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:

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

$$
=\frac{1}{2}\sum_{ijab}(T_{ij}^{ab})^*\langle a^\lambda b||ij\rangle + \frac{1}{2}\sum_{ijab}(T_{ij}^{ab})^*\langle ab||i^\lambda j\rangle + \frac{1}{2}\sum_{ijab}T_{ij}^{ab}\langle i^\lambda j||ab\rangle + \frac{1}{2}\sum_{ijab}T_{ij}^{ab}\langle ij||a^\lambda b\rangle
$$

$$
-\frac{1}{2}\sum_{ijab}T_{ij}^{ab}(T_{ij}^{ab})^*(\varepsilon_i^\lambda - \varepsilon_a^\lambda) \tag{8}
$$

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

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

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:

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

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

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

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:

$$\frac{1}{2} \sum_{ijab} T_{ij}^{ab} (T_{ij}^{ab})^* \varepsilon_a^\lambda = \frac{1}{2} \sum_{ijab} T_{ij}^{ab} (T_{ij}^{ab})^* \Big(Q_{aa}^\lambda + \sum_{gm} [U_{gm}^\lambda \langle am||ag \rangle + (U_{gm}^\lambda)^* \langle ag||am \rangle] \Big)$$

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

$$\tag{13}$$

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:

$$-\frac{1}{2} \sum_{ijab} \sum_k (T_{ij}^{ab})^* \langle kb||ij \rangle S_{ak}^\lambda - \frac{1}{2} \sum_{ijab} \sum_k T_{ij}^{ab} \langle ij||kb \rangle S_{ak}^\lambda$$

$$= -\frac{1}{2} \sum_{ijkab} S_{ak}^\lambda \Big(\frac{\langle ij||ab \rangle \langle kb||ij \rangle + \langle ab||ij \rangle \langle ij||kb \rangle}{\Delta_{ab}^{ij}} \Big) \tag{16}$$

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

Now putting these all back into eqn (10):

$$\frac{\partial E^{(2)}}{\partial \lambda} = -\frac{1}{2} \sum_{ijkab} S_{ak}^\lambda \Big(T_{ij}^{ab} \langle ij||kb \rangle + (T_{ij}^{ab})^* \langle kb||ij \rangle \Big)$$

$$-\frac{1}{2} \sum_{ijab} \sum_{f \neq a} (T_{ij}^{ab})^* \langle fb||ij \rangle S_{af}^\lambda - \frac{1}{2} \sum_{ijab} \sum_{k \neq i} T_{ij}^{ab} \langle kj||ab \rangle S_{ik}^\lambda$$

$$+\frac{1}{2} \sum_{ijab} \sum_f (T_{ij}^{ab})^* \langle ab||fi \rangle U_{fi}^\lambda + \frac{1}{2} \sum_{ijab} \sum_f T_{ij}^{ab} \langle fj||ab \rangle (U_{fi}^\lambda)^*$$

$$-\frac{1}{2} \sum_{ijab} \sum_k (T_{ij}^{ab})^* \langle kb||ij \rangle U_{ak}^\lambda - \frac{1}{2} \sum_{ijab} \sum_k T_{ij}^{ab} \langle ij||kb \rangle (U_{ak}^\lambda)^*$$

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

$$-\frac{1}{2} \sum_{ijabk} (T_{ij}^{ab})^* T_{kj}^{ab} \Big(Q_{ki}^\lambda + \sum_{gm} [U_{gm}^\lambda \langle km||ig \rangle + (U_{gm}^\lambda)^* \langle kg||im \rangle] \Big) \tag{17}$$

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}
$$

$$+ \sum_{ai} \sum_{jk} D_{jk} \langle ji||ka \rangle U_{ai}^{\lambda} + \sum_{ai} \sum_{jk} D_{jk} \langle ja||ki \rangle (U_{ai}^{\lambda})^{*}$$

$$= \sum_{ai} S_{ai}^{\lambda} I_{ai} + \sum_{ab} S_{ab}^{\lambda} I_{ab} + \sum_{ij} S_{ij}^{\lambda} I_{ij} + \sum_{ab} D_{ab} Q_{ab}^{\lambda} + \sum_{ij} D_{ij} Q_{ij}^{\lambda}$$

$$+ \text{ something like } \sum_{ai} X_{ai} U_{ai}^{\lambda} \tag{23}$$

$\sum_{a \neq b}$ 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):

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

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

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

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