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

3.1 Perturbed Orthonormality Condition

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

$$S_{pq} = \langle p|q\rangle = \delta_{pq} \tag{33}$$

$$\sum_{\mu\nu} C^*_{\mu p} S_{\mu\nu} C_{\nu q} = \delta_{pq} \tag{34}$$

Parameterization of the MO coefficients:

$$\mathbf{C}(\lambda) = \mathbf{C}(0)\mathbf{U}(\lambda) \tag{35}$$

$$C_{\mu p}(\lambda) = \sum_r C_{\mu r}(0) U_{rp}(\lambda) \tag{36}$$

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

Now the orthonomality condition using this parameterization:

$$\sum_{\mu\nu} \Big(\sum_r U^*_{rp}(\lambda) C^*_{\mu r}(0)\Big) S_{\mu\nu}(\lambda) \Big(\sum_s C_{\nu s}(0) U_{sq}(\lambda)\Big) = \delta_{pq} \tag{37}$$

Introducing the transformed overlap matrix:

$$\mathcal{S}_{pq}(\lambda) = \sum_{\mu\nu} C^*_{\mu p}(0) S_{\mu\nu}(\lambda) C_{\nu q}(0) \tag{38}$$

we have:

$$\sum_{rs} U^*_{rp}(\lambda) \mathcal{S}_{rs}(\lambda) U_{sq}(\lambda) = \delta_{pq} \tag{39}$$

differentiating both sides of the equation gives:

$$\sum_{rs} \frac{\mathrm{d}U^*_{rp}(\lambda)}{\mathrm{d}\lambda} \mathcal{S}_{rs}(\lambda) U_{sq}(\lambda) + \sum_{rs} U^*_{rp}(\lambda) \frac{\mathrm{d}\mathcal{S}_{rs}(\lambda)}{\mathrm{d}\lambda} U_{sq}(\lambda) + \sum_{rs} U^*_{rp}(\lambda) \mathcal{S}_{rs}(\lambda) \frac{\mathrm{d}U_{sq}(\lambda)}{\mathrm{d}\lambda} = 0 \tag{40}$$

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:

$$\sum_{rs} (U^\lambda_{rp})^* \delta_{rs}\delta_{sq} + \sum_{rs} \delta_{rp} \mathcal{S}^\lambda_{rs} \delta_{sq} + \sum_{rs} \delta_{rp}\delta_{rs} U^\lambda_{sq} = 0 \tag{41}$$

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

$$(U^\lambda_{qp})^* + \mathcal{S}^\lambda_{pq} + U^\lambda_{pq} = 0 \tag{42}$$

3.2 Perturbed Brillouin Condition

The SCF density matrix is defined as:

$$D^{\text{SCF}}_{\mu\nu} = \sum_i^N C^*_{\mu i} C_{\nu i} \tag{43}$$

in which the MO coefficients are parameterized as:

$$C_{\mu p}(\lambda) = \sum_q C_{\mu q}(0) U(\lambda)_{qp} \tag{44}$$

$$\mathbf{C}(\lambda) = \mathbf{C}(0)\mathbf{U}(\lambda) \tag{45}$$

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

$$\begin{aligned} h_{pq} &= \langle p|\hat{h}|q\rangle = \sum_{\mu\nu} C^*_{\mu p} h^{\text{AO}}_{\mu\nu} C_{\nu q} & g_{pq} &= \sum_i \langle pi||qi\rangle = \sum_i \sum_{\mu\nu} C^*_{\mu p} \langle \mu i||\nu i\rangle C_{\nu q} \\ h^{\text{AO}}_{\mu\nu} &= \langle \mu|\hat{h}|\nu\rangle & g^{\text{AO}}_{\mu\nu} &= \sum_i \langle \mu i||\nu i\rangle = \sum_{\rho\sigma} D_{\rho\sigma} \langle \mu\rho||\nu\sigma\rangle \\ \mathbf{h} &= \mathbf{C}^\dagger \mathbf{h}^{\text{AO}} \mathbf{C} & & \\ & & \mathbf{g} &= \mathbf{C}^\dagger \mathbf{g}^{\text{AO}} \mathbf{C} \end{aligned} \tag{46}$$

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

$$\begin{aligned} F_{pq} &= h_{pq} + \sum_i \langle pi||qi\rangle \\ &= \sum_{\mu\nu} C^*_{\mu p} h^{\text{AO}}_{\mu\nu} C_{\nu q} + \sum_{\mu\nu} C^*_{\mu p} g^{\text{AO}}_{\mu\nu} C_{\nu q} \\ &= \sum_{\mu\nu} C^*_{\mu p} \langle \mu|\hat{h}|\nu\rangle C_{\nu q} + \sum_{\mu\nu} C^*_{\mu p} \big(\sum_{\rho\sigma} D_{\rho\sigma} \langle \mu\rho||\nu\sigma\rangle \big) C_{\nu q} \end{aligned} \tag{47}$$

$$F^{\text{AO}}_{\mu\nu} = h^{\text{AO}}_{\mu\nu} + g^{\text{AO}}_{\mu\nu} = \langle \mu|\hat{h}|\nu\rangle + \sum_{\rho\sigma} D_{\rho\sigma} \langle \mu\rho||\nu\sigma\rangle \tag{48}$$

$$\begin{aligned} \mathbf{F} &= \mathbf{h} + \mathbf{g}[\mathbf{D}^{\text{SCF}}] \\ &= \mathbf{C}^\dagger \mathbf{h}^{\text{AO}} \mathbf{C} + \mathbf{C}^\dagger \mathbf{g}^{\text{AO}} [\mathbf{D}^{\text{SCF}}] \mathbf{C} \\ &= \mathbf{C}^\dagger \mathbf{F}^{\text{AO}} [\mathbf{D}^{\text{SCF}}] \mathbf{C} \end{aligned} \tag{49}$$

$$\mathbf{F}^{\text{AO}}[\mathbf{D}^{\text{SCF}}] = \mathbf{h}^{\text{AO}} + \mathbf{g}^{\text{AO}}[\mathbf{D}^{\text{SCF}}] \tag{50}$$

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

$$\begin{aligned} \mathbf{F}^\lambda &= \frac{\mathrm{d}\mathbf{F}(\lambda)}{\mathrm{d}\lambda}\Big|_{\lambda=0} = \Big(\mathbf{C}^\dagger(\lambda) \mathbf{F}^{\text{AO}} [\mathbf{D}^{\text{SCF}}(\lambda)](\lambda) \mathbf{C}(\lambda) \Big)^\lambda \\ &= \mathbf{C}^{\lambda\dagger}(\lambda) \mathbf{F}^{\text{AO}} [\mathbf{D}^{\text{SCF}}(\lambda)](\lambda) \mathbf{C}(\lambda) + \mathbf{C}^\dagger(\lambda) \mathbf{F}^{\text{AO}} [\mathbf{D}^{\text{SCF}}(\lambda)](\lambda) \mathbf{C}^\lambda(\lambda) \\ &\quad + \mathbf{C}^\dagger(\lambda) \Big(\mathbf{h}^{\text{AO}}(\lambda) + \mathbf{g}^{\text{AO}} [\mathbf{D}^{\text{SCF}}(\lambda)](\lambda) \Big)^\lambda \mathbf{C}(\lambda) \\ &= \mathbf{U}^{\lambda\dagger}(\lambda) \underbrace{\mathbf{U}^\dagger(0)\mathbf{C}^\dagger(0)}_{\mathbf{C}^\dagger(\lambda=0)} \mathbf{F}^{\text{AO}} [\mathbf{D}^{\text{SCF}}(\lambda)](\lambda) \mathbf{C}(\lambda) + \mathbf{C}^\dagger(\lambda) \mathbf{F}^{\text{AO}} [\mathbf{D}^{\text{SCF}}(\lambda)](\lambda) \underbrace{\mathbf{C}(0)\mathbf{U}(0)}_{\mathbf{C}(\lambda=0)} \mathbf{U}^\lambda(\lambda) \\ &\quad + \mathbf{C}^\dagger(\lambda) \Big(\mathbf{h}^{\text{AO},\lambda}(\lambda) + \mathbf{g}^{\text{AO},\lambda} [\mathbf{D}^{\text{SCF}}(\lambda)](\lambda) + \mathbf{g}^{\text{AO}} [\mathbf{D}^{\text{SCF},\lambda}(\lambda)](\lambda) \Big) \mathbf{C}(\lambda) \\ &= \mathbf{U}^{\lambda\dagger} \mathbf{F} + \mathbf{F} \mathbf{U}^\lambda + \mathbf{C}^\dagger \mathbf{h}^{\text{AO},\lambda} \mathbf{C} + \mathbf{C}^\dagger \mathbf{g}^{\text{AO},\lambda} [\mathbf{D}^{\text{SCF}}] \mathbf{C} + \mathbf{C}^\dagger \mathbf{g}^{\text{AO}} [\mathbf{D}^{\text{SCF},\lambda}] \mathbf{C} \end{aligned} \tag{51}$$

The perturbed Brillouin condition is:

$$F^\lambda_{ai} = 0 \tag{52}$$

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

$$(\mathbf{U}^{\lambda\dagger}\mathbf{F})_{ai} = U^{\lambda *}_{ia} \varepsilon_i = \frac{\mathrm{d}U^*_{ia}}{\mathrm{d}\lambda}\Big|_{\lambda=0} \varepsilon_i \tag{53}$$

$$(\mathbf{F}\mathbf{U}^{\lambda})_{ai} = \varepsilon_a U_{ai}^{\lambda} = \varepsilon_a \frac{\mathrm{d}U_{ai}}{\mathrm{d}\lambda}\Big|_{\lambda=0} \tag{54}$$

$$(\mathbf{C}^{\dagger}\mathbf{h}^{\mathrm{AO},\lambda}\mathbf{C})_{ai} = \sum_{\mu\nu} C_{\mu a}^{*} h_{\mu\nu}^{\lambda} C_{\nu i} = \sum_{\mu\nu} C_{\nu a}^{*} \frac{\mathrm{d}h_{\mu\nu}}{\mathrm{d}\lambda}\Big|_{\lambda=0} C_{\nu i} \tag{55}$$

$$\begin{aligned}(\mathbf{C}^{\dagger}\mathbf{g}^{\mathrm{AO},\lambda}[\mathbf{D}^{\mathrm{SCF}}]\mathbf{C})_{ai} &= \sum_{\mu\nu} C_{\mu a}^{*} (\sum_{\rho\sigma} D_{\rho\sigma} \langle\mu\rho||\nu\sigma\rangle^{\lambda}) C_{\nu i} \\ &= \sum_{\mu\nu} C_{\mu a}^{*} (\sum_{\rho\sigma} D_{\rho\sigma} \frac{\mathrm{d}\langle\mu\rho||\nu\sigma\rangle}{\mathrm{d}\lambda}\Big|_{\lambda=0}) C_{\nu i}\end{aligned} \tag{56}$$

$$\begin{aligned}(\mathbf{C}^{\dagger}\mathbf{g}^{\mathrm{AO}}[\mathbf{D}^{\mathrm{SCF},\lambda}]\mathbf{C})_{ai} &= \sum_{\mu\nu} C_{\mu a}^{*} (\sum_{\rho\sigma} D_{\rho\sigma}^{\lambda} \langle\mu\rho||\nu\sigma\rangle) C_{\nu i} \\ &= \sum_{\mu\nu} C_{\mu a}^{*} (\sum_{\rho\sigma} \frac{\mathrm{d}D_{\rho\sigma}}{\mathrm{d}\lambda}\Big|_{\lambda=0} \langle\mu\rho||\nu\sigma\rangle) C_{\nu i}\end{aligned} \tag{57}$$