1 Stationary Lagrangian

The CC Lagrangian is given as:

$$\mathcal{L}_{\text{CC}} = \langle \Phi_0 | (1 + \hat{\Lambda}) \mathcal{H} | \Phi_0 \rangle + \sum_{ai} f_{ai} z_{ai} + \sum_{pq} I_{pq} (\sum_{\mu\nu} C^*_{\mu p} S_{\mu\nu} C_{\nu q} - \delta_{pq}) \tag{1}$$

(Question: do I need to include other blocks of the Fock matrix?)
in which:

$$\hat{\Lambda} = \hat{\Lambda}_1 + \hat{\Lambda}_2 + \cdots = \sum_{ia} \lambda_a^i \{\hat{i}^\dagger \hat{a}\} + \frac{1}{4} \sum_{ijab} \lambda_{ab}^{ij} \{\hat{i}^\dagger \hat{j}^\dagger \hat{b} \hat{a}\} + \dots \tag{2}$$

The first term in the Lagrangian is used to include CC energy expression and CC amplitude constraints:

$$\begin{aligned}\langle \Phi_0 | (1 + \Lambda) \mathcal{H} | \Phi_0 \rangle =& \langle \Phi_0 | \mathcal{H} | \Phi_0 \rangle + \langle \Phi_0 | \hat{\Lambda} \mathcal{H} | \Phi_0 \rangle \\ =& \Delta E + \sum_{\mu} \lambda_\mu \langle \Phi_\mu | \mathcal{H} | \Phi_0 \rangle \end{aligned} \tag{3}$$

We need to impose the stationary conditions, w.r.t.:

- λ_μ: resulting the CC amplitude equations
- t_μ: resulting the CC lambda equations
- z_{ai}: the HF condition
- κ_{ai}: resulting the z-vector equations
- I_{pq}: resulting the orthonomality condition

1.1 CC Amplitude Equations

$$\begin{aligned}\frac{\partial \mathcal{L}_{\text{CC}}}{\partial \lambda_\mu} &= \frac{\partial}{\partial \lambda_\mu} \left(\langle \Phi_0 | \mathcal{H} | \Phi_0 \rangle + \langle \Phi_0 | \hat{\Lambda} \mathcal{H} | \Phi_0 \rangle + \sum_{ia} f_{ia} z_{ia} + \sum_{pq} I_{pq} (\sum_{\mu\nu} C^*_{\mu p} S_{\mu\nu} C_{\nu q} - \delta_{pq}) \right) \\ &= \langle \Phi_\mu | \mathcal{H} | \Phi_0 \rangle \end{aligned} \tag{4}$$

Hence imposing the stationary condition:

$$\frac{\partial \mathcal{L}_{\text{CC}}}{\partial \lambda_\mu} = 0 \tag{5}$$

we get:

$$\langle \Phi_\mu | \mathcal{H} | \Phi_0 \rangle = 0 \tag{6}$$

which are the CC amplitude equations. The alternative form is:

$$\hat{Q} \mathcal{H} \hat{P} = 0 \tag{7}$$

1.2 CC Lambda Equations

By:

$$\begin{aligned}\mathcal{H} &= (\hat{H}_{\text{N}} e^{\hat{T}})_{\text{C}} \\ &= (\hat{H}_{\text{N}} + \hat{H}_{\text{N}} \hat{T} + \frac{1}{2} \hat{H}_{\text{N}} \hat{T}^2 + \frac{1}{6} \hat{H}_{\text{N}} \hat{T}^3 + \frac{1}{24} \hat{H}_{\text{N}} \hat{T}^4)_{\text{C}} \end{aligned} \tag{8}$$

and:

$$\mathcal{L}_{\mathrm{CC}} = \langle\Phi_0|(1+\hat{\Lambda})\mathcal{H}|\Phi_0\rangle + \sum_{p>q} f_{pq} z_{pq} \tag{9}$$

We can find the partial derivative $\partial\mathcal{L}_{\mathrm{CC}}/\partial t_\mu$. First let's consider (CCSD):
(Should I truncate to four-fold then take derivatives, or the other way around? Or can I show they're equivalent?)

$$\frac{\partial\mathcal{H}}{\partial t_i^a} = \frac{\partial}{\partial t_i^a}\left(\hat{H}_{\mathrm{N}}(1+\hat{T}+\frac{1}{2}\hat{T}^2+\frac{1}{6}\hat{T}^3+\frac{1}{24}\hat{T}^4+\dots)\right)_{\mathrm{C}} \tag{10}$$

$$\frac{\partial\hat{H}_{\mathrm{N}}}{\partial t_i^a} = 0 \tag{11}$$

$$\frac{\partial}{\partial t_i^a}\left(\hat{H}_{\mathrm{N}}\hat{T}\right) = \frac{\partial}{\partial t_i^a}\left(\hat{H}_{\mathrm{N}}(\hat{T}_1+\hat{T}_2)\right) = \hat{H}_{\mathrm{N}}\{\hat{a}^\dagger\hat{i}\} \tag{12}$$

$$\begin{aligned}\frac{\partial}{\partial t_i^a}\left(\frac{1}{2}\hat{H}_{\mathrm{N}}\hat{T}^2\right) &= \frac{1}{2}\hat{H}_{\mathrm{N}}\frac{\partial}{\partial t_i^a}\left(\hat{T}_1^2+2\hat{T}_1\hat{T}_2+\hat{T}_2^2\right) \\ &= \frac{1}{2}\hat{H}_{\mathrm{N}}(2\hat{T}_1+2\hat{T}_2)\{\hat{a}^\dagger\hat{i}\} \\ &= \hat{H}_{\mathrm{N}}\hat{T}\{\hat{a}^\dagger\hat{i}\}\end{aligned} \tag{13}$$

$$\begin{aligned}\frac{\partial}{\partial t_i^a}\left(\frac{1}{6}\hat{H}_{\mathrm{N}}\hat{T}^3\right) &= \frac{1}{6}\hat{H}_{\mathrm{N}}\frac{\partial}{\partial t_i^a}\left(\hat{T}_1^3+3\hat{T}_1^2\hat{T}_2+3\hat{T}_1\hat{T}_2^2+\hat{T}_2^3\right) \\ &= \frac{1}{6}\hat{H}_{\mathrm{N}}(3\hat{T}_1^2+6\hat{T}_1\hat{T}+3\hat{T}_2^2)\{\hat{a}^\dagger\hat{i}\} \\ &= \frac{1}{2}\hat{H}_{\mathrm{N}}\hat{T}^2\{\hat{a}^\dagger\hat{i}\}\end{aligned} \tag{14}$$

$$\begin{aligned}\frac{\partial}{\partial t_i^a}\left(\frac{1}{24}\hat{H}_{\mathrm{N}}\hat{T}^4\right) &= \frac{1}{24}\hat{H}_{\mathrm{N}}\frac{\partial}{\partial t_i^a}\left(\hat{T}_1^4+4\hat{T}_1^3\hat{T}_2+6\hat{T}_1^2\hat{T}_2^2+4\hat{T}_1\hat{T}_2^3+\hat{T}_2^4\right) \\ &= \frac{1}{24}\hat{H}_{\mathrm{N}}(4\hat{T}_1^3+12\hat{T}_1\hat{2}\hat{T}_2+12\hat{T}_1\hat{T}_2^2+4\hat{T}_2^3)\{\hat{a}^\dagger\hat{i}\} \\ &= \frac{1}{6}\hat{H}_{\mathrm{N}}\hat{T}^3\{\hat{a}^\dagger\hat{i}\} \\ &\dots\end{aligned} \tag{15}$$

Therefore:

$$\begin{aligned}\frac{\partial\mathcal{H}}{\partial t_i^a} &= (\hat{H}_{\mathrm{N}}(1+\hat{T}+\frac{1}{2}\hat{T}^2+\frac{1}{6}\hat{T}^3+...))_{\mathrm{C}}\{\hat{a}^\dagger\hat{i}\} \\ &= (\hat{H}_{\mathrm{N}}e^{\hat{T}})_{\mathrm{C}}\{\hat{a}^\dagger\hat{i}\} \\ &= \mathcal{H}\{\hat{a}^\dagger\hat{i}\}\end{aligned} \tag{16}$$

Compare results with commutators?
By BCH:

$$\begin{aligned}\mathcal{H} =& \hat{H}_{\mathrm{N}} + [\hat{H}_{\mathrm{N}},\hat{T}] + \frac{1}{2!}[[\hat{H}_{\mathrm{N}},\hat{T}],\hat{T}] + \frac{1}{3!}[[[\hat{H}_{\mathrm{N}},\hat{T}],\hat{T}],\hat{T}] \\ &+ \frac{1}{4!}[[[[\hat{H}_{\mathrm{N}},\hat{T}],\hat{T}],\hat{T}],\hat{T}] + \dots\end{aligned} \tag{17}$$

Can't truncate yet, for the sake of taking derivatives.
Then take derivative w.r.t amplitude t_i^a:

$$\frac{\partial\mathcal{H}}{\partial t_i^a} = \frac{\partial\hat{H}_{\mathrm{N}}}{\partial t_i^a} + \frac{\partial}{\partial t_i^a}[\hat{H}_{\mathrm{N}},\hat{T}] + \dots \tag{18}$$

$$
\begin{aligned}
\frac{\partial \hat{H}_{\mathrm{N}}}{\partial t_i^a} =& 0 & (19)\\
\frac{\partial}{\partial t_i^a}[\hat{H}_{\mathrm{N}}, \hat{T}] =& \frac{\partial}{\partial t_i^a}[\hat{H}_{\mathrm{N}}, \hat{T}_1] + 0 = [\hat{H}_{\mathrm{N}}, \{\hat{a}^\dagger\hat{i}\}] & (20)\\
\frac{\partial}{\partial t_i^a}[[\hat{H}_{\mathrm{N}}, \hat{T}], \hat{T}] =& \frac{\partial}{\partial t_i^a}\Big([[\hat{H}_{\mathrm{N}}, \hat{T}_1], \hat{T}_1] + [[\hat{H}_{\mathrm{N}}, \hat{T}_1], \hat{T}_2] + [[\hat{H}_{\mathrm{N}}, \hat{T}_2], \hat{T}_1] + [[\hat{H}_{\mathrm{N}}, \hat{T}_2], \hat{T}_2]\Big) & \\
=& [[\hat{H}_{\mathrm{N}}, \frac{\partial \hat{T}_1}{\partial t_i^a}], \hat{T}_1] + [[\hat{H}_{\mathrm{N}}, \hat{T}_1], \frac{\partial \hat{T}_1}{\partial t_i^a}] + [[\hat{H}_{\mathrm{N}}, \frac{\partial \hat{T}_1}{\partial t_i^a}], \hat{T}_2] + [[\hat{H}_{\mathrm{N}}, \hat{T}_2], \frac{\partial \hat{T}_1}{\partial t_i^a}] & \\
=& [[\hat{H}_{\mathrm{N}}, \{\hat{a}^\dagger\hat{i}\}], \hat{T}_1] + [[\hat{H}_{\mathrm{N}}, \hat{T}_1], \{\hat{a}^\dagger\hat{i}\}] + [[\hat{H}_{\mathrm{N}}, \{\hat{a}^\dagger\hat{i}\}], \hat{T}_2] + [[\hat{H}_{\mathrm{N}}, \hat{T}_2], \{\hat{a}^\dagger\hat{i}\}] & \\
=& [[\hat{H}_{\mathrm{N}}, \{\hat{a}^\dagger\hat{i}\}], \hat{T}] + [[\hat{H}_{\mathrm{N}}, \hat{T}], \{\hat{a}^\dagger\hat{i}\}] & (21)\\
\frac{\partial}{\partial t_i^a}[[[\hat{H}_{\mathrm{N}}, \hat{T}], \hat{T}], \hat{T}] =& \dots &
\end{aligned}
$$

(At the end of this tedious evaluation, we can find:)

$$
\begin{aligned}
\frac{\partial \mathcal{H}}{\partial t_i^a} =& [\mathcal{H}, \{\hat{a}^\dagger\hat{i}\}] & (22)\\
\frac{\partial \mathcal{H}}{\partial t_{ij}^{ab}} =& [\mathcal{H}, \frac{1}{4}\{\hat{a}^\dagger\hat{b}^\dagger\hat{j}\hat{i}\}] & (23)
\end{aligned}
$$

I think the commutator expression may be more convenient, for the following derivation:
Now to find $\partial\mathcal{L}_{\mathrm{CC}}/\partial t_\mu$:

$$
\begin{aligned}
\frac{\partial \mathcal{L}_{\mathrm{CC}}}{\partial t_i^a} =& \langle\Phi_0|(1+\hat{\Lambda})[\mathcal{H}, \{\hat{a}^\dagger\hat{i}\}]|\Phi_0\rangle \\
=& \langle\Phi_0|(1+\hat{\Lambda})\mathcal{H}\{\hat{a}^\dagger\hat{i}\}|\Phi_0\rangle - \langle\Phi_0|(1+\hat{\Lambda})\{\hat{a}^\dagger\hat{i}\}\mathcal{H}|\Phi_0\rangle \\
=& \langle\Phi_0|(1+\hat{\Lambda})\mathcal{H}|\Phi_i^a\rangle - \langle\Phi_0|(1+\hat{\Lambda})\Delta E|\Phi_i^a\rangle \\
=& \langle\Phi_0|(1+\hat{\Lambda})(\mathcal{H}-\Delta E)|\Phi_i^a\rangle \qquad (24)
\end{aligned}
$$

Similarly:

$$
\frac{\partial \mathcal{L}_{\mathrm{CC}}}{\partial t_{ij}^{ab}} = \langle\Phi_0|(1+\hat{\Lambda})(\mathcal{H}-\Delta E)|\Phi_{ij}^{ab}\rangle \qquad (25)
$$

These expressions are the same as the Λ equations obtained in previous section.

1.3 HF Condition

Taking the derivative of $\mathcal{L}_{\mathrm{CC}}$ w.r.t the z-vector results in the Brillouin's condition:

$$
\frac{\partial \mathcal{L}_{\mathrm{CC}}}{\partial z_{ai}} = f_{ai} = 0 \qquad (26)
$$

which is equivalent to the HF equation.

1.4 z-vector Equations

Question: (related to frozen-core approximation I suppose) W.r.t what block of $\boldsymbol{\kappa}$ do I need to take derivatives for $\mathcal{L}_{\mathrm{CC}}$? Virtual-inactive block (κ_{bj}) is shown below because this type of orbital rotation is always non-redundant.

$$
\frac{\partial \mathcal{L}_{\mathrm{CC}}}{\partial \kappa_{bj}} = \frac{\partial}{\partial \kappa_{bj}}\left(\langle\Phi_0|(1+\hat{\Lambda})\mathcal{H}|\Phi_0\rangle + \sum_{ai} f_{ai}z_{ai} + \sum_{pq} I_{pq}(\sum_{\mu\nu} C_{\mu p}^* S_{\mu\nu} C_{\nu q} - \delta_{pq})\right)
$$

$$=\frac{\partial}{\partial\kappa_{bj}}\langle\Phi_0|(1+\hat{\Lambda})\mathcal{H}|\Phi_0\rangle+\sum_{ai}\frac{\partial f_{ai}}{\partial\kappa_{bj}}z_{ai}+\sum_{pq}I_{pq}(\sum_{\mu\nu}U^*_{\mu p}\frac{\partial\mathcal{S}_{\mu\nu}}{\partial\kappa_{bj}}U_{\nu q}) \tag{27}$$

in which:

$$\mathbf{U}=e^{-\hat{\kappa}} \tag{28}$$

$$\hat{\kappa}=\sum_{p>q}\kappa_{pq}E^-_{pq} \tag{29}$$

$$\boldsymbol{\mathcal{S}}=\mathbf{C}^\dagger(0)\mathbf{S}\mathbf{C}(0) \tag{30}$$

To evaluate term by term, the CC energy part:

$$\begin{aligned}\frac{\partial}{\partial\kappa_{bj}}\langle\Phi_0(\hat{\kappa})|(1+\hat{\Lambda})\mathcal{H}|\Phi_0(\hat{\kappa})\rangle=&\frac{\partial}{\partial\kappa_{bj}}\langle\Phi_0|e^{\hat{\kappa}}(1+\hat{\Lambda})\mathcal{H}e^{-\hat{\kappa}}|\Phi_0\rangle\\=&\frac{\partial}{\partial\kappa_{bj}}\langle\Phi_0|e^{\hat{\kappa}}\mathcal{H}e^{-\hat{\kappa}}|\Phi_0\rangle+\frac{\partial}{\partial\kappa_{bj}}\langle\Phi_0|e^{\hat{\kappa}}\hat{\Lambda}\mathcal{H}e^{-\hat{\kappa}}|\Phi_0\rangle\end{aligned} \tag{31}$$

The first term (using BCH expansion):

$$\begin{aligned}\frac{\partial}{\partial\kappa_{bj}}\langle\Phi_0(\hat{\kappa})|\mathcal{H}|\Phi_0(\hat{\kappa})\rangle=&\frac{\partial}{\partial\kappa_{bj}}\langle\Phi_0|\mathcal{H}+[\mathcal{H},-\hat{\kappa}]+\frac{1}{2!}[[\mathcal{H},-\hat{\kappa}],-\hat{\kappa}]+\frac{1}{3!}[[[\mathcal{H},-\hat{\kappa}],-\hat{\kappa}],-\hat{\kappa}]+\ldots|\Phi_0\rangle\\=&\langle\Phi_0|\mathcal{H}+[\mathcal{H},-E^-_{bj}]+[[\mathcal{H},-E^-_{bj}],-\hat{\kappa}]+[[\mathcal{H},-\hat{\kappa}],-E^-_{bj}]+\ldots|\Phi_0\rangle\\=&\langle\Phi_0|e^{\hat{\kappa}}[\mathcal{H},E^-_{jb}]e^{-\hat{\kappa}}|\Phi_0\rangle\\=&\langle\Phi_0(\hat{\kappa})|[\mathcal{H},E^-_{jb}]|\Phi_0(\hat{\kappa})\rangle\end{aligned} \tag{32}$$

The second term:
(TODO: show that $\hat{\Lambda}$ and $\hat{\kappa}$ commute.)

1.5 Orthonormality Condition