

$$\begin{aligned} (\mathbf{C}^\dagger \mathbf{g}^{\text{AO},\lambda} [\mathbf{D}^{\text{SCF}}] \mathbf{C})_{ai} &= \sum_{\mu\nu} C_{\mu a}^* \left( \sum_{\rho\sigma} D_{\rho\sigma} \langle \mu\rho || \nu\sigma \rangle^\lambda \right) C_{\nu i} \\ &= \sum_{\mu\nu} C_{\mu a}^* \left( \sum_{\rho\sigma} D_{\rho\sigma} \left. \frac{d\langle \mu\rho || \nu\sigma \rangle}{d\lambda} \right|_{\lambda=0} \right) C_{\nu i} \end{aligned} \quad (76)$$

$$\begin{aligned} (\mathbf{C}^\dagger \mathbf{g}^{\text{AO}} [\mathbf{D}^{\text{SCF},\lambda}] \mathbf{C})_{ai} &= \sum_{\mu\nu} C_{\mu a}^* \left( \sum_{\rho\sigma} D_{\rho\sigma}^\lambda \langle \mu\rho || \nu\sigma \rangle \right) C_{\nu i} \\ &= \sum_{\mu\nu} C_{\mu a}^* \left( \sum_{\rho\sigma} \left. \frac{dD_{\rho\sigma}}{d\lambda} \right|_{\lambda=0} \langle \mu\rho || \nu\sigma \rangle \right) C_{\nu i} \end{aligned} \quad (77)$$

### 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!**

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

$$\frac{\partial \mathcal{L}_{\text{MP2}}}{\partial \mathbf{U}} = \frac{\partial E_{\text{HF}}}{\partial \mathbf{U}} + \frac{\partial E_{\text{H}}}{\partial \mathbf{U}} + \sum_{ai} z_{ai} \frac{\partial f_{ai}}{\partial \mathbf{U}} = 0 \quad (79)$$

The Hylleraas part (assuming real):

$$E_{\text{H}} = \sum_{ij} h_{ij} \gamma_{ij} + \sum_{ab} h_{ab} \gamma_{ab} + \sum_{ijab} \langle ab || ij \rangle \Gamma_{ij}^{ab} + \sum_{ijkl} \langle ij || kl \rangle \Gamma_{kl}^{ij} + \sum_{ijab} \langle ai || bj \rangle \Gamma_{bj}^{ai} \quad (80)$$

**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 multiplier in  $C_{ON}$  condition.

Could treat  $\mathbf{U}$  and  $\mathbf{U}^*$  as independent variables, i.e.:

$$\frac{\partial U_{pq}}{\partial U_{rs}^*} = 0 \quad (81)$$

Or just treat real and imaginary parts separately.

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

Similarly:

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

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

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

Other blocks of the 2e-integrals are similar.

note:

$$\frac{dU_{pq}}{dU_{rs}} = \delta_{pr} \delta_{qs} \tag{85}$$

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:

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

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  $\boldsymbol{\kappa}$ :

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

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

**NO! Take derivatives!:**

$$\begin{aligned}
 \mathbf{I} &= \mathbf{S}(\lambda) \\
 &= \mathbf{C}^\dagger(\lambda) \mathbf{S}^{\text{AO}}(\lambda) \mathbf{C}(\lambda) \\
 &= (\mathbf{C}(0) \exp[-\boldsymbol{\kappa}(\lambda)])^\dagger \mathbf{S}^{\text{AO}}(\lambda) \mathbf{C}(0) \exp[-\boldsymbol{\kappa}(\lambda)] \\
 &= \exp\left[-\boldsymbol{\kappa}^\dagger(\lambda)\right] \mathbf{C}^\dagger(0) \mathbf{S}^{\text{AO}}(\lambda) \mathbf{C}(0) \exp[-\boldsymbol{\kappa}(\lambda)] \\
 &= \exp[\boldsymbol{\kappa}(\lambda)] \mathcal{S}(\lambda) \exp[-\boldsymbol{\kappa}(\lambda)] \\
 &= \left[\mathbf{I} + \boldsymbol{\kappa}(\lambda) + \frac{1}{2} \boldsymbol{\kappa}^2(\lambda) + \dots\right] \mathcal{S}(\lambda) \left[\mathbf{I} - \boldsymbol{\kappa}(\lambda) + \frac{1}{2} \boldsymbol{\kappa}^2(\lambda) + \dots\right] \\
 \Leftrightarrow \delta_{pq} &= \sum_{\mu\nu} C_{\mu p}^*(\lambda) S_{\mu\nu}^{\text{AO}}(\lambda) C_{\nu q}(\lambda) \\
 &= \sum_{\mu\nu} \left( \sum_r C_{\mu r}^*(0) \exp[-\boldsymbol{\kappa}(\lambda)]_{rp}^* \right) S_{\mu\nu}^{\text{AO}}(\lambda) \left( \sum_s C_{\nu s} \exp[-\boldsymbol{\kappa}(\lambda)]_{sq} \right) \\
 &= \sum_{\mu\nu rs} \exp[\boldsymbol{\kappa}(\lambda)]_{pr} \left( C_{\mu r}^*(0) S_{\mu\nu}^{\text{AO}}(\lambda) C_{\nu s}(0) \right) \exp[-\boldsymbol{\kappa}(\lambda)]_{sq} \\
 &= \sum_{rs} \exp[\boldsymbol{\kappa}(\lambda)]_{pr} \mathcal{S}_{rs}(\lambda) \exp[-\boldsymbol{\kappa}(\lambda)]_{sq} \\
 &= \sum_{rs} \left[ \delta_{pr} + \kappa_{pr}(\lambda) + \frac{1}{2} \sum_x \kappa_{px}(\lambda) \kappa_{xr}(\lambda) \right] \mathcal{S}_{rs}(\lambda) \left[ \delta_{sq} + \kappa_{sq}(\lambda) + \frac{1}{2} \sum_y \kappa_{sy}(\lambda) \kappa_{yq}(\lambda) \right]
 \end{aligned} \tag{94}$$

$$\tag{95}$$

**index  $x$  &  $y$  look weird, find other appropriate indices.**

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

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

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

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

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

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

$$\frac{\partial E_{\text{HF}}}{\partial \boldsymbol{\kappa}} = \quad (99)$$

$$\frac{\partial E_{\text{H}}}{\partial \boldsymbol{\kappa}} = \quad (100)$$

$$\frac{\partial f_{ai}}{\partial \boldsymbol{\kappa}} = \quad (101)$$

The specific blocks:

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

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

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

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

$$\mathcal{S} = \mathbf{C}^\dagger(0) \mathbf{S}^{\text{AO}}(\lambda) \mathbf{C}(0) \quad (105)$$

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

In this way:

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

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

$$\mathbf{S}^\lambda = \left. \frac{\partial \mathbf{S}(\lambda)}{\partial \lambda} \right|_{\lambda=0} = \mathbf{0} \quad (107)$$

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

$$\mathcal{S}^{-\frac{1}{2}\dagger} \mathcal{S} \mathcal{S}^{-\frac{1}{2}} = \mathbf{I} \quad (108)$$

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

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

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

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

Then the relevant integrals could be expressed as:

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

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

$$\frac{\partial \delta_{pq}}{\partial \kappa_{rs}} = 0 \quad (113)$$

$$\frac{\partial \kappa_{pq}}{\partial \kappa_{rs}} = \delta_{pr} \delta_{qs} \quad (114)$$

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

$$\begin{aligned} &= \sum_{\mu\nu rstu} C_{\mu r}^* \mathcal{S}_{rt}^{-\frac{1}{2}*} \exp[\boldsymbol{\kappa}]_{pt} h_{\mu\nu}^{\text{AO}} C_{vs} \mathcal{S}_{su}^{-\frac{1}{2}} \exp[-\boldsymbol{\kappa}]_{uq} \\ &= \sum_{\mu\nu rstu} C_{\mu r}^* \mathcal{S}_{rt}^{-\frac{1}{2}*} [\delta_{pt} + \kappa_{pt} + \dots] h_{\mu\nu}^{\text{AO}} C_{vs} \mathcal{S}_{su}^{-\frac{1}{2}} [\delta_{uq} - \kappa_{uq} + \dots] \\ &= \sum_{\mu\nu rstu} C_{\mu r}^* \mathcal{S}_{rt}^{-\frac{1}{2}*} h_{\mu\nu}^{\text{AO}} C_{vs} \mathcal{S}_{su}^{-\frac{1}{2}} [\delta_{pt} \delta_{uq} - \delta_{pt} \kappa_{uq} + \delta_{uq} \kappa_{pt} - \kappa_{pt} \kappa_{uq}] \end{aligned} \quad (116)$$

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

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

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

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

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

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



hence:

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

Now the two-electron integral:

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

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

$$\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} \left( \frac{\partial \kappa_{pg}}{\partial \kappa_{xy}} \Big|_{\lambda=0} \delta_{qh} \delta_{mr} \delta_{ns} \right. \\ &\quad \left. + \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} \right) \\ &= \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} \quad (122)$$

Therefore, the orbital response for fock matrix is:

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

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

thus the only non-redundant orbital response is:

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

Then, the orbital response for the Hylleraas functional:

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

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

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

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

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

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

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

$$\begin{aligned}
 \sum_{ij} \left. \frac{\partial h_{ij}}{\partial \kappa_{em}} \gamma_{ij} \right|_{\lambda=0} &= \sum_{ij} (h_{jm} \delta_{ie} - h_{ie} \delta_{jm}) \gamma_{ij} \\
 &= - \sum_i h_{ie} \gamma_{im}
 \end{aligned} \tag{131}$$

$$\begin{aligned}
 \sum_{ab} \left. \frac{\partial h_{ab}}{\partial \kappa_{em}} \gamma_{ab} \right|_{\lambda=0} &= \sum_{ab} (h_{bm} \delta_{ae} - h_{ae} \delta_{bm}) \gamma_{ab} \\
 &= \sum_b h_{bm} \gamma_{eb} = \sum_a h_{am} \gamma_{ea}
 \end{aligned} \tag{132}$$

$$\sum_{ijab} \left. \frac{\partial \langle ab || ij \rangle}{\partial \kappa_{em}} \Gamma_{ij}^{ab} \right|_{\lambda=0} = \sum_{ijab} \left( \langle mb || ij \rangle \delta_{ae} + \langle am || ij \rangle \delta_{be} - \langle ab || ej \rangle \delta_{im} - \langle ab || ie \rangle \delta_{jm} \right) \Gamma_{ij}^{ab}$$

$$\begin{aligned}
 &= \sum_{ijb} \langle mb || ij \rangle \Gamma_{ij}^{eb} + \sum_{ija} \langle am || ij \rangle \Gamma_{ij}^{ae} - \sum_{jab} \langle ab || ej \rangle \Gamma_{mj}^{ab} - \sum_{iab} \langle ab || ie \rangle \Gamma_{im}^{ab} \\
 &= \sum_{ija} \langle ma || ij \rangle \Gamma_{ij}^{ea} + \sum_{ija} \langle am || ij \rangle \Gamma_{ij}^{ae} - \sum_{iab} \langle ab || ei \rangle \Gamma_{mi}^{ab} - \sum_{iab} \langle ab || ie \rangle \Gamma_{im}^{ab} \\
 &= \sum_{ija} \langle am || ji \rangle \Gamma_{ij}^{ea} + \sum_{ija} \langle am || ji \rangle \Gamma_{ji}^{ae} - \sum_{iab} \langle ab || ei \rangle \Gamma_{mi}^{ab} - \sum_{iab} \langle ab || ei \rangle \Gamma_{im}^{ba} \\
 &= 2 \sum_{ija} \langle am || ji \rangle \Gamma_{ij}^{ea} - 2 \sum_{iab} \langle ab || ei \rangle \Gamma_{mi}^{ab} \tag{133}
 \end{aligned}$$

in which the symmetry of MP2 amplitudes is exploited:

$$T_{ij}^{ab} = T_{ji}^{ba} \Leftrightarrow \Gamma_{ij}^{ab} = \Gamma_{ji}^{ba} \tag{134}$$

Then:

$$\begin{aligned}
 \sum_{ijkl} \frac{\partial \langle ij || kl \rangle}{\partial \kappa_{em}} \Gamma_{kl}^{ij} \Big|_{\lambda=0} &= \sum_{ijkl} \left( \cancel{\langle mj || kt \rangle \delta_{ie}} + \cancel{\langle im || kt \rangle \delta_{je}} - \langle ij || el \rangle \delta_{km} - \langle ij || ke \rangle \delta_{lm} \right) \Gamma_{kl}^{ij} \\
 &= - \sum_{ijl} \langle ij || el \rangle \Gamma_{ml}^{ij} - \sum_{ijk} \langle ij || ke \rangle \Gamma_{km}^{ij} \\
 &= - \sum_{ijk} \langle ij || ek \rangle \Gamma_{mk}^{ij} - \sum_{ijk} \langle ij || ek \rangle \Gamma_{km}^{ji} \tag{135}
 \end{aligned}$$

No symmetry for  $\Gamma_{kl}^{ij}$  could be used to simplify the expression.

$$\begin{aligned}
 \sum_{ijab} \frac{\partial \langle ai || bj \rangle}{\partial \kappa_{em}} \Gamma_{bj}^{ai} \Big|_{\lambda=0} &= \sum_{ijab} \left( \langle mi || bj \rangle \delta_{ae} + \cancel{\langle am || bj \rangle \delta_{ie}} - \cancel{\langle ai || ej \rangle \delta_{bm}} - \langle ai || be \rangle \delta_{jm} \right) \Gamma_{bj}^{ai} \\
 &= \sum_{ijb} \langle mi || bj \rangle \Gamma_{bj}^{ei} - \sum_{iab} \langle ai || be \rangle \Gamma_{bm}^{ai} \tag{136}
 \end{aligned}$$

Therefore, the overall Hylleraas response is:

$$\begin{aligned}
 \frac{\partial E_H}{\partial \kappa_{bj}} \Big|_{\lambda=0} &= \sum_a h_{aj} \gamma_{ba} - \sum_i h_{ib} \gamma_{ij} \\
 &\quad + 2 \sum_{ika} \langle aj || ki \rangle \Gamma_{ik}^{ba} - 2 \sum_{iac} \langle ac || bi \rangle \Gamma_{ji}^{ac} \\
 &\quad - \sum_{ikl} \langle ik || bl \rangle \Gamma_{jl}^{ik} - \sum_{ikl} \langle ik || bl \rangle \Gamma_{lj}^{ki} \\
 &\quad + \sum_{ikc} \langle ji || ck \rangle \Gamma_{ck}^{bi} - \sum_{iac} \langle ai || cb \rangle \Gamma_{cj}^{ai} \tag{137}
 \end{aligned}$$

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

$$E_{\text{HF}} = \sum_i h_{ii} + \frac{1}{2} \sum_{ik} \langle ik || ik \rangle \tag{138}$$

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

$$\begin{aligned}
 & + \frac{1}{2} \sum_{ik} \left( \cancel{\langle jk||ik \rangle \delta_{ib}} + \cancel{\langle ij||ik \rangle \delta_{kb}} - \langle ik||bk \rangle \delta_{ij} - \langle ik||ib \rangle \delta_{kj} \right) \\
 & = -h_{jb} - \frac{1}{2} \sum_k \langle jk||bk \rangle - \frac{1}{2} \sum_i \langle ij||ib \rangle \\
 & = -h_{jb} - \sum_i \langle ji||bi \rangle \\
 & = -f_{jb} \\
 & = 0
 \end{aligned} \tag{139}$$

The Lagrangian constraint on orbital rotation:

$$\frac{\partial \mathcal{L}_{\text{MP2}}}{\partial \kappa_{bj}} \Big|_{\lambda=0} = \frac{\partial E_{\text{HF}}}{\partial \kappa_{bj}} \Big|_{\lambda=0} + \frac{\partial E_{\text{H}}}{\partial \kappa_{bj}} \Big|_{\lambda=0} + \sum_{ai} z_{ai} \frac{\partial f_{ai}}{\partial \kappa_{bj}} \Big|_{\lambda=0} = 0 \tag{140}$$

Now the Z-Vector equation becomes:

$$\sum_{ai} z_{ai} \frac{\partial f_{ai}}{\partial \kappa_{bj}} \Big|_{\lambda=0} = - \frac{\partial E_{\text{H}}}{\partial \kappa_{bj}} \Big|_{\lambda=0} \tag{141}$$

in which the RHS is the orbital gradient for MP2.

$$\begin{aligned}
 \text{LHS} & = \sum_{ai} (\varepsilon_i - \varepsilon_a) \delta_{ab} \delta_{ij} z_{ai} \\
 & = (\varepsilon_j - \varepsilon_b) z_{bj}
 \end{aligned} \tag{142}$$

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

$$\begin{aligned}
 (\varepsilon_b - \varepsilon_j) z_{bj} & = \sum_a h_{aj} \gamma_{ba} - \sum_i h_{ib} \gamma_{ij} \\
 & + 2 \sum_{ika} \langle aj||ki \rangle \Gamma_{ik}^{ba} - 2 \sum_{iac} \langle ac||bi \rangle \Gamma_{ji}^{ac} \\
 & - \sum_{ikl} \langle ik||bl \rangle \Gamma_{jl}^{ik} - \sum_{ikl} \langle ik||bl \rangle \Gamma_{lj}^{ki} \\
 & + \sum_{ikc} \langle ji||ck \rangle \Gamma_{ck}^{bi} - \sum_{iac} \langle ai||cb \rangle \Gamma_{cj}^{ai}
 \end{aligned} \tag{143}$$

## 4 !!EUREKA: Summary of MP2 Gradient

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

$$\begin{aligned}\mathcal{L}_{\text{MP2}} &= E_{\text{HF}} + E_{\text{H}} + \frac{1}{2} \sum_{ai} (z_{ai} f_{ai} + z_{ai}^* f_{ai}^*) \\ &= \sum_{pq} h_{pq} \gamma_{pq} + \sum_{pqrs} \Gamma_{rs}^{pq} \langle pq || rs \rangle + \frac{1}{2} \sum_{ai} (z_{ai} f_{ai} + z_{ai}^* f_{ai}^*)\end{aligned}\quad (144)$$

Constraints:

$$\frac{\partial \mathcal{L}_{\text{MP2}}}{\partial z_{ai}} = f_{ai} = 0 \quad \text{Hartree-Fock Condition} \quad (145)$$

$$\frac{\partial \mathcal{L}_{\text{MP2}}}{\partial T_{ij}^{ab}} = \frac{\partial E_{\text{H}}}{\partial T_{ij}^{ab}} = 0 \quad \text{MP2 Condition} \quad (146)$$

$$\frac{\partial \mathcal{L}_{\text{MP2}}}{\partial \kappa_{bj}} = \frac{\partial E_{\text{H}}}{\partial \kappa_{bj}} + \frac{1}{2} \sum_{ai} \left( z_{ai} \frac{\partial f_{ai}}{\partial \kappa_{bj}} + \bar{z}_{ai} \frac{\partial f_{ai}^*}{\partial \kappa_{bj}} \right) = 0 \quad \text{Z-Vector Equations} \quad (147)$$

Densities:

$$\gamma_{pq} = \gamma_{pq}^{\text{HF}} + \gamma_{pq}^{\text{H}} \quad (148)$$

$$\Gamma_{rs}^{pq} = (\Gamma^{\text{HF}})_{rs}^{pq} + (\Gamma^{\text{H}})_{rs}^{pq} \quad (149)$$

$$\gamma_{ij}^{\text{H}} = \frac{1}{2} \sum_{kab} (T_{jk}^{ab})^* T_{ki}^{ab} \quad \gamma_{ij}^{\text{HF}} = \delta_{ij} \quad (150)$$

$$\gamma_{ab}^{\text{H}} = -\frac{1}{2} \sum_{ijc} (T_{ij}^{ac})^* T_{ij}^{cb} \quad (151)$$

$$(\Gamma^{\text{H}})_{ij}^{ab} = \frac{1}{2} (T_{ij}^{ab})^* \quad (152)$$

$$(\Gamma^{\text{H}})_{kl}^{ij} = \frac{1}{2} \sum_{mab} (T_{km}^{ab})^* T_{mi}^{ab} \delta_{jl} \quad (\Gamma^{\text{HF}})_{kl}^{ij} = \frac{1}{2} \delta_{ik} \delta_{jl} \quad (153)$$

$$(\Gamma^{\text{H}})_{bj}^{ai} = -\frac{1}{2} \sum_{klc} (T_{kl}^{ac})^* T_{kl}^{cb} \delta_{ij} \quad (154)$$

### 4.1 Hartree-Fock

$$f_{ai} = h_{ai} + \sum_j \langle aj || ij \rangle = 0 \quad (155)$$

$$\begin{aligned}E_{\text{HF}} &= \sum_i h_{ii} + \frac{1}{2} \sum_{ij} \langle ij || ij \rangle \\ &= \sum_{i\mu\nu} C_{\mu i}^* C_{\nu i} h_{\mu\nu} + \frac{1}{2} \sum_{ij} \sum_{\mu\nu\sigma\tau} C_{\mu i}^* C_{\nu j}^* C_{\sigma i} C_{\tau j} \langle \mu\nu || \sigma\tau \rangle \\ &= \sum_{\mu\nu} D_{\mu\nu}^{\text{HF}} h_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\sigma\tau} D_{\mu\sigma}^{\text{HF}} D_{\nu\tau}^{\text{HF}} \langle \mu\nu || \sigma\tau \rangle\end{aligned}\quad (156)$$

**4.2 MP2**

$$E_H = \sum_{ij} h_{ij} \gamma_{ij}^H + \sum_{ab} h_{ab} \gamma_{ab}^H + \sum_{ijab} \langle ab || ij \rangle (\Gamma^H)_{ij}^{ab} + \sum_{ijkl} \langle ij || kl \rangle (\Gamma^H)_{kl}^{ij} + \sum_{ijab} \langle ai || bj \rangle (\Gamma^H)_{bj}^{ai} \quad (157)$$

$$\sum_{ij} h_{ij} \gamma_{ij}^H = \sum_{ij\mu\nu} C_{\mu i}^* C_{\nu j} h_{\mu\nu} \gamma_{ij}^H \quad (158)$$

$$\sum_{ab} h_{ab} \gamma_{ab}^H = \sum_{ab\mu\nu} C_{\mu a}^* C_{\nu b} h_{\mu\nu} \gamma_{ab}^H \quad (159)$$

$$D_{\mu\nu}^H = \sum_{ij} C_{\mu i}^* C_{\nu j} \gamma_{ij}^H + \sum_{ab} C_{\mu a}^* C_{\nu b} \gamma_{ab}^H \quad (160)$$

$$\frac{\partial \gamma_{ij}^H}{\partial T_{ij}^{ab}} = \quad (161)$$