1 Λ Equations

1.1 Derivation of Λ Equations

This is a summary of the article Salter et al., J. Chem. Phys. 90, 1752 (1989).

For a perturbation χ, we define the following notations here:

$$T = T(\chi)\Big|_{\chi=0} \qquad T^{\chi} = \frac{\partial T(\chi)}{\partial \chi}\Big|_{\chi=0}$$
$$\Delta E = \Delta E(\chi)\Big|_{\chi=0} \qquad \Delta E^{\chi} = \frac{\partial \Delta E(\chi)}{\partial \chi}\Big|_{\chi=0}$$
$$H_{\mathrm{N}} = f_{\mathrm{N}} + W_{\mathrm{N}} = (f_{\mathrm{N}}(\chi) + W_{\mathrm{N}}(\chi))\Big|_{\chi=0}$$
$$H_{\mathrm{N}}^{\chi} = f_{\mathrm{N}}^{\chi} + W_{\mathrm{N}}^{\chi} = \Big(\frac{\partial f_{\mathrm{N}}(\chi)}{\partial \chi} + \frac{\partial W_{\mathrm{N}}(\chi)}{\partial \chi}\Big)\Big|_{\chi=0}$$

We also define the orthonormal determinant space as $|P\rangle$, in which $T(\chi)$ and $\Delta E(\chi)$ are determined:

$$|P\rangle = |0\rangle + |\Phi\rangle \tag{1}$$

where $|0\rangle$ is the ground-state determinant and $|\Phi\rangle$ represent the excited determinant space. We know that:

$$|P\rangle\langle P| = |0\rangle\langle 0| + |\Phi\rangle\langle\Phi| = \hat{1} \tag{2}$$

We have the CC equations as:

$$\langle 0|\mathcal{H}|0\rangle = \langle 0|(H_{\mathrm{N}}e^{T})_{\mathrm{C}}|0\rangle = \Delta E \tag{3}$$
$$\langle \Phi|\mathcal{H}|0\rangle = \langle \Phi|(H_{\mathrm{N}}e^{T})_{\mathrm{C}}|0\rangle = 0 \tag{4}$$

By taking derivatives w.r.t. χ on both sides of the eigenvalue equation $\mathcal{H}|0\rangle = \Delta E|0\rangle$, we have:

$$\begin{aligned}\Delta E^{\chi}|0\rangle &= (-T^{\chi}e^{-T}H_{\mathrm{N}}e^{T} + e^{-T}H_{\mathrm{N}}^{\chi}e^{T} + e^{-T}H_{\mathrm{N}}e^{T}T^{\chi})|0\rangle \\ &= \{[\mathcal{H}, T^{\chi}] + (H_{\mathrm{N}}e^{T})_{\mathrm{C}}\}|0\rangle \\ &= \{[(H_{\mathrm{N}}e^{T})_{\mathrm{C}}T^{\chi}]_{\mathrm{C}} + (H_{\mathrm{N}}e^{T})_{\mathrm{C}}\}|0\rangle\end{aligned} \tag{5}$$

Project $|P\rangle$ on both sides of the equation we obtain the equations for energy derivative and amplitude derivatives:

$$\langle 0|[(H_{\mathrm{N}}e^{T})_{\mathrm{C}}T^{\chi}]_{\mathrm{C}} + (H_{\mathrm{N}}^{\chi}e^{T})_{\mathrm{C}}|0\rangle = \Delta E^{\chi} \tag{6}$$
$$\langle \Phi|[(H_{\mathrm{N}}e^{T})_{\mathrm{C}}T^{\chi}]_{\mathrm{C}} + (H_{\mathrm{N}}^{\chi}e^{T})_{\mathrm{C}}|0\rangle = 0 \tag{7}$$

We could solve the amplitude derivative equation for T^{χ} and use that to obtain ΔE^{χ}. However, this is difficult as well as unnecessary. Instead, we can manipulate the equations in the following manner to get rid of the T^{χ} dependence in the energy derivative equation.

First, we have the derivative eigenvalue equation as:

$$\begin{aligned}\Delta E^{\chi}|0\rangle &= \{[(H_{\mathrm{N}}e^{T})_{\mathrm{C}}, T^{\chi}] + (H_{\mathrm{N}}e^{T})_{\mathrm{C}}\}|0\rangle \\ &= \{(H_{\mathrm{N}}e^{T})_{\mathrm{C}}T^{\chi} - T^{\chi}(H_{\mathrm{N}}e^{T})_{\mathrm{C}} + (H_{\mathrm{N}}^{\chi}e^{T})_{\mathrm{C}}\}|0\rangle\end{aligned} \tag{8}$$

Insert, on the RHS, that $\hat{1} = |P\rangle\langle P|$

$$\Delta E^{\chi}|0\rangle = (H_{\mathrm{N}}e^{T})_{\mathrm{C}}|P\rangle\langle P|T^{\chi}|0\rangle - T^{\chi}|P\rangle\langle P|(H_{\mathrm{N}}e^{T})_{\mathrm{C}}|0\rangle + (H_{\mathrm{N}}^{\chi}e^{T})_{\mathrm{C}}|0\rangle \tag{9}$$

Projecting onto $\langle 0|$ we get:

$$
\begin{aligned}
\Delta E^{\chi} =& \langle 0|(H_{\mathrm{N}}e^{T})_{\mathrm{C}}|P\rangle\langle P|T^{\chi}|0\rangle - \langle 0|T^{\chi}|P\rangle\langle P|(H_{\mathrm{N}}e^{T})_{\mathrm{C}}|0\rangle + \langle 0|(H_{\mathrm{N}}^{\chi}e^{T})_{\mathrm{C}}|0\rangle \\
=& \langle 0|(H_{\mathrm{N}}e^{T})_{\mathrm{C}}|0\rangle\langle 0|T^{\chi}|0\rangle - \langle 0|T^{\chi}|0\rangle\langle 0|(H_{\mathrm{N}}e^{T})_{\mathrm{C}}|0\rangle + \langle 0|(H_{\mathrm{N}}^{\chi}e^{T})_{\mathrm{C}}|0\rangle \\
&+ \langle 0|(H_{\mathrm{N}}e^{T})_{\mathrm{C}}|\Phi\rangle\langle\Phi|T^{\chi}|0\rangle - \langle 0|T^{\chi}|\Phi\rangle\langle\Phi|(H_{\mathrm{N}}e^{T})_{\mathrm{C}}|0\rangle\rangle \\
=& \Delta E \times 0 - 0 \times \Delta E + \langle 0|(H_{\mathrm{N}}^{\chi}e^{T})_{\mathrm{C}}|0\rangle + \langle 0|(H_{\mathrm{N}}e^{T})_{\mathrm{C}}|\Phi\rangle\langle\Phi|T^{\chi}|0\rangle - 0 \times 0 \\
=& \langle 0|(H_{\mathrm{N}}^{\chi}e^{T})_{\mathrm{C}}|0\rangle + \langle 0|(H_{\mathrm{N}}e^{T})_{\mathrm{C}}|\Phi\rangle\langle\Phi|T^{\chi}|0\rangle
\end{aligned} \tag{10}
$$

where we used the fact that $\langle 0|T^{\chi}|0\rangle = \langle 0|T^{\chi}|\Phi\rangle = 0$ since T^{χ} is an excitation operator. Similarly, projecting onto $\langle\Phi|$ gives:

$$
\begin{aligned}
0 =& \langle\Phi|(H_{\mathrm{N}}e^{T})_{\mathrm{C}}|P\rangle\langle P|T^{\chi}|0\rangle - \langle\Phi|T^{\chi}|P\rangle\langle P|(H_{\mathrm{N}}e^{T})_{\mathrm{C}}|0\rangle + \langle\Phi|(H_{\mathrm{N}}^{\chi}e^{T})_{\mathrm{C}}|0\rangle \\
=& \langle\Phi|(H_{\mathrm{N}}e^{T})_{\mathrm{C}}|0\rangle\langle 0|T^{\chi}|0\rangle - \langle\Phi|T^{\chi}|0\rangle\langle 0|(H_{\mathrm{N}}e^{T})_{\mathrm{C}}|0\rangle + \langle\Phi|(H_{\mathrm{N}}^{\chi}e^{T})_{\mathrm{C}}|0\rangle \\
&+ \langle\Phi|(H_{\mathrm{N}}e^{T})_{\mathrm{C}}|\Phi\rangle\langle\Phi|T^{\chi}|0\rangle - \langle\Phi|T^{\chi}|\Phi\rangle\langle\Phi|(H_{\mathrm{N}}e^{T})_{\mathrm{C}}|0\rangle\rangle \\
=& 0 \times 0 - \langle\Phi|T^{\chi}|0\rangle\Delta E + \langle\Phi|(H_{\mathrm{N}}^{\chi}e^{T})_{\mathrm{C}}|0\rangle + \langle\Phi|(H_{\mathrm{N}}e^{T})_{\mathrm{C}}|\Phi\rangle\langle\Phi|T^{\chi}|0\rangle - \langle\Phi|T^{\chi}|\Phi\rangle \times 0 \\
=& \langle\Phi|(H_{\mathrm{N}}^{\chi}e^{T})_{\mathrm{C}}|0\rangle + \langle\Phi|(H_{\mathrm{N}}e^{T})_{\mathrm{C}}|\Phi\rangle\langle\Phi|T^{\chi}|0\rangle - \langle\Phi|T^{\chi}|0\rangle\Delta E
\end{aligned} \tag{11}
$$

From this we can get the expression for the integral containing T^{χ}:

$$
\begin{aligned}
\langle\Phi|T^{\chi}|0\rangle\Big(\langle\Phi|(H_{\mathrm{N}}e^{T})_{\mathrm{C}}|\Phi\rangle - \Delta E\Big) =& - \langle\Phi|(H_{\mathrm{N}}^{\chi}e^{T})_{\mathrm{C}}|0\rangle \\
\langle\Phi|T^{\chi}|0\rangle =& \frac{\langle\Phi|(H_{\mathrm{N}}^{\chi}e^{T})_{\mathrm{C}}|0\rangle}{\Delta E - \langle\Phi|(H_{\mathrm{N}}e^{T})_{\mathrm{C}}|\Phi\rangle}
\end{aligned} \tag{12}
$$

Sub this back into the expression for ΔE^{χ}:

$$
\Delta E^{\chi} = \frac{\langle 0|(H_{\mathrm{N}}e^{T})_{\mathrm{C}}|\Phi\rangle\langle\Phi|(H_{\mathrm{N}}^{\chi}e^{T})_{\mathrm{C}}|0\rangle}{\Delta E - \langle\Phi|(H_{\mathrm{N}}e^{T})_{\mathrm{C}}|\Phi\rangle} + \langle 0|(H_{\mathrm{N}}^{\chi}e^{T})_{\mathrm{C}}|0\rangle \tag{13}
$$

Here we define a new operator such that:

$$
\langle 0|\Lambda|\Phi\rangle = \frac{\langle 0|(H_{\mathrm{N}}e^{T})_{\mathrm{C}}|\Phi\rangle}{\Delta E - \langle\Phi|(H_{\mathrm{N}}e^{T})_{\mathrm{C}}|\Phi\rangle} \tag{14}
$$

Λ is a de-excitation operator:

$$
\Lambda = \sum_{\mu} \Lambda_{\mu} \tag{15}
$$

$$
\Lambda_{\mu} = \sum_{\substack{a,b,\ldots \\ i,j,\ldots}} \frac{1}{(m!)^2}\{\hat{i}^{\dagger}\hat{a}\hat{j}^{\dagger}\hat{b}\ldots\} \tag{16}
$$

With this definition (and the fact that, as a de-excitation operator, $\langle 0|\Lambda|0\rangle = 0$), we can re-write the ΔE^{χ} equation as:

$$
\begin{aligned}
\Delta E^{\chi} =& \langle 0|(H_{\mathrm{N}}^{\chi}e^{T})_{\mathrm{C}}|0\rangle + \langle 0|\Lambda|\Phi\rangle\langle\Phi|(H_{\mathrm{N}}^{\chi}e^{T})_{\mathrm{C}}|0\rangle \\
=& \langle 0|(H_{\mathrm{N}}^{\chi}e^{T})_{\mathrm{C}}|0\rangle + \langle 0|\Lambda|\Phi\rangle\langle\Phi|(H_{\mathrm{N}}^{\chi}e^{T})_{\mathrm{C}}|0\rangle + \langle 0|\Lambda|0\rangle\langle 0|(H_{\mathrm{N}}^{\chi}e^{T})_{\mathrm{C}}|0\rangle \\
=& \langle 0|(H_{\mathrm{N}}^{\chi}e^{T})_{\mathrm{C}}|0\rangle + \langle 0|\Lambda\Big(|0\rangle\langle 0| + |\Phi\rangle\langle\Phi|\Big)(H_{\mathrm{N}}^{\chi}e^{T})_{\mathrm{C}}|0\rangle \\
=& \langle 0|(H_{\mathrm{N}}^{\chi}e^{T})_{\mathrm{C}}|0\rangle + \langle 0|\Lambda(H_{\mathrm{N}}^{\chi}e^{T})_{\mathrm{C}}|0\rangle
\end{aligned} \tag{17}
$$

We also have the Λ equation as:

$$
\frac{\langle 0|(H_{\mathrm{N}}e^{T})_{\mathrm{C}}|\Phi\rangle}{\Delta E - \langle\Phi|(H_{\mathrm{N}}e^{T})_{\mathrm{C}}|\Phi\rangle} = \langle 0|\Lambda|\Phi\rangle \Leftrightarrow
$$

$$\begin{aligned}\langle 0|\Lambda|\Phi\rangle\langle\Phi|(H_\mathrm{N}e^T)_\mathrm{C} - \Delta E|\Phi\rangle + \langle 0|(H_\mathrm{N}e^T)_\mathrm{C}|\Phi\rangle =& 0 \Leftrightarrow \\ \langle 0|\Lambda\Big(|\Phi\rangle\langle\Phi| + |0\rangle\langle 0|\Big)\Big((H_\mathrm{N}e^T)_\mathrm{C} - \Delta E\Big)|\Phi\rangle + \langle 0|(H_\mathrm{N}e^T)_\mathrm{C}|\Phi\rangle =& 0 \Leftrightarrow \\ \langle 0|\Lambda(H_\mathrm{N}e^T)_\mathrm{C}|\Phi\rangle - \Delta E\langle 0|\Lambda|\Phi\rangle + \langle 0|(H_\mathrm{N}e^T)_\mathrm{C}|\Phi\rangle =& 0 \end{aligned} \tag{18}$$

By considering $\langle 0|(H_\mathrm{N}e^T)_\mathrm{C}\Lambda|\Phi\rangle$:

$$\begin{aligned}\langle 0|(H_\mathrm{N}e^T)_\mathrm{C}\Lambda|\Phi\rangle =& \langle 0|(H_\mathrm{N}e^T)_\mathrm{C}\Big(|0\rangle\langle 0| + |\Phi\rangle\langle\Phi|\Big)\Lambda|\Phi\rangle \\ =& \langle 0|(H_\mathrm{N}e^T)_\mathrm{C}|0\rangle\langle 0|\Lambda|\Phi\rangle + \langle 0|(H_\mathrm{N}e^T)_\mathrm{C}|\Phi\rangle\langle\Phi|\Lambda|\Phi\rangle \\ =& \Delta E\langle 0|\Lambda|\Phi\rangle + \langle 0|(H_\mathrm{N}e^T)_\mathrm{C}|\Phi\rangle\langle\Phi|\Lambda|\Phi\rangle \end{aligned} \tag{19}$$

We can obtain the Λ equation as:

$$\begin{aligned}\langle 0|\Lambda(H_\mathrm{N}e^T)_\mathrm{C}|\Phi\rangle - \langle 0|(H_\mathrm{N}e^T)_\mathrm{C}\Lambda|\Phi\rangle + \langle 0|(H_\mathrm{N}e^T)_\mathrm{C}|\Phi\rangle\langle\Phi|\Lambda|\Phi\rangle + \langle 0|(H_\mathrm{N}e^T)_\mathrm{C}|\Phi\rangle =& 0 \Leftrightarrow \\ \langle 0|[\Lambda, (H_\mathrm{N}e^T)_\mathrm{C}]|\Phi\rangle + \langle 0|(H_\mathrm{N}e^T)_\mathrm{C}|\Phi\rangle\langle\Phi|\Lambda|\Phi\rangle + \langle 0|(H_\mathrm{N}e^T)_\mathrm{C}|\Phi\rangle =& 0 \end{aligned} \tag{20}$$

This together with the ΔE^χ equation, are the CC energy derivative equations:

$$\Delta E^\chi = \langle 0|(H_\mathrm{N}^\chi e^T)_\mathrm{C}|0\rangle + \langle 0|\Lambda(H_\mathrm{N}^\chi e^T)_\mathrm{C}|0\rangle \tag{21}$$

$$0 = \langle 0|[\Lambda, (H_\mathrm{N}e^T)_\mathrm{C}]|\Phi\rangle + \langle 0|(H_\mathrm{N}e^T)_\mathrm{C}|\Phi\rangle\langle\Phi|\Lambda|\Phi\rangle + \langle 0|(H_\mathrm{N}e^T)_\mathrm{C}|\Phi\rangle \tag{22}$$

Alternatively, the Λ equation could be written in a more compact form:

$$\begin{aligned}\langle 0|[\Lambda, (H_\mathrm{N}e^T)_\mathrm{C}]|\Phi\rangle + \langle 0|(H_\mathrm{N}e^T)_\mathrm{C}|\Phi\rangle\langle\Phi|\Lambda|\Phi\rangle + \langle 0|(H_\mathrm{N}e^T)_\mathrm{C}|\Phi\rangle =& 0 \Leftrightarrow \\ \langle 0|\Lambda(H_\mathrm{N}e^T)_\mathrm{C}|\Phi\rangle - \langle 0|(H_\mathrm{N}e^T)_\mathrm{C}\Lambda|\Phi\rangle + \langle 0|(H_\mathrm{N}e^T)_\mathrm{C}|\Phi\rangle\langle\Phi|\Lambda|\Phi\rangle + \langle 0|(H_\mathrm{N}e^T)_\mathrm{C}|\Phi\rangle =& 0 \Leftrightarrow \\ \langle 0|\Lambda(H_\mathrm{N}e^T)_\mathrm{C}|\Phi\rangle - \langle 0|(H_\mathrm{N}e^T)_\mathrm{C}|0\rangle\langle 0|\Lambda|\Phi\rangle + \langle 0|(H_\mathrm{N}e^T)_\mathrm{C}|\Phi\rangle =& 0 \Leftrightarrow \\ \langle 0|\Lambda(H_\mathrm{N}e^T)_\mathrm{C} - \Lambda\Delta E + (H_\mathrm{N}e^T)_\mathrm{C}|\Phi\rangle =& 0 \\ & \Updownarrow \\ \langle 0|(1+\Lambda)((\mathcal{H} - \Delta E)|\Phi\rangle =& 0 \end{aligned} \tag{23}$$