

Unitary Coupled Cluster Theory

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1 Derivation of Polarisation Propogator $G_{pr,rs}$ in the new unitary transformed excitation/deexcitation scheme

The Polarisation Propogator in superoperator representation is given by :

$$\begin{aligned} G_{pq,rs}(\omega) &= \langle \Psi_{gr} | [a_p a_q^\dagger, (\omega \hat{I} - \hat{H})^{-1} a_r^\dagger a_s] | \Psi_{gr} \rangle \\ &= \langle \Psi_{gr} | [q_I, (\omega \hat{I} - \hat{H})^{-1} q_J^\dagger] | \Psi_{gr} \rangle \end{aligned}$$

A Binary Product can be defined as follows :

$$(A|B) = \langle \Psi_{gr} | [A^\dagger, B] | \Psi \rangle$$

Another definition used in this derivation is :

$$(A|\hat{O}|B) \equiv (A|\hat{O}B)$$

Polarisation Propogator can be written in terms of binary product notation as :

$$G(\omega) = (q_i^\dagger | (\omega \hat{I} - \hat{H})^{-1} q_j^\dagger)$$

In our self consistant polarisation propagation theory, the unitary transformed excitation/deexcitation operators are defined as :

$$y_i^\dagger = \exp(\sigma) b_i^\dagger \exp(-\sigma)$$

Using the resolution of identity in G :

$$\begin{aligned} \hat{I} &= \sum_I \{ |y_I^\dagger\rangle \langle y_I^\dagger| - |y_I\rangle \langle y_I| \} \\ G(\omega) &= (q_I | y_I^\dagger) (y_I^\dagger | (\omega \hat{I} - \hat{H})^{-1} q_j^\dagger) - (q_I | y_I) (y_I | (\omega \hat{I} - \hat{H})^{-1} q_j^\dagger) \end{aligned}$$

Taking the second half of the expression and expanding through tailors expansion :

$$\begin{aligned}
(y_I | (\omega \hat{I} - \hat{H})^{-1} q_j^\dagger) &= \langle \Psi_{gr} | [y_I, (\omega \hat{I} - \hat{H})^{-1} q_j^\dagger] | \Psi_{gr} \rangle \\
&= \langle \Psi_{gr} | [y_I, \frac{1}{\omega} \left((\hat{I} - \hat{H}) \right)^{-1} q_j^\dagger] | \Psi_{gr} \rangle \\
&= \langle \Psi_{gr} | [y_I, \frac{1}{\omega} \left((\hat{I} + \frac{1}{\omega} \hat{H} + \frac{1}{\omega^2} \hat{H}^2 \dots) \right) q_j^\dagger] | \Psi_{gr} \rangle \\
&= \frac{1}{\omega} \left(\langle \Psi_{gr} | [y_I, (\hat{I} q_j^\dagger)] | \Psi_{gr} \rangle + \langle \Psi_{gr} | [y_I, \frac{1}{\omega} \hat{H} q_j^\dagger] | \Psi_{gr} \rangle + \langle \Psi_{gr} | [y_I, \frac{1}{\omega^2} \hat{H}^2 q_j^\dagger] | \Psi_{gr} \rangle \right) \\
&= \frac{1}{\omega} \left((y_I | (\hat{I} q_j^\dagger)) + (y_I | \frac{1}{\omega} \hat{H} q_j^\dagger) + (y_I | \frac{1}{\omega^2} \hat{H}^2 q_j^\dagger) \right) \\
&= \frac{1}{\omega} \left((y_I | (\hat{I} q_j^\dagger)) + (y_I | \frac{1}{\omega} \hat{H} q_j^\dagger) + (y_I | \frac{1}{\omega^2} \hat{H}^2 q_j^\dagger) \dots \right) \\
&= \frac{1}{\omega} (y_I | (\hat{I} + \frac{1}{\omega} \hat{H} + \frac{1}{\omega^2} \hat{H}^2 \dots) q_j^\dagger) \\
&= \frac{1}{\omega} (y_I | (\hat{I} - \frac{\hat{H}}{\omega})^{-1} q_j^\dagger) \\
&= (y_I | (\omega \hat{I} - \hat{H})^{-1} q_j^\dagger)
\end{aligned}$$

Using this result in the previously derived expression :

$$\begin{aligned}
\hat{I} &= \sum_I \{ |y_I^\dagger\rangle \langle y_I^\dagger| - |y_I\rangle \langle y_I| \} \\
G(\omega) &= (q_I^\dagger | y_I^\dagger) (y_I^\dagger | (\omega \hat{I} - \hat{H})^{-1} q_j^\dagger) - (q_I^\dagger | y_I) (y_I | (\omega \hat{I} - \hat{H})^{-1} q_j^\dagger) \\
&= (q_I^\dagger | y_I^\dagger) (y_I^\dagger | (\omega \hat{I} - \hat{H})^{-1} q_j^\dagger) - (q_I^\dagger | y_I) (y_I | (\omega \hat{I} - \hat{H})^{-1} q_j^\dagger)
\end{aligned}$$

Again using resolution of Identity Operator :

$$\begin{aligned}
G(\omega) &= (q_I^\dagger | y_I^\dagger) (y_I^\dagger | (\omega \hat{I} - \hat{H})^{-1} | y_J^\dagger \rangle \langle y_J^\dagger | q_j^\dagger) - (q_I^\dagger | y_I) (y_I | (\omega \hat{I} - \hat{H})^{-1} | y_J^\dagger \rangle \langle y_J^\dagger | q_j^\dagger) \\
&\quad - (q_I^\dagger | y_I^\dagger) (y_I^\dagger | (\omega \hat{I} - \hat{H})^{-1} | y_J \rangle \langle y_J | q_j^\dagger) + (q_I^\dagger | y_I) (y_I | (\omega \hat{I} - \hat{H})^{-1} | y_J \rangle \langle y_J | q_j^\dagger) \\
&= M L^{-1} M^\dagger
\end{aligned}$$

2 Resolution of Identity

2.1 Proof for the Identity for the notation

$$\begin{aligned}
(A|B) &= \sum_I (A|y_I^\dagger)(y_I^\dagger|B) - (A|y_I)(y_I|B) \\
\sum_I (A|y_I^\dagger)(y_I^\dagger|B) &= \sum_I [\langle \Psi_{gr} | A^\dagger y_I^\dagger - y_I^\dagger A^\dagger | \Psi_{gr} \rangle \langle \Psi_{gr} | y_I B - B y_I | \Psi_{gr} \rangle] \\
&= \langle \Psi_{gr} | A^\dagger y_I^\dagger | \Psi_{gr} \rangle \langle \Psi_{gr} | y_I B | \Psi_{gr} \rangle - \langle \Psi_{gr} | A^\dagger y_I^\dagger | \Psi_{gr} \rangle \langle \Psi_{gr} | B y_I | \Psi_{gr} \rangle \\
&\quad - \langle \Psi_{gr} | y_I^\dagger A^\dagger | \Psi_{gr} \rangle \langle \Psi_{gr} | y_I B | \Psi_{gr} \rangle + \langle \Psi_{gr} | y_I^\dagger A^\dagger | \Psi_{gr} \rangle \langle \Psi_{gr} | B y_I | \Psi_{gr} \rangle \\
&= \langle \Psi_{gr} | A^\dagger B | \Psi_{gr} \rangle
\end{aligned}$$

Similarly using Vaccume Anihilation Conditions :

$$\begin{aligned}
\sum_I (A|y_I)(y_I|B) &= \sum_I [\langle \Psi_{gr} | A^\dagger y_I - y_I A^\dagger | \Psi_{gr} \rangle \langle \Psi_{gr} | y_I^\dagger B - B y_I^\dagger | \Psi_{gr} \rangle] \\
&= \langle \Psi_{gr} | A^\dagger y_I | \Psi_{gr} \rangle \langle \Psi_{gr} | y_I^\dagger B | \Psi_{gr} \rangle - \langle \Psi_{gr} | A^\dagger y_I | \Psi_{gr} \rangle \langle \Psi_{gr} | B y_I^\dagger | \Psi_{gr} \rangle \\
&\quad - \langle \Psi_{gr} | y_I A^\dagger | \Psi_{gr} \rangle \langle \Psi_{gr} | y_I^\dagger B | \Psi_{gr} \rangle + \langle \Psi_{gr} | y_I A^\dagger | \Psi_{gr} \rangle \langle \Psi_{gr} | B y_I^\dagger | \Psi_{gr} \rangle \\
&= -\langle \Psi_{gr} | B A^\dagger | \Psi_{gr} \rangle
\end{aligned}$$

Adding both terms, we prove our identity:

$$\begin{aligned}
(A|B) &= \sum_I (A|y_I^\dagger)(y_I^\dagger|B) - (A|y_I)(y_I|B) \\
&= \langle \Psi_{gr} | A^\dagger B | \Psi_{gr} \rangle - \langle \Psi_{gr} | B A^\dagger | \Psi_{gr} \rangle \\
&= \langle \Psi_{gr} | [A^\dagger, B] | \Psi_{gr} \rangle \\
&= (A|B)
\end{aligned}$$

2.2 Resolution of Identity 2

Placing I at the second place in our notation:

conditions : $\hat{O}\Psi_{gr} = E\Psi_{gr}$ ans using the Vaccume Anihilation conditions :

$$\begin{aligned}
(A|\hat{O}|B) &= (A|\hat{O}|y_I^\dagger)(y_I^\dagger|B) - (A|\hat{O}|y_I)(y_I|B) \\
(A|\hat{O}|y_I^\dagger)(y_I^\dagger|B) &= \{(A|Oy_I^\dagger) - (A|y_I^\dagger O)\}(y_I^\dagger|B) \\
&= \langle \Psi_{gr} | [A^\dagger, Oy_I^\dagger] - [A^\dagger, y_I^\dagger O] | \Psi_{gr} \rangle \langle \Psi_{gr} | [y_I B] | \Psi_{gr} \rangle \\
&= \langle \Psi_{gr} | A^\dagger Oy_I^\dagger | \Psi_{gr} \rangle \langle \Psi_{gr} | y_I B | \Psi_{gr} \rangle - \langle \Psi_{gr} | Oy_I^\dagger A^\dagger | \Psi_{gr} \rangle \langle \Psi_{gr} | y_I B | \Psi_{gr} \rangle \\
&\quad - \langle \Psi_{gr} | A^\dagger y_I^\dagger O | \Psi_{gr} \rangle \langle \Psi_{gr} | y_I B | \Psi_{gr} \rangle + \langle \Psi_{gr} | y_I^\dagger O A^\dagger | \Psi_{gr} \rangle \langle \Psi_{gr} | y_I B | \Psi_{gr} \rangle \\
&\quad - \langle \Psi_{gr} | A^\dagger Oy_I^\dagger | \Psi_{gr} \rangle \langle \Psi_{gr} | By_I | \Psi_{gr} \rangle + \langle \Psi_{gr} | Oy_I^\dagger A^\dagger | \Psi_{gr} \rangle \langle \Psi_{gr} | By_I | \Psi_{gr} \rangle \\
&\quad + \langle \Psi_{gr} | A^\dagger y_I^\dagger O | \Psi_{gr} \rangle \langle \Psi_{gr} | By_I | \Psi_{gr} \rangle - \langle \Psi_{gr} | y_I^\dagger O A^\dagger | \Psi_{gr} \rangle \langle \Psi_{gr} | By_I | \Psi_{gr} \rangle \\
&= \langle \Psi_{gr} | A^\dagger OB | \Psi_{gr} \rangle - E \langle \Psi_{gr} | A^\dagger B | \Psi_{gr} \rangle
\end{aligned}$$

Similarly :

$$(A|\hat{O}|y_I)(y_I|B) = -\langle \Psi_{gr} | BOA^\dagger | \Psi_{gr} \rangle + E \langle \Psi_{gr} | BA^\dagger | \Psi_{gr} \rangle$$

Adding both we get :

$$\begin{aligned}
(A|\hat{O}|B) &= \langle \Psi_{gr} | A^\dagger OB | \Psi_{gr} \rangle - E \langle \Psi_{gr} | A^\dagger B | \Psi_{gr} \rangle \\
&\quad + \langle \Psi_{gr} | BOA^\dagger | \Psi_{gr} \rangle - E \langle \Psi_{gr} | BA^\dagger | \Psi_{gr} \rangle
\end{aligned}$$