Derivation of formula for GVB-LCC

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GVB-BCCC wave function:$\Psi^{GVB-BCCC} = e^{\hat{T}}|\Phi_0\rangle$, Φ_0 is GVB wave function

$$\hat{H}\Psi^{GVB-BCCC} = E\Psi^{GVB-BCCC} \Rightarrow \hat{H}e^{\hat{T}}|\Phi_0\rangle = Ee^{\hat{T}}|\Phi_0\rangle \Rightarrow e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = E|\Phi_0\rangle$$

$$\begin{cases} \langle\Phi_0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = E & \text{Energy equation} \\ \\ \langle\Phi_a|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = 0 & \text{Amplitude Equation} \end{cases}$$

where $|\Phi_a\rangle$ is ath excited state, and excited states

$$\psi_A = \hat{T}\Phi_0 = \sum_{a=1}^{n_A} t_a|\Phi_a\rangle$$

linear CC expansion: $e^{-\hat{T}}\hat{H}e^{\hat{T}} = \hat{H} + [\hat{H}, \hat{T}] \qquad [\hat{H}, \hat{T}] = \hat{H}\hat{T} - \hat{T}\hat{H}$

$$E = \langle\Phi_0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = \langle\Phi_0|\hat{H} + \left[\hat{H}, \hat{T}\right]|\Phi_0\rangle$$

$$= \langle\Phi_0|\hat{H}|\Phi_0\rangle + \langle\Phi_0|\left[\hat{H}, \hat{T}\right]|\Phi_0\rangle = \langle\Phi_0|\hat{H}|\Phi_0\rangle + \langle\Phi_0|\hat{H}\hat{T}|\Phi_0\rangle - \langle\Phi_0|\hat{T}\hat{H}|\Phi_0\rangle$$

$$= \langle\Phi_0|\hat{H}|\Phi_0\rangle + \langle\Phi_0|\hat{H}\hat{T}|\Phi_0\rangle = \langle\Phi_0|\hat{H}|\Phi_0\rangle + \langle\Phi_0|\hat{H}|\psi_A\rangle$$

$$= E_0 + \sum_{a=1}^{n_A} t_a\langle\Phi_0|\hat{H}|\Phi_a\rangle$$

Correlation Energy: $\Delta E = E - E_0 = \sum_{a=1}^{n_A} t_a\langle\Phi_0|\hat{H}|\Phi_a\rangle$

$$0 = \langle\Phi_a|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = \langle\Phi_a|\left[\hat{H}, \hat{T}\right]|\Phi_0\rangle$$

$$= \langle\Phi_a|\hat{H}|\Phi_0\rangle + \langle\Phi_a|\hat{H}\hat{T}|\Phi_0\rangle - \langle\Phi_a|\hat{T}\hat{H}|\Phi_0\rangle$$

$$= \langle\Phi_a|\hat{H}|\Phi_0\rangle + \langle\Phi_a|\hat{H}|\psi_A\rangle - \langle\Phi_a|\hat{T}\hat{H}|\Phi_0\rangle$$

$$= \langle\Phi_a|\hat{H}|\Phi_0\rangle + \sum_{b=1}^{n_A} t_b\langle\Phi_a|\hat{H}|\Phi_b\rangle - \langle\Phi_a|\hat{T}\hat{H}|\Phi_0\rangle$$

$$\langle\Phi_a|\hat{T}\hat{H}|\Phi_0\rangle = \langle\Phi_a|\hat{T}\left(\sum_{b\neq 0}^{n_A}|\Phi_b\rangle\langle\Phi_b| + |\Phi_0\rangle\langle\Phi_0|\right)\hat{H}|\Phi_0\rangle$$

$$= \langle\Phi_a|\hat{T}\sum_{b\neq 0}^{n_A}|\Phi_b\rangle\langle\Phi_b|\hat{H}|\Phi_0\rangle + \langle\Phi_a|\hat{T}|\Phi_0\rangle\langle\Phi_0|\hat{H}|\Phi_0\rangle$$

$$= \sum_{b\neq 0}^{n_A}\langle\Phi_a|\hat{T}|\Phi_b\rangle\langle\Phi_b|\hat{H}|\Phi_0\rangle + E_0\langle\Phi_a|\hat{T}|\Phi_0\rangle$$

Based on spin orbital: $\hat{H} = \sum_{pq} \langle p|h|q\rangle p^{+} q + \frac{1}{2} \sum_{pqrs} \langle pq|rs\rangle p^{+} q^{+} sr$

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

$\hat{H}_N = \sum_{pq} \langle p|f|q\rangle q^{+} q + \frac{1}{4} \sum_{pqrs} \langle pq||rs\rangle p^{+} q^{+} sr$

Based on space orbital:

$$\hat{H} = \sum_{pq} \sum_{\lambda} \langle p|h|q\rangle p_{\lambda}^{+} q_{\lambda} + \frac{1}{4} \sum_{pqrs} \sum_{\lambda\sigma} \langle pq||rs\rangle p_{\lambda}^{+} q_{\sigma}^{+} s_{\sigma} r_{\lambda}$$
$$= \sum_{p_\alpha q_\alpha} \langle p|h|q\rangle p_{\alpha}^{+} q_{\alpha}^{-} + \sum_{p_\beta q_\beta} \langle p|h|q\rangle p_{\beta}^{+} q_{\beta}^{-}$$
$$+ \frac{1}{4} \sum_{p_\alpha q_\alpha r_\alpha s_\alpha} \langle pq||rs\rangle p_{\alpha}^{+} q_{\alpha}^{+} s_{\alpha}^{-} r_{\alpha}^{-} + \frac{1}{4} \sum_{p_\beta q_\beta r_\beta s_\beta} \langle pq||rs\rangle p_{\beta}^{+} q_{\beta}^{+} s_{\beta}^{-} r_{\beta}^{-} + \sum_{p_\alpha q_\beta r_\alpha s_\beta} \langle pq||rs\rangle p_{\alpha}^{+} q_{\beta}^{+} s_{\beta}^{-} r_{\alpha}^{-}$$

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