1 Expected Value of Operators

For a general operator $\hat{O}$, the expectation value is:

$$\bar{O} = \langle \hat{O} \rangle = \frac{\langle \Psi | \hat{O} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \tag{1}$$

It could be written in the normal product form:

$$\begin{aligned} \hat{O} &= \sum_{pq} \langle p | \hat{o} | q \rangle \hat{p}^\dagger \hat{q} \\ &= \sum_{pq} o_{pq} (\{\hat{p}^\dagger \hat{q}\} + \{\overbrace{\hat{p}^\dagger \hat{q}}\}) \\ &= \sum_{pq} o_{pq} \{\hat{p}^\dagger \hat{q}\} + \sum_{i} o_{ii} \end{aligned} \tag{2}$$

since

$$\{\overbrace{\hat{p}^\dagger \hat{q}}\} = \delta pq \delta_{p \in \mathrm{occ}} \tag{3}$$

Then normal one-body operator expectation value is then:

$$\bar{O}_{\mathrm{N}} = \frac{\langle 0 | e^{\hat{T}^\dagger} \hat{O}_{\mathrm{N}} e^{\hat{T}^\dagger} | 0 \rangle}{\langle 0 | e^{\hat{T}^\dagger} e^{\hat{T}} | 0 \rangle} \tag{4}$$

From *Bartlett & Shavitt §11.1*, we have (valid for all normal-ordered operators):

$$\langle 0 | e^{\hat{T}^\dagger} \hat{O}_{\mathrm{N}} e^{\hat{T}} | 0 \rangle = \langle 0 | e^{\hat{T}^\dagger} e^{\hat{T}} | 0 \rangle \langle 0 | e^{\hat{T}^\dagger} \hat{O}_{\mathrm{N}} e^{\hat{T}} | 0 \rangle_{\mathrm{C}} \tag{5}$$

and therefore,

$$\bar{O}_{\mathrm{N}} = \langle 0 | e^{\hat{T}^\dagger} \hat{O}_{\mathrm{N}} e^{\hat{T}} | 0 \rangle_{\mathrm{C}} \tag{6}$$

We can use this result to obtain the correlation energy for CC, as:

$$E_{\mathrm{corr}} = \langle \hat{H}_{\mathrm{N}} \rangle = \frac{\langle 0 | e^{\hat{T}^\dagger} \hat{H}_{\mathrm{N}} e^{\hat{T}} | 0 \rangle}{\langle 0 | e^{\hat{T}^\dagger} e^{\hat{T}} | 0 \rangle} = \langle 0 | e^{\hat{T}^\dagger} \hat{H}_{\mathrm{N}} e^{\hat{T}} | 0 \rangle_{\mathrm{C}} \tag{7}$$

The more familiar form of CC correlation energy is:

$$E_{\mathrm{corr}} = \langle 0 | \hat{H}_{\mathrm{N}} e^{\hat{T}} | 0 \rangle_{\mathrm{C}} = \langle 0 | e^{-\hat{T}} \hat{H}_{\mathrm{N}} e^{\hat{T}} | 0 \rangle \tag{8}$$

These two forms are actually equivalent, demonstrated with the aid of the fact that $e^{\hat{T}(\hat{P}+\hat{Q})}e^{-\hat{T}} = \hat{1}$, where $\hat{P} = |0\rangle\langle 0|$ and $Q = \hat{1} - \hat{P} = \sum_{i \neq 0} |i\rangle\langle i|$, as following:

$$\begin{aligned} E_{\mathrm{corr}} =& \frac{\langle 0 | e^{\hat{T}^\dagger} \hat{H}_{\mathrm{N}} e^{\hat{T}} | 0 \rangle}{\langle 0 | e^{\hat{T}^\dagger} e^{\hat{T}} | 0 \rangle} \\ =& \frac{\langle 0 | e^{\hat{T}^\dagger} e^{\hat{T}} (\hat{P} + \hat{Q}) e^{-\hat{T}} \hat{H}_{\mathrm{N}} e^{\hat{T}} | 0 \rangle}{\langle 0 | e^{\hat{T}^\dagger} e^{\hat{T}} | 0 \rangle} \\ =& \frac{\langle 0 | e^{\hat{T}^\dagger} e^{\hat{T}} \hat{P} e^{-\hat{T}} \hat{H}_{\mathrm{N}} e^{\hat{T}} | 0 \rangle}{\langle 0 | e^{\hat{T}^\dagger} e^{\hat{T}} | 0 \rangle} + \frac{\langle 0 | e^{\hat{T}^\dagger} e^{\hat{T}} \hat{Q} e^{-\hat{T}} \hat{H}_{\mathrm{N}} e^{\hat{T}} | 0 \rangle}{\langle 0 | e^{\hat{T}^\dagger} e^{\hat{T}} | 0 \rangle} \\ =& \frac{\langle 0 | e^{\hat{T}^\dagger} e^{\hat{T}} | 0 \rangle \langle 0 | e^{-\hat{T}} \hat{H}_{\mathrm{N}} e^{\hat{T}} | 0 \rangle}{\langle 0 | e^{\hat{T}^\dagger} e^{\hat{T}} | 0 \rangle} \\ =& \langle 0 | e^{-\hat{T}} \hat{H}_{\mathrm{N}} e^{\hat{T}} | 0 \rangle \end{aligned} \tag{9}$$

$$=\langle 0|\hat{H}_{\mathrm{N}} e^{\hat{T}}|0\rangle_{\mathrm{C}}$$

in which we used the fact that:

$$\hat{Q} e^{-\hat{T}} \hat{H}_{\mathrm{N}} e^{\hat{T}}|0\rangle = \hat{Q}\hat{\mathcal{H}}|0\rangle = 0 \tag{10}$$

which is equivalently:

$$\langle \Phi_{ij\ldots}^{ab\ldots}|\hat{\mathcal{H}}|0\rangle = 0 \tag{11}$$

which are the CC amplitudes equations.