Supporting Information: Superposition of Fragment Excitations for Excited States of Large Clusters with Application to Helium Clusters

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1 Derivation of Matrix Elements

We consider each case on the right hand side of the ALMO-CIS equations.

$$\left\langle \Psi^{b}_{\cdot j} \right| \hat{H} \left| \Psi^{i}_{\cdot a} \right\rangle t^{a}_{\cdot i} = \omega_{CIS} \left\langle \Psi^{b}_{\cdot j} \middle| \Psi^{i}_{\cdot a} \right\rangle t^{a}_{\cdot i} \tag{1}$$

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Using standard definitions of the Fock operator

$$f^p_{\cdot q} = \left\langle \psi^p \left| \hat{f} \right| \psi_q \right\rangle = \left\langle \psi^p \left| \hat{h} \right| \psi_q \right\rangle + \sum_{k \in \{\Psi_0\}} \left\langle \psi^p \psi^k \,||\, \psi_q \psi_k \right\rangle \tag{2}$$

and the ground state energy

$$E_0 = \left\langle \Psi_0 \left| \hat{H} \right| \Psi_0 \right\rangle = \sum_{k \in \{\Psi_0\}} \left\langle \psi^k \left| \hat{h} \right| \psi_k \right\rangle + \frac{1}{2} \sum_{k,l \in \{\Psi_0\}} \left\langle \psi^k \psi^l \,||\, \psi_k \psi_l \right\rangle \tag{3}$$

1. $i \neq j$ and $a \neq b$

$$\left\langle \Psi^b_{\cdot j} \left| \hat{H} \right| \Psi^i_{\cdot a} \right\rangle = \left\langle \psi^i \psi^b \,||\, \psi_a \psi_j \right\rangle = \Pi^{ib}_{\cdot\cdot ja} \tag{4}$$

2. $i = j$ and $a \neq b$

$$\begin{aligned} \left\langle \Psi^b_{\cdot i} \left| \hat{H} \right| \Psi^i_{\cdot a} \right\rangle &= \left\langle \psi^b \left| \hat{h} \right| \psi_a \right\rangle + \sum_{k \in \{\Psi_0, \neg \psi_i\}} \left\langle \psi^b \psi^k \,||\, \psi_a \psi_k \right\rangle \\ &= \left\langle \psi^b \left| \hat{h} \right| \psi_a \right\rangle + \sum_{k \in \{\Psi_0\}} \left\langle \psi^b \psi^k \,||\, \psi_a \psi_k \right\rangle - \left\langle \psi^b \psi^i \,||\, \psi_a \psi_i \right\rangle \\ &= \left\langle \psi^b \left| \hat{f} \right| \psi_a \right\rangle - \left\langle \psi^b \psi^i \,||\, \psi_a \psi_i \right\rangle = f^b_{\cdot a} - \Pi^{bi}_{\cdot\cdot ai} \end{aligned} \tag{5}$$

3. $i \neq j$ and $a = b$

$$\begin{aligned} \left\langle \Psi^a_{\cdot j} \left| \hat{H} \right| \Psi^i_{\cdot a} \right\rangle &= -\left\langle \psi^i \left| \hat{h} \right| \psi_j \right\rangle - \sum_{k \in \{\Psi_0, a\}} \left\langle \psi^i \psi^k \,||\, \psi_j \psi_k \right\rangle \\ &= -\left\langle \psi^i \left| \hat{h} \right| \psi_j \right\rangle - \sum_{k \in \{\Psi_0\}} \left\langle \psi^i \psi^k \,||\, \psi_j \psi_k \right\rangle - \left\langle \psi^i \psi^a \,||\, \psi_j \psi_a \right\rangle \\ &= -\left\langle \psi^i \left| \hat{f} \right| \psi_j \right\rangle - \left\langle \psi^i \psi^a \,||\, \psi_j \psi_a \right\rangle = -f^i_{\cdot j} - \Pi^{ia}_{\cdot\cdot ja} \end{aligned} \tag{6}$$

Note negative sign appears due to placing the determinants in maximum coincidence because of electron anti-symmetry:

$$\begin{aligned} \left|\Psi^{i}_{\cdot a}\right\rangle &= \left|\psi_1 \dots \psi_a \psi_j \dots \psi_n\right\rangle \\ \implies \left|\Psi^{j}_{\cdot a}\right\rangle &= \left|\psi_1 \dots \psi_i \psi_a \dots \psi_n\right\rangle = -\left|\psi_1 \dots \psi_a \psi_i \dots \psi_n\right\rangle . \end{aligned} \tag{7}$$

4. $i = j$ and $a = b$

$$\begin{aligned} \left\langle \Psi^{a}_{\cdot i} \middle| \hat{H} \middle| \Psi^{i}_{\cdot a} \right\rangle =& \sum_{k \in \{\Psi_0, \neg i, a\}} \left\langle \psi^k \middle| \hat{h} \middle| \psi_k \right\rangle + \frac{1}{2} \sum_{k,l \in \{\Psi_0, \neg i, a\}} \left\langle \psi^k \psi^l \,||\, \psi_k \psi_l \right\rangle \\ =& \sum_{k \in \{\Psi_0\}} \left\langle \psi^k \middle| \hat{h} \middle| \psi_k \right\rangle - \left\langle \psi^i \middle| \hat{h} \middle| \psi_i \right\rangle + \left\langle \psi^a \middle| \hat{h} \middle| \psi_a \right\rangle + \frac{1}{2} \sum_{k,l \in \{\Psi_0\}} \left\langle \psi^k \psi^l \,||\, \psi_k \psi_l \right\rangle \\ &+ \sum_{k \in \{\Psi_0\}} \left(\left\langle \psi^a \psi^k \,||\, \psi_a \psi_k \right\rangle - \left\langle \psi^i \psi^k \,||\, \psi_i \psi_k \right\rangle \right) - \left\langle \psi^i \psi^a \,||\, \psi_i \psi_a \right\rangle \\ =& \sum_{k \in \{\Psi_0\}} \left(\left\langle \psi^k \middle| \hat{h} \middle| \psi_k \right\rangle + \frac{1}{2} \left\langle \psi^k \psi^l \,||\, \psi_k \psi_l \right\rangle \right) + \\ & \left\langle \psi^a \middle| \hat{h} \middle| \psi_a \right\rangle + \sum_{k \in \{\Psi_0\}} \left\langle \psi^a \psi^k \,||\, \psi_a \psi_k \right\rangle - \\ & \left\langle \psi^i \middle| \hat{h} \middle| \psi_i \right\rangle - \sum_{k \in \{\Psi_0\}} \left\langle \psi^i \psi^k \,||\, \psi_i \psi_k \right\rangle - \left\langle \psi^i \psi^a \,||\, \psi_i \psi_a \right\rangle \\ =& E_0 + f^{a}_{\cdot a} - f^{i}_{\cdot i} - \Pi^{ia}_{\cdot\cdot ia} \end{aligned} \tag{8}$$

Combining all cases and making use of the two-electron integral permutational symmetry we obtain

$$\left\langle \Psi^{b}_{\cdot j} \middle| \hat{H} \middle| \Psi^{i}_{\cdot a} \right\rangle = E_0 \delta^{b}_{\cdot a} \delta^{i}_{\cdot j} + f^{b}_{\cdot a} \delta^{i}_{\cdot j} - f^{i}_{\cdot j} \delta^{b}_{\cdot a} + \Pi^{ib}_{\cdot\cdot aj} \tag{9}$$

Noting that for real functions

$$
\begin{aligned}
\langle \psi^p \psi^q \,||\, \psi_r \psi_s \rangle &= \langle \psi^q \psi^p \,||\, \psi_s \psi_r \rangle = - \langle \psi^q \psi^p \,||\, \psi_r \psi_s \rangle = - \langle \psi^p \psi^q \,||\, \psi_s \psi_r \rangle \\
&= \langle \psi^r \psi^s \,||\, \psi_p \psi_q \rangle = \langle \psi^s \psi^r \,||\, \psi_q \psi_p \rangle = - \langle \psi^r \psi^s \,||\, \psi_q \psi_p \rangle = - \langle \psi^s \psi^r \,||\, \psi_p \psi_q \rangle
\end{aligned}
\tag{10}
$$

2 Resolution of the Identity Corrections to the two electron integrals

While the primary components of the two electron integrals are evaluated exactly, they must be corrected due to the non-orthogonal ALMOs. This section details the derivation of the integral corrections which are evaluated with using the RI approximation.

2.1 Coulomb integrals

$$
\begin{aligned}
(\psi_i \phi_a \mid \psi_j \phi_b) =& N^2 \Big\{ (\psi_i \psi_a \mid \psi_j \psi_b) \\
& -2 \left(\psi_i \psi_a \,|\psi_j \psi_k \right) \left(\psi^k \mid \psi_b \right) + \left(\psi_i \psi_k \mid \psi_j \psi_l \right) \left(\psi^k \,|\psi_\alpha \right) \left(\psi^l \,|\psi_b \right) \Big\}
\end{aligned}
\tag{11}
$$

$$
J = \mathcal{N}^2 (J1 - 2 \cdot J23 + J4) \tag{12}
$$

1. $J23$

$$
\left(\psi_i \psi_a \,|\psi_j \psi_k \right) \left(\psi^k \mid \psi_b \right) = \left(\psi_i \psi_a \,|\chi_P \right) \left(\chi^P \mid \chi^Q \right) \left(\chi_Q |\, \psi_j \, \psi_k \right) \left(\psi^k \mid \psi_b \right)
$$

$$
\implies J23 = v_{iaP} v^{PQ} v_{jkQ} \sigma^k_b \tag{13}
$$

2. $J4$

$$(\psi_i\psi_k \mid \psi_j\psi_l) \left(\psi^k \,|\psi_a\right) \left(\psi^l \,|\psi_b\right) = \left(\psi^k \middle| \psi_a \right) (\psi_i\psi_k| \, \chi_P) \left(\chi^P \mid \chi^Q\right) (\chi_Q| \, \psi_j \, \psi_l) \left(\psi^l \mid \psi_b\right)$$

$$\implies J4 = \sigma_a^k v_{ikP} v^{PQ} v_{jlQ} \sigma_b^l \tag{14}$$

2.2 Exchange integrals

$$\begin{aligned}(\psi_i\psi_j \,|\phi_a\phi_b) =& \mathcal{N}^2 \Big\{(\psi_i\psi_j \,|\psi_a\psi_b) \\ & -2 \,(\psi_i\psi_j \,|\psi_a\psi_k) \left(\psi^k \,|\psi_b\right) + (\psi_i\psi_j \mid \psi_k\psi_l) \left(\psi^k \,|\psi_a\right) \left(\psi^l \,|\psi_b\right)\Big\} \qquad (15) \\ K =& \mathcal{N}^2(K1 - 2 \cdot K23 + K4) \qquad (16)\end{aligned}$$

1. K23

$$(\psi_i\psi_j \,|\psi_a\psi_k) \left(\psi^k \,|\psi_b\right) = \Big(\psi_i\psi_j \mid \chi_P\Big) \left(\chi^P \mid \chi^Q\right) (\chi_Q \mid \psi_a\psi_k) \left(\psi^k \,|\psi_b\right) \tag{17}$$

$$\implies K23 = v_{ijP} v^{PQ} v_{akQ} \sigma_b^k \tag{18}$$

2. K4

$$(\psi_i\psi_j \mid \psi_k\psi_l)\left(\psi^k \mid \psi_a\right)\left(\psi^l \mid \psi_b\right) = \left(\psi_i\psi_j \mid \chi_P\right)\left(\chi^P \mid \chi^Q\right)(\chi_Q \mid \psi_k\psi_l)\left(\psi^k \mid \psi_a\right)\left(\psi^l \mid \psi_b\right) \tag{19}$$

$$\Longrightarrow \; K4 = v_{ijP}v^{PQ}v_{klQ}\sigma_a^k\sigma_b^l \tag{20}$$