1 Basic Ansatz

The Hamiltonian

The Hamiltonian in general form:

$$\hat{H} = \sum_{pq} \langle p|\hat{h}|q\rangle \hat{p}^\dagger \hat{q} + \frac{1}{4} \sum_{pqrs} \langle pq||rs\rangle \hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r} \tag{1}$$

Using Wick's theorem:

$$\begin{aligned}\hat{H} =& \sum_{pq} h_{pq} \{\hat{p}^\dagger \hat{q}\} + \sum_i h_{ii} + \frac{1}{4} \sum_{pqrs} \langle pq||rs\rangle \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\} + \frac{1}{2} \sum_{ij} \langle ij||ij\rangle + \sum_{pqi} \langle pi||qi\rangle \{\hat{p}^\dagger \hat{q}\} \\ =& E_{\mathrm{HF}} + \sum_{pq} f_{pq} \{\hat{p}^\dagger \hat{q}\} + \frac{1}{4} \sum_{pqrs} \langle pq||rs\rangle \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\} \end{aligned} \tag{2}$$

and the normal-ordered Hamiltonian:

$$\hat{H}_{\mathrm{N}} = \sum_{pq} f_{pq} \{\hat{p}^\dagger \hat{q}\} + \frac{1}{4} \sum_{pqrs} \langle pq||rs\rangle \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\} \tag{3}$$

Coupled-Cluster Energy

$$\hat{H}|\Psi_{\mathrm{CC}}\rangle = E_{\mathrm{CC}}|\Psi_{\mathrm{CC}}\rangle \tag{4}$$

$$\Leftrightarrow \hat{H}e^{\hat{T}}|\Phi_0\rangle = E_{\mathrm{CC}}e^{\hat{T}}|\Phi_0\rangle$$

$$\Leftrightarrow e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = E_{\mathrm{CC}}|\Phi_0\rangle$$

$$\Leftrightarrow \mathcal{H}|\Phi_0\rangle = E_{\mathrm{CC}}|\Phi_0\rangle \tag{5}$$

Projecting $\langle\Phi_0|$ onto equation 5:

$$\begin{aligned} E_{\mathrm{CC}} =& \langle\Phi_0|\mathcal{H}|\Phi_0\rangle \\ =& \sum_{pq} h_{pq} \langle\Phi_0|e^{-\hat{T}}\hat{p}^\dagger \hat{q} e^{\hat{T}}|\Phi_0\rangle + \frac{1}{4}\sum_{pqrs} \langle pq||rs\rangle \langle\Phi_0|e^{-\hat{T}}\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}e^{\hat{T}}|\Phi_0\rangle \\ =& E_{\mathrm{HF}} + \sum_{pq} f_{pq} \langle\Phi_0|e^{-\hat{T}}\{\hat{p}^\dagger \hat{q}\}e^{\hat{T}}|\Phi_0\rangle + \frac{1}{4}\sum_{pqrs} \langle pq||rs\rangle \langle\Phi_0|e^{-\hat{T}}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}e^{\hat{T}}|\Phi_0\rangle \end{aligned} \tag{6}$$

Also, by intermediate normalisation, projecting $\langle\Phi_0|$ onto equation 4:

$$\begin{aligned} E_{\mathrm{CC}} =& \langle\Phi_0|\hat{H}|\Psi_{\mathrm{CC}}\rangle \\ =& \langle\Phi_0|\hat{H}e^{\hat{T}}|\Phi_0\rangle \\ =& \sum_{pq} h_{pq} \langle\Phi_0|\hat{p}^\dagger \hat{q} e^{\hat{T}}|\Phi_0\rangle + \frac{1}{4}\sum_{pqrs} \langle pq||rs\rangle \langle\Phi_0|\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}e^{T}|\Phi_0\rangle \\ =& E_{\mathrm{HF}} + \sum_{pq} f_{pq} \langle\Phi_0|\{\hat{p}^\dagger \hat{q}\}e^{\hat{T}}|\Phi_0\rangle + \frac{1}{4}\sum_{pqrs} \langle pq||rs\rangle \langle\Phi_0|\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}e^{\hat{T}}|\Phi_0\rangle \end{aligned} \tag{7}$$

Reduced Density Matrices

Consider only CC energy:

$$E_{\mathrm{CC}} = \langle\Phi_0|\mathcal{H}|\Phi_0\rangle$$

$$
\begin{aligned}
&= \sum_{pq} h_{pq} \langle \Phi_0 | e^{-\hat{T}} \hat{p}^\dagger \hat{q} e^{\hat{T}} | \Phi_0 \rangle + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \langle \Phi_0 | e^{-\hat{T}} \hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r} e^{\hat{T}} | \Phi_0 \rangle \\
&= E_{\mathrm{HF}} + \sum_{pq} f_{pq} \langle \Phi_0 | e^{-\hat{T}} \{ \hat{p}^\dagger \hat{q} \} e^{\hat{T}} | \Phi_0 \rangle + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \langle \Phi_0 | e^{-\hat{T}} \{ \hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r} \} e^{\hat{T}} | \Phi_0 \rangle
\end{aligned} \tag{8}
$$

Defining the one-body reduced density matrix:

$$
\gamma_{pq} = \frac{\langle \Psi_{\mathrm{CC}} | \hat{p}^\dagger \hat{q} | \Psi_{\mathrm{CC}} \rangle}{\langle \Psi_{\mathrm{CC}} | \Psi_{\mathrm{CC}} \rangle} = \frac{\langle \Phi_0 | e^{\hat{T}^\dagger} \hat{p}^\dagger \hat{q} e^{\hat{T}} | \Phi_0 \rangle}{\langle \Phi_0 | e^{\hat{T}^\dagger} e^{\hat{T}} | \Phi_0 \rangle} \tag{9}
$$

and two-body reduced density matrix:

$$
\Gamma^{pq}_{rs} = \frac{\langle \Psi_{\mathrm{CC}} | \hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r} | \Psi_{\mathrm{CC}} \rangle}{\langle \Psi_{\mathrm{CC}} | \Psi_{\mathrm{CC}} \rangle} = \frac{\langle \Phi_0 | e^{\hat{T}^\dagger} \hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r} e^{\hat{T}} | \Phi_0 \rangle}{\langle \Phi_0 | e^{\hat{T}^\dagger} e^{\hat{T}} | \Phi_0 \rangle} \tag{10}
$$

Then CC energy could be expressed as:

$$
\begin{aligned}
E_{\mathrm{CC}} &= \sum_{pq} h_{pq} \gamma_{pq} + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \Gamma^{pq}_{rs} \\
&= \frac{\langle \Phi_0 | e^{\hat{T}^\dagger} (\sum_{pq} h_{pq} \hat{p}^\dagger \hat{q}) e^{\hat{T}} | \Phi_0 \rangle}{\langle \Phi_0 | e^{\hat{T}^\dagger} e^{\hat{T}} | \Phi_0 \rangle} + \frac{\langle \Phi_0 | e^{\hat{T}^\dagger} (\frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r}) e^{\hat{T}} | \Phi_0 \rangle}{\langle \Phi_0 | e^{\hat{T}^\dagger} e^{\hat{T}} | \Phi_0 \rangle} \\
&= \frac{\langle \Phi_0 | e^{\hat{T}^\dagger} \hat{H} e^{\hat{T}} | \Phi_0 \rangle}{\langle \Phi_0 | e^{\hat{T}^\dagger} e^{\hat{T}} | \Phi_0 \rangle}
\end{aligned} \tag{11}
$$

inserting the resolution of identity $e^{\hat{T}} (\hat{P} + \hat{Q}) e^{-\hat{T}} = \hat{1}$:

$$
\begin{aligned}
E_{\mathrm{CC}} &= \frac{\langle \Phi_0 | e^{\hat{T}^\dagger} e^{\hat{T}} (\hat{P} + \hat{Q}) e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle}{\langle \Phi_0 | e^{\hat{T}^\dagger} e^{\hat{T}} | \Phi_0 \rangle} \\
&= \frac{\langle \Phi_0 | e^{\hat{T}^\dagger} e^{\hat{T}} | \Phi_0 \rangle}{\langle \Phi_0 | e^{\hat{T}^\dagger} e^{\hat{T}} | \Phi_0 \rangle} \langle \Phi_0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle + 0 \\
&= \langle \Phi_0 | \mathcal{H} | \Phi_0 \rangle
\end{aligned} \tag{12}
$$

as expected. Note that we used that $\hat{Q} \mathcal{H} | \Phi_0 \rangle = 0$ which is the CC amplitude constraint.

Similarly, we could define the normal-ordered one- and two-body reduced density matrices as:

$$
(\gamma_{\mathrm{N}})_{pq} = \frac{\langle \Psi_{\mathrm{CC}} | \{ \hat{p}^\dagger \hat{q} \} | \Psi_{\mathrm{CC}} \rangle}{\langle \Psi_{\mathrm{CC}} | \Psi_{\mathrm{CC}} \rangle} = \frac{\langle \Phi_0 | e^{\hat{T}^\dagger} \{ \hat{p}^\dagger \hat{q} \} e^{\hat{T}} | \Phi_0 \rangle}{\langle \Phi_0 | e^{\hat{T}^\dagger} e^{\hat{T}} | \Phi_0 \rangle} \tag{13}
$$

$$
(\Gamma_{\mathrm{N}})^{pq}_{rs} = \frac{\langle \Psi_{\mathrm{CC}} | \{ \hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r} \} | \Psi_{\mathrm{CC}} \rangle}{\langle \Psi_{\mathrm{CC}} | \Psi_{\mathrm{CC}} \rangle} = \frac{\langle \Phi_0 | e^{\hat{T}^\dagger} \{ \hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r} \} e^{\hat{T}} | \Phi_0 \rangle}{\langle \Phi_0 | e^{\hat{T}^\dagger} e^{\hat{T}} | \Phi_0 \rangle} \tag{14}
$$

Accordingly, the correlation contribution of CC energy could be expressed as:

$$
\begin{aligned}
\Delta E_{\mathrm{CC}} &= E_{\mathrm{CC}} - E_{\mathrm{HF}} \\
&= \sum_{pq} f_{pq} (\gamma_{\mathrm{N}})_{pq} + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle (\Gamma_{\mathrm{N}})^{pq}_{rs}
\end{aligned} \tag{15}
$$

Generally, for one- and two-body operators, the expectation value could be evaluated as:

$$\begin{aligned}\langle\hat{O}\rangle &= \sum_{pq} o_{pq}\gamma_{pq} \qquad (16)\\ \langle\hat{G}\rangle &= \frac{1}{4}\sum_{pqrs}\langle pq|\hat{g}|rs\rangle_{\mathrm{A}}\Gamma^{pq}_{rs} \qquad (17)\end{aligned}$$

Response Density Matrices

Consider the Lagrangian which only includes the CC energy and amplitude constraints:

$$\begin{aligned}\mathcal{L}_{\mathrm{CC}} =& E_{\mathrm{CC}} + \sum_{\mu}\lambda_\mu\langle\Phi_\mu|\mathcal{H}|\Phi_0\rangle\\ =&\langle\Phi_0|\mathcal{H}|\Phi_0\rangle + \langle\Phi_0|\hat{\Lambda}\mathcal{H}|\Phi_0\rangle\\ =&\langle\Phi_0|(1+\hat{\Lambda})\mathcal{H}|\Phi_0\rangle\\ =&\langle\Phi_0|(1+\hat{\Lambda})e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle\\ =&\sum_{pq}h_{pq}\langle\Phi_0|(1+\hat{\Lambda})e^{-\hat{T}}\hat{p}^\dagger\hat{q}e^{\hat{T}}|\Phi_0\rangle + \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\langle\Phi_0|(1+\hat{\Lambda})e^{-\hat{T}}\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}e^{\hat{T}}|\Phi_0\rangle\\ =&E_{\mathrm{HF}} + \sum_{pq}f_{pq}\langle\Phi_0|(1+\hat{\Lambda})e^{-\hat{T}}\{\hat{p}^\dagger\hat{q}\}e^{\hat{T}}|\Phi_0\rangle + \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\langle\Phi_0|(1+\hat{\Lambda})e^{-\hat{T}}\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}e^{\hat{T}}|\Phi_0\rangle\end{aligned} \qquad (18)$$

By defining the response density matrices:

$$\begin{aligned}\gamma_{pq} &= \langle\Phi_0|(1+\hat{\Lambda})e^{-\hat{T}}\hat{p}^\dagger\hat{q}e^{\hat{T}}|\Phi_0\rangle \qquad (19)\\ \Gamma^{pq}_{rs} &= \langle\Phi_0|(1+\hat{\Lambda})e^{-\hat{T}}\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}e^{\hat{T}}|\Phi_0\rangle \qquad (20)\\ (\gamma_{\mathrm{N}})_{pq} &= \langle\Phi_0|(1+\hat{\Lambda})e^{-\hat{T}}\{\hat{p}^\dagger\hat{q}\}e^{\hat{T}}|\Phi_0\rangle \qquad (21)\\ (\Gamma_{\mathrm{N}})^{pq}_{rs} &= \langle\Phi_0|(1+\hat{\Lambda})e^{-\hat{T}}\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}e^{\hat{T}}|\Phi_0\rangle \qquad (22)\end{aligned}$$

the Lagrangian coulde be written as:

$$\mathcal{L}_{\mathrm{CC}} = E_{\mathrm{HF}} + \sum_{pq}f_{pq}(\gamma_{\mathrm{N}})_{pq} + \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle(\Gamma_{\mathrm{N}})^{pq}_{rs} \qquad (23)$$

2 CC Lagrangian

To construct the complete Lagrangian for CC ansatz, the constraints of Brillouin condition and orthonomality should also be included. From now on, denote $\mathcal{H} = e^{-\hat{T}}\hat{H}_{\mathrm{N}}e^{\hat{T}}$:

$$\begin{aligned}\mathcal{L}^{\mathrm{N}}_{\mathrm{CC}} =&\langle\Phi_0|(1+\hat{\Lambda})e^{-\hat{T}}\hat{H}_{\mathrm{N}}e^{\hat{T}}|\Phi_0\rangle + \sum_{ai}z_{ai}f_{ai}\\ =&\langle\Phi_0|(1+\hat{\Lambda})\mathcal{H}|\Phi_0\rangle + \sum_{ai}z_{ai}f_{ai}\end{aligned} \qquad (24)$$

3 Stationary Lagrangian

The CC Lagrangian is given as:

$$\mathcal{L}_{\mathrm{CC}} = \langle\Phi_0|(1+\hat{\Lambda})\mathcal{H}|\Phi_0\rangle + \sum_{ai} f_{ai} z_{ai} + \sum_{pq} I_{pq}(\sum_{\mu\nu} C^*_{\mu p} S_{\mu\nu} C_{\nu q} - \delta_{pq}) \tag{25}$$

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

$$\hat{\Lambda} = \hat{\Lambda}_1 + \hat{\Lambda}_2 + \cdots = \sum_{ia} \lambda_a^i \{\hat{i}^\dagger \hat{a}\} + \frac{1}{4}\sum_{ijab} \lambda_{ab}^{ij} \{\hat{i}^\dagger \hat{j}^\dagger \hat{b}\hat{a}\} + \dots \tag{26}$$

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

$$\begin{aligned}\langle\Phi_0|(1+\Lambda)\mathcal{H}|\Phi_0\rangle =& \langle\Phi_0|\mathcal{H}|\Phi_0\rangle + \langle\Phi_0|\hat{\Lambda}\mathcal{H}|\Phi_0\rangle \\ =& \Delta E + \sum_{\mu} \lambda_\mu \langle\Phi_\mu|\mathcal{H}|\Phi_0\rangle\end{aligned} \tag{27}$$

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

3.1 CC Amplitude Equations

$$\begin{aligned}\frac{\partial\mathcal{L}_{\mathrm{CC}}}{\partial\lambda_\mu} &= \frac{\partial}{\partial\lambda_\mu}\left(\langle\Phi_0|\mathcal{H}|\Phi_0\rangle + \langle\Phi_0|\hat{\Lambda}\mathcal{H}|\Phi_0\rangle + \sum_{ia} f_{ia} z_{ia} + \sum_{pq} I_{pq}(\sum_{\mu\nu} C^*_{\mu p} S_{\mu\nu} C_{\nu q} - \delta_{pq})\right) \\ &= \langle\Phi_\mu|\mathcal{H}|\Phi_0\rangle\end{aligned} \tag{28}$$

Hence imposing the stationary condition:

$$\frac{\partial\mathcal{L}_{\mathrm{CC}}}{\partial\lambda_\mu} = 0 \tag{29}$$

we get:

$$\langle\Phi_\mu|\mathcal{H}|\Phi_0\rangle = 0 \tag{30}$$

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

$$\hat{Q}\mathcal{H}\hat{P} = 0 \tag{31}$$

3.2 CC Lambda Equations

By:

$$\begin{aligned}\mathcal{H} &= (\hat{H}_{\mathrm{N}} e^{\hat{T}})_{\mathrm{C}} \\ &= (\hat{H}_{\mathrm{N}} + \hat{H}_{\mathrm{N}}\hat{T} + \frac{1}{2}\hat{H}_{\mathrm{N}}\hat{T}^2 + \frac{1}{6}\hat{H}_{\mathrm{N}}\hat{T}^3 + \frac{1}{24}\hat{H}_{\mathrm{N}}\hat{T}^4)_{\mathrm{C}}\end{aligned} \tag{32}$$

and:

$$\mathcal{L}_{\mathrm{CC}} = \langle \Phi_0 | (1+\hat{\Lambda}) \mathcal{H} | \Phi_0 \rangle + \sum_{p>q} f_{pq} z_{pq} \tag{33}$$

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?)

$$\frac{\partial \mathcal{H}}{\partial t_i^a} = \frac{\partial}{\partial t_i^a} \left(\hat{H}_{\mathrm{N}} (1 + \hat{T} + \frac{1}{2}\hat{T}^2 + \frac{1}{6}\hat{T}^3 + \frac{1}{24}\hat{T}^4 + \dots) \right)_{\mathrm{C}} \tag{34}$$

$$\frac{\partial \hat{H}_{\mathrm{N}}}{\partial t_i^a} = 0 \tag{35}$$

$$\frac{\partial}{\partial t_i^a}\left(\hat{H}_{\mathrm{N}}\hat{T}\right) = \frac{\partial}{\partial t_i^a}\left(\hat{H}_{\mathrm{N}}(\hat{T}_1 + \hat{T}_2)\right) = \hat{H}_{\mathrm{N}}\{\hat{a}^\dagger \hat{i}\} \tag{36}$$

$$\begin{aligned}
\frac{\partial}{\partial t_i^a}\left(\frac{1}{2}\hat{H}_{\mathrm{N}}\hat{T}^2\right) &= \frac{1}{2}\hat{H}_{\mathrm{N}}\frac{\partial}{\partial t_i^a}\left(\hat{T}_1^2 + 2\hat{T}_1\hat{T}_2 + \hat{T}_2^2\right) \\
&= \frac{1}{2}\hat{H}_{\mathrm{N}}(2\hat{T}_1 + 2\hat{T}_2)\{\hat{a}^\dagger \hat{i}\} \\
&= \hat{H}_{\mathrm{N}}\hat{T}\{\hat{a}^\dagger \hat{i}\}
\end{aligned} \tag{37}$$

$$\begin{aligned}
\frac{\partial}{\partial t_i^a}\left(\frac{1}{6}\hat{H}_{\mathrm{N}}\hat{T}^3\right) &= \frac{1}{6}\hat{H}_{\mathrm{N}}\frac{\partial}{\partial t_i^a}\left(\hat{T}_1^3 + 3\hat{T}_1^2\hat{T}_2 + 3\hat{T}_1\hat{T}_2^2 + \hat{T}_2^3\right) \\
&= \frac{1}{6}\hat{H}_{\mathrm{N}}(3\hat{T}_1^2 + 6\hat{T}_1\hat{T} + 3\hat{T}_2^2)\{\hat{a}^\dagger \hat{i}\} \\
&= \frac{1}{2}\hat{H}_{\mathrm{N}}\hat{T}^2\{\hat{a}^\dagger \hat{i}\}
\end{aligned} \tag{38}$$

$$\begin{aligned}
\frac{\partial}{\partial t_i^a}\left(\frac{1}{24}\hat{H}_{\mathrm{N}}\hat{T}^4\right) &= \frac{1}{24}\hat{H}_{\mathrm{N}}\frac{\partial}{\partial t_i^a}\left(\hat{T}_1^4 + 4\hat{T}_1^3\hat{T}_2 + 6\hat{T}_1^2\hat{T}_2^2 + 4\hat{T}_1\hat{T}_2^3 + \hat{T}_2^4\right) \\
&= \frac{1}{24}\hat{H}_{\mathrm{N}}(4\hat{T}_1^3 + 12\hat{T}_1\hat{2}\hat{T}_2 + 12\hat{T}_1\hat{T}_2^2 + 4\hat{T}_2^3)\{\hat{a}^\dagger \hat{i}\} \\
&= \frac{1}{6}\hat{H}_{\mathrm{N}}\hat{T}^3\{\hat{a}^\dagger \hat{i}\} \\
&\dots
\end{aligned} \tag{39}$$

Therefore:

$$\begin{aligned}
\frac{\partial \mathcal{H}}{\partial t_i^a} &= (\hat{H}_{\mathrm{N}}(1 + \hat{T} + \frac{1}{2}\hat{T}^2 + \frac{1}{6}\hat{T}^3 + \dots))_{\mathrm{C}}\{\hat{a}^\dagger \hat{i}\} \\
&= (\hat{H}_{\mathrm{N}} e^{\hat{T}})_{\mathrm{C}}\{\hat{a}^\dagger \hat{i}\} \\
&= \mathcal{H}\{\hat{a}^\dagger \hat{i}\}
\end{aligned} \tag{40}$$

Compare results with commutators?
By BCH:

$$\begin{aligned}
\mathcal{H} =& \hat{H}_{\mathrm{N}} + [\hat{H}_{\mathrm{N}}, \hat{T}] + \frac{1}{2!}[[\hat{H}_{\mathrm{N}}, \hat{T}], \hat{T}] + \frac{1}{3!}[[[\hat{H}_{\mathrm{N}}, \hat{T}], \hat{T}], \hat{T}] \\
&+ \frac{1}{4!}[[[[\hat{H}_{\mathrm{N}}, \hat{T}], \hat{T}], \hat{T}], \hat{T}] + \dots
\end{aligned} \tag{41}$$

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

$$\frac{\partial \mathcal{H}}{\partial t_i^a} = \frac{\partial \hat{H}_{\mathrm{N}}}{\partial t_i^a} + \frac{\partial}{\partial t_i^a}[\hat{H}_{\mathrm{N}}, \hat{T}] + \dots \tag{42}$$

$$\frac{\partial \hat{H}_\mathrm{N}}{\partial t_i^a} = 0 \tag{43}$$

$$\frac{\partial}{\partial t_i^a}[\hat{H}_\mathrm{N}, \hat{T}] = \frac{\partial}{\partial t_i^a}[\hat{H}_\mathrm{N}, \hat{T}_1] + 0 = [\hat{H}_\mathrm{N}, \{\hat{a}^\dagger \hat{i}\}] \tag{44}$$

$$\begin{aligned}
\frac{\partial}{\partial t_i^a}[[\hat{H}_\mathrm{N}, \hat{T}], \hat{T}] =& \frac{\partial}{\partial t_i^a}\Big([[\hat{H}_\mathrm{N}, \hat{T}_1], \hat{T}_1] + [[\hat{H}_\mathrm{N}, \hat{T}_1], \hat{T}_2] + [[\hat{H}_\mathrm{N}, \hat{T}_2], \hat{T}_1] + [[\hat{H}_\mathrm{N}, \hat{T}_2], \hat{T}_2]\Big) \\
=& [[\hat{H}_\mathrm{N}, \frac{\partial \hat{T}_1}{\partial t_i^a}], \hat{T}_1] + [[\hat{H}_\mathrm{N}, \hat{T}_1], \frac{\partial \hat{T}_1}{\partial t_i^a}] + [[\hat{H}_\mathrm{N}, \frac{\partial \hat{T}_1}{\partial t_i^a}], \hat{T}_2] + [[\hat{H}_\mathrm{N}, \hat{T}_2], \frac{\partial \hat{T}_1}{\partial t_i^a}] \\
=& [[\hat{H}_\mathrm{N}, \{\hat{a}^\dagger \hat{i}\}], \hat{T}_1] + [[\hat{H}_\mathrm{N}, \hat{T}_1], \{\hat{a}^\dagger \hat{i}\}] + [[\hat{H}_\mathrm{N}, \{\hat{a}^\dagger \hat{i}\}], \hat{T}_2] + [[\hat{H}_\mathrm{N}, \hat{T}_2], \{\hat{a}^\dagger \hat{i}\}] \\
=& [[\hat{H}_\mathrm{N}, \{\hat{a}^\dagger \hat{i}\}], \hat{T}] + [[\hat{H}_\mathrm{N}, \hat{T}], \{\hat{a}^\dagger \hat{i}\}]
\end{aligned} \tag{45}$$

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

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

$$\frac{\partial \mathcal{H}}{\partial t_i^a} = [\mathcal{H}, \{\hat{a}^\dagger \hat{i}\}] \tag{46}$$

$$\frac{\partial \mathcal{H}}{\partial t_{ij}^{ab}} = [\mathcal{H}, \frac{1}{4}\{\hat{a}^\dagger \hat{b}^\dagger \hat{j} \hat{i}\}] \tag{47}$$

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

$$\begin{aligned}
\frac{\partial \mathcal{L}_\mathrm{CC}}{\partial t_i^a} =& \langle \Phi_0 | (1+\hat{\Lambda}) [\mathcal{H}, \{\hat{a}^\dagger \hat{i}\}] | \Phi_0 \rangle \\
=& \langle \Phi_0 | (1+\hat{\Lambda}) \mathcal{H} \{\hat{a}^\dagger \hat{i}\} | \Phi_0 \rangle - \langle \Phi_0 | (1+\hat{\Lambda}) \{\hat{a}^\dagger \hat{i}\} \mathcal{H} | \Phi_0 \rangle \\
=& \langle \Phi_0 | (1+\hat{\Lambda}) \mathcal{H} | \Phi_i^a \rangle - \langle \Phi_0 | (1+\hat{\Lambda}) \Delta E | \Phi_i^a \rangle \\
=& \langle \Phi_0 | (1+\hat{\Lambda}) (\mathcal{H} - \Delta E) | \Phi_i^a \rangle
\end{aligned} \tag{48}$$

Similarly:

$$\frac{\partial \mathcal{L}_\mathrm{CC}}{\partial t_{ij}^{ab}} = \langle \Phi_0 | (1+\hat{\Lambda}) (\mathcal{H} - \Delta E) | \Phi_{ij}^{ab} \rangle \tag{49}$$

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

3.3 HF Condition

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

$$\frac{\partial \mathcal{L}_\mathrm{CC}}{\partial z_{ai}} = f_{ai} = 0 \tag{50}$$

which is equivalent to the HF equation.

3.4 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.

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

$$=\frac{\partial}{\partial\kappa_{bj}}\langle\Phi_0|(1+\hat{\Lambda})\mathcal{H}|\Phi_0\rangle+\sum_{ai}\frac{\partial f_{ai}}{\partial\kappa_{bj}}z_{ai}+\sum_{pq}I_{pq}(\sum_{\mu\nu}U^*_{\mu p}\frac{\partial\mathcal{S}_{\mu\nu}}{\partial\kappa_{bj}}U_{\nu q}) \tag{51}$$

in which:

$$\mathbf{U}=e^{-\hat{\kappa}} \tag{52}$$

$$\hat{\kappa}=\sum_{p>q}\kappa_{pq}E^-_{pq} \tag{53}$$

$$\boldsymbol{\mathcal{S}}=\mathbf{C}^\dagger(0)\mathbf{S}\mathbf{C}(0) \tag{54}$$

To evaluate term by term, the CC energy part:

$$\begin{aligned}\frac{\partial}{\partial\kappa_{bj}}\langle\Phi_0(\hat{\kappa})|(1+\hat{\Lambda})\mathcal{H}|\Phi_0(\hat{\kappa})\rangle=&\frac{\partial}{\partial\kappa_{bj}}\langle\Phi_0|e^{\hat{\kappa}}(1+\hat{\Lambda})\mathcal{H}e^{-\hat{\kappa}}|\Phi_0\rangle\\=&\frac{\partial}{\partial\kappa_{bj}}\langle\Phi_0|e^{\hat{\kappa}}\mathcal{H}e^{-\hat{\kappa}}|\Phi_0\rangle+\frac{\partial}{\partial\kappa_{bj}}\langle\Phi_0|e^{\hat{\kappa}}\hat{\Lambda}\mathcal{H}e^{-\hat{\kappa}}|\Phi_0\rangle\end{aligned} \tag{55}$$

The first term (using BCH expansion):

$$\begin{aligned}\frac{\partial}{\partial\kappa_{bj}}\langle\Phi_0(\hat{\kappa})|\mathcal{H}|\Phi_0(\hat{\kappa})\rangle=&\frac{\partial}{\partial\kappa_{bj}}\langle\Phi_0|\mathcal{H}+[\mathcal{H},-\hat{\kappa}]+\frac{1}{2!}[[\mathcal{H},-\hat{\kappa}],-\hat{\kappa}]+\frac{1}{3!}[[[\mathcal{H},-\hat{\kappa}],-\hat{\kappa}],-\hat{\kappa}]+\ldots|\Phi_0\rangle\\=&\langle\Phi_0|\mathcal{H}+[\mathcal{H},-E^-_{bj}]+[[\mathcal{H},-E^-_{bj}],-\hat{\kappa}]+[[\mathcal{H},-\hat{\kappa}],-E^-_{bj}]+\ldots|\Phi_0\rangle\\=&\langle\Phi_0|e^{\hat{\kappa}}[\mathcal{H},E^-_{jb}]e^{-\hat{\kappa}}|\Phi_0\rangle\\=&\langle\Phi_0(\hat{\kappa})|[\mathcal{H},E^-_{jb}]|\Phi_0(\hat{\kappa})\rangle\end{aligned} \tag{56}$$

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

3.5 Orthonormality Condition