CID equations

Derivation in KM tensor notation

The electronic Hamiltonian can be expressed as follows.

$$H_e = E_{\text{HF}} + H_c \qquad E_{\text{HF}} = \langle\Phi|H_e|\Phi\rangle \qquad H_c = f_p^q \tilde{a}_q^p + \tfrac{1}{4}\overline{g}_{pq}^{rs}\tilde{a}_{rs}^{pq} \tag{1}$$

The CID ansatz parametrizes the wavefunction as $\Psi \approx (c_0 + \hat{C}_2)\Phi$ where[1] $\hat{C}_2 = \frac{1}{4}c_{ab}^{ij}a_{ij}^{ab}$, and the CID correlation energy can obtained by solving the following system of linear equations

$$\langle\Phi|H_c(c_0+\hat{C}_2)|\Phi\rangle = E_c c_0 \qquad \Longrightarrow \qquad \tfrac{1}{4}\langle\Phi|H_c|\Phi_{kl}^{cd}\rangle c_{cd}^{kl} = E_c c_0 \tag{2}$$

$$\langle\Phi_{ij}^{ab}|H_c(c_0+\hat{C}_2)|\Phi\rangle = E_c c_{ab}^{ij} \qquad \Longrightarrow \qquad \langle\Phi_{ij}^{ab}|H_c|\Phi\rangle c_0 + \tfrac{1}{4}\langle\Phi_{ij}^{ab}|H_c|\Phi_{kl}^{cd}\rangle c_{cd}^{kl} = E_c c_{ab}^{ij} \tag{3}$$

which come from projecting the Schrödinger equation in the form $H_c\Psi = E_c\Psi$ by Φ and Φ_{ij}^{ab}. This is equivalent to solving for a root of the CID matrix

$$\begin{bmatrix} \langle\Phi|H_c|\Phi\rangle & \langle\Phi|H_c|\mathbf{D}\rangle \\ \langle\mathbf{D}|H_c|\Phi\rangle & \langle\mathbf{D}|H_c|\mathbf{D}\rangle \end{bmatrix} \begin{bmatrix} c_0 \\ \mathbf{c_D} \end{bmatrix} = E_c \begin{bmatrix} c_0 \\ \mathbf{c_D} \end{bmatrix} \qquad \mathbf{D} = \{\Phi_{ij}^{ab}\},\ \mathbf{c_D} = \{c_{ij}^{ab}\} \tag{4}$$

where the lowest root corresponds to the ground state correlation energy. The relevant matrix elements are

$$\langle\Phi|H_c|\Phi\rangle = 0 \qquad \langle\Phi|H_c|\Phi_{ij}^{ab}\rangle = \overline{g}_{ij}^{ab} \qquad \langle\Phi_{ij}^{ab}|H_c|\Phi_{kl}^{cd}\rangle = f_p^q(\tilde{a}_{ab}^{ij}\tilde{a}_q^p\tilde{a}_{kl}^{cd})_{\text{f.c.}} + \tfrac{1}{4}\overline{g}_{pq}^{rs}(\tilde{a}_{ab}^{ij}\tilde{a}_{rs}^{pq}\tilde{a}_{kl}^{cd})_{\text{f.c.}} \tag{5}$$

where $(\tilde{a}_{ab}^{ij}\tilde{a}_q^p\tilde{a}_{kl}^{cd})_{\text{f.c.}}$ and $(\tilde{a}_{ab}^{ij}\tilde{a}_{rs}^{pq}\tilde{a}_{kl}^{cd})_{\text{f.c.}}$ can be determined using Wick's theorem

$$\begin{aligned}
(\tilde{a}_{ab}^{ij}\tilde{a}_q^p\tilde{a}_{kl}^{cd})_{\text{f.c.}} &= \hat{P}_{(a/b|k/l)}^{(c/d)} \vdots\tilde{a}_{a^{\circ 1}b^{\circ 3}}^{i^{\bullet 1}j^{\bullet 2}}\tilde{a}_{q^{\circ 2}}^{p^{\circ 1}}\tilde{a}_{k^{\bullet 1}l^{\bullet 2}}^{c^{\circ 2}d^{\circ 3}}\vdots + \hat{P}_{(k/l)}^{(i/j|c/d)} \vdots\tilde{a}_{a^{\circ 1}b^{\circ 2}}^{i^{\bullet 1}j^{\bullet 3}}\tilde{a}_{q^{\bullet 1}}^{p^{\bullet 2}}\tilde{a}_{k^{\bullet 2}l^{\bullet 3}}^{c^{\circ 1}d^{\circ 2}}\vdots \\
&= -\hat{P}_{(a/b|k/l)}^{(c/d)}\tilde{a}_{a^{\circ 1}q^{\circ 2}b^{\circ 3}k^{\bullet 1}l^{\bullet 2}}^{p^{\circ 1}c^{\circ 2}d^{\circ 3}i^{\bullet 1}j^{\bullet 2}} - \hat{P}_{(k/l)}^{(i/j|c/d)}\tilde{a}_{q^{\bullet 1}k^{\bullet 2}l^{\bullet 3}a^{\circ 1}b^{\circ 2}}^{i^{\bullet 1}p^{\bullet 2}j^{\bullet 3}c^{\circ 1}d^{\circ 2}} \\
&= \hat{P}_{(a/b|k/l)}^{(c/d)}\eta_a^p\eta_q^c\eta_b^d\kappa_k^i\kappa_l^j - \hat{P}_{(k/l)}^{(i/j|c/d)}\kappa_q^i\kappa_k^p\kappa_l^j\eta_a^c\eta_b^d \\
(\tilde{a}_{ab}^{ij}\tilde{a}_{rs}^{pq}\tilde{a}_{kl}^{cd})_{\text{f.c.}} &= \hat{P}_{(a/b|k/l)}^{(c/d)} \vdots\tilde{a}_{a^{\circ 1}b^{\circ 2}}^{i^{\bullet 1}j^{\bullet 2}}\tilde{a}_{r^{\circ 3}s^{\circ 4}}^{p^{\circ 1}q^{\circ 2}}\tilde{a}_{k^{\bullet 1}l^{\bullet 2}}^{c^{\circ 3}d^{\circ 4}}\vdots + \hat{P}_{(k/l)}^{(i/j|c/d)} \vdots\tilde{a}_{a^{\circ 1}b^{\circ 2}}^{i^{\bullet 1}j^{\bullet 2}}\tilde{a}_{r^{\bullet 1}s^{\bullet 2}}^{p^{\bullet 3}q^{\bullet 4}}\tilde{a}_{k^{\bullet 3}l^{\bullet 4}}^{c^{\circ 1}d^{\circ 2}}\vdots \\
&\quad + \hat{P}_{(r/s|k/l|a/b)}^{(p/q|i/j|c/d)} \vdots\tilde{a}_{a^{\circ 1}b^{\circ 3}}^{i^{\bullet 1}j^{\bullet 3}}\tilde{a}_{r^{\bullet 1}s^{\circ 2}}^{p^{\bullet 2}q^{\circ 1}}\tilde{a}_{k^{\bullet 2}l^{\bullet 3}}^{c^{\circ 2}d^{\circ 3}}\vdots \\
&= \hat{P}_{(a/b|k/l)}^{(c/d)}\tilde{a}_{a^{\circ 1}b^{\circ 2}r^{\circ 3}s^{\circ 4}k^{\bullet 1}l^{\bullet 2}}^{p^{\circ 1}q^{\circ 2}c^{\circ 3}d^{\circ 4}i^{\bullet 1}j^{\bullet 2}} + \hat{P}_{(k/l)}^{(i/j|c/d)}\tilde{a}_{r^{\bullet 1}s^{\bullet 2}k^{\bullet 3}l^{\bullet 4}a^{\circ 1}b^{\circ 2}}^{i^{\bullet 1}j^{\bullet 2}p^{\bullet 3}q^{\bullet 4}c^{\circ 1}d^{\circ 2}} + \hat{P}_{(r/s|k/l|a/b)}^{(p/q|i/j|c/d)}\tilde{a}_{r^{\bullet 1}k^{\bullet 2}l^{\bullet 3}a^{\circ 1}s^{\circ 2}b^{\circ 3}}^{i^{\bullet 1}p^{\bullet 2}j^{\bullet 3}q^{\circ 1}c^{\circ 2}d^{\circ 3}} \\
&= \hat{P}_{(a/b|k/l)}^{(c/d)}\eta_a^p\eta_b^q\eta_r^c\eta_s^d\kappa_k^i\kappa_l^j + \hat{P}_{(k/l)}^{(i/j|c/d)}\kappa_r^i\kappa_s^j\kappa_k^p\kappa_l^q\eta_a^c\eta_b^d - \hat{P}_{(r/s|k/l|a/b)}^{(p/q|i/j|c/d)}\kappa_r^i\kappa_k^p\kappa_l^j\eta_a^q\eta_s^c\eta_b^d
\end{aligned}$$

giving

$$\langle\Phi_{ij}^{ab}|H_c|\Phi_{kl}^{cd}\rangle = \hat{P}_{(a/b|k/l)}^{(c/d)}f_a^c\delta_b^d\delta_k^i\delta_l^j - \hat{P}_{(k/l)}^{(i/j|c/d)}f_k^i\delta_l^j\delta_a^c\delta_b^d + \hat{P}_{(k/l)}\overline{g}_{ab}^{cd}\delta_k^i\delta_l^j + \hat{P}^{(c/d)}\overline{g}_{kl}^{ij}\delta_a^c\delta_b^d - \hat{P}_{(k/l|a/b)}^{(i/j|c/d)}\overline{g}_{ka}^{ic}\delta_l^j\delta_b^d \tag{6}$$

for the matrix elements of the doubles block, $\langle\mathbf{D}|H_c|\mathbf{D}\rangle$. Efficient CI implementations utilize a "direct algorithm", in which the Hamiltonian matrix $\tilde{\mathbf{H}} = [\langle\Phi_P|H_c|\Phi_Q\rangle]$ is never constructed and stored in memory. Instead, the product $\tilde{\mathbf{H}}\mathbf{c}$ is computed directly (hence the name) for a given trial vector $\mathbf{c}$. This matrix-vector product is called the "sigma vector", $\boldsymbol{\sigma}$, with elements $\sigma_P = \sum_Q \langle\Phi_P|H_c|\Phi_Q\rangle c_Q$. Elements of the CID sigma vector are given by the left-hand sides of equations 2 and 3. Using equations 5 and 6, the working expressions for σ_0 and σ_{ab}^{ij} are as follows.

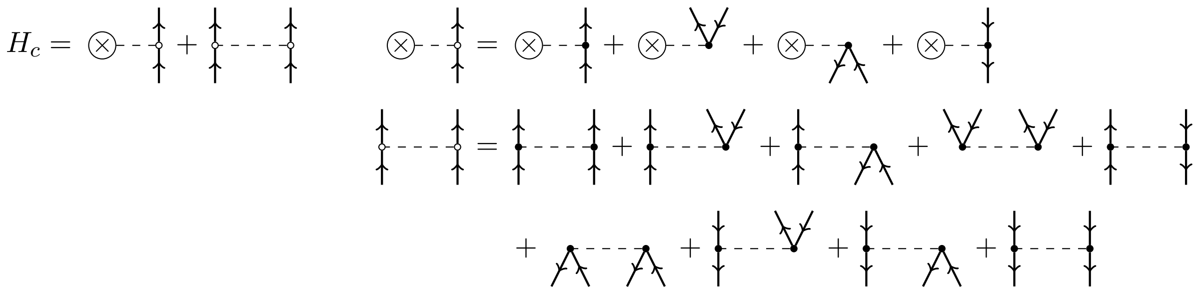
$$\sigma_0 = \tfrac{1}{4}\overline{g}_{kl}^{cd}c_{cd}^{kl} \qquad \left(\sigma_0 \equiv \tfrac{1}{4}\langle\Phi|H_c|\Phi_{kl}^{cd}\rangle c_{cd}^{kl}\right) \tag{7}$$

$$\sigma_{ab}^{ij} = \overline{g}_{ab}^{ij}c_0 + \hat{P}_{(a/b)}f_a^c c_{cb}^{ij} - \hat{P}^{(i/j)}f_k^i c_{ab}^{kj} + \tfrac{1}{2}\overline{g}_{ab}^{cd}c_{cd}^{ij} + \tfrac{1}{2}\overline{g}_{kl}^{ij}c_{ab}^{kl} - \hat{P}_{(a/b)}^{(i/j)}\overline{g}_{ka}^{ic}c_{cb}^{kj} \qquad \left(\sigma_{ab}^{ij} \equiv \tfrac{1}{4}\langle\Phi_{ij}^{ab}|H_c|\Phi_{kl}^{cd}\rangle c_{cd}^{kl}\right) \tag{8}$$

[1] We write the CI coefficients here as c_{ab}^{ij} instead of c_{ij}^{ab} in order to be consistent with Einstein notation.

Derivation in diagrammatic notation

In diagrammatic notation, H_c is given by the following.



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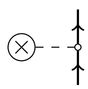
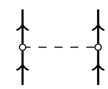
Where the diagrams with open-circle interaction points are



$$\equiv f_p^q \tilde{a}_q^p$$



$$\equiv \tfrac{1}{4}\bar{g}_{pq}^{rs}\tilde{a}_{rs}^{pq} \tag{11}$$

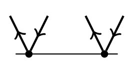
and those with closed-circle interaction points are their expansions in terms of quasiparticle operators $\{b_p\} = \{a_i^\dagger\} \cup \{a_a\}$ and $\{b_p^\dagger\} = \{a_i\} \cup \{a_a^\dagger\}$. In terms of KM notation, using the original set of operators, these diagram expansions correspond to the following equations.

$$f_p^q \tilde{a}_q^p = f_a^b \tilde{a}_b^a + f_a^i \tilde{a}_i^a + f_i^a \tilde{a}_a^i + f_i^j \tilde{a}_j^i \tag{12}$$

$$\tfrac{1}{4}\bar{g}_{pq}^{rs}\tilde{a}_{rs}^{pq} = \tfrac{1}{4}\bar{g}_{ab}^{cd}\tilde{a}_{cd}^{ab} + \tfrac{1}{2}\bar{g}_{ab}^{ci}\tilde{a}_{ci}^{ab} + \tfrac{1}{2}\bar{g}_{ai}^{bc}\tilde{a}_{bc}^{ai} + \tfrac{1}{4}\bar{g}_{ab}^{ij}\tilde{a}_{ij}^{ab} + \bar{g}_{ai}^{bj}\tilde{a}_{bj}^{ai} + \tfrac{1}{4}\bar{g}_{ij}^{ab}\tilde{a}_{ab}^{ij} + \tfrac{1}{2}\bar{g}_{ia}^{jk}\tilde{a}_{jk}^{ia} + \tfrac{1}{2}\bar{g}_{ij}^{ka}\tilde{a}_{ka}^{ij} + \tfrac{1}{4}\bar{g}_{ij}^{kl}\tilde{a}_{kl}^{ij} \tag{13}$$

The CI double excitation operator is given by

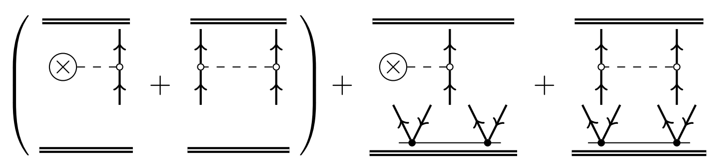
$$\hat{C}_2 = \frac{1}{4}\sum_{ijab} c_{ab}^{ij} b_a^\dagger b_b^\dagger b_j^\dagger b_i^\dagger =$$



$$\left(= \tfrac{1}{4}c_{ab}^{ij} a_{ij}^{ab} = \tfrac{1}{4}c_{ab}^{ij}\tilde{a}_{ij}^{ab} \text{ in KM notation}\right). \tag{14}$$

The sigma vector elements are therefore given by

$$\sigma_0 = \langle\Phi|H_c(c_0 + \hat{C}_2)|\Phi\rangle = c_0$$



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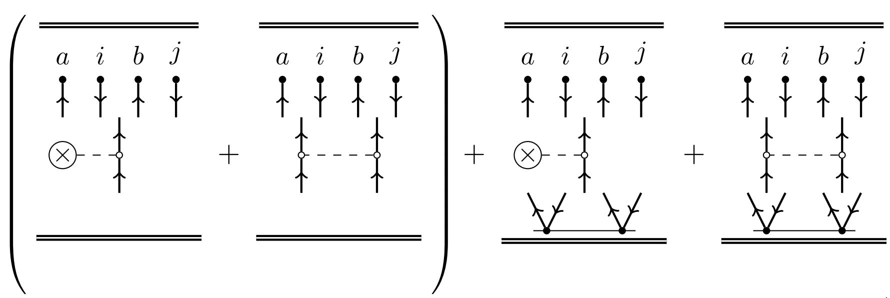
$$\sigma_{ab}^{ij} = \langle\Phi_{ij}^{ab}|H_c(c_0 + \hat{C}_2)|\Phi\rangle = c_0$$



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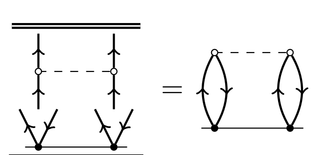
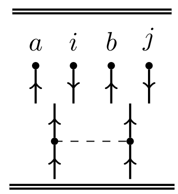
In the σ_0 expression, only the final diagram is non-vanishing.

$$\sigma_0 =$$



$$= \tfrac{1}{4}\bar{g}_{kl}^{cd} c_{cd}^{kl} \tag{17}$$

In the σ_{ab}^{ij} expression, the first diagram vanishes and the second diagram evaluates as follows.



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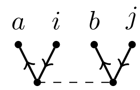

$$= \overline{g}_{ab}^{ij} \tag{18}$$