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:

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

in which E_{H} is the Hylleraas functional, C_{Bri} is the Brillouin condition, and C_{ON} is the orthonormality condition.

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:

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

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:

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

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

$$\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:

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

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

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

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

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.

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

in which

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

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

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

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

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

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 orthonomality 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. $F_{pq} = \delta_{pq}\varepsilon_p$):

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