Supporting Information For: An Efficient Implementation of the Second-Order Quasidegenerate Perturbation Theory with Density-Fitting and Cholesky Decomposition Approximations: Is It Possible to Use Hartree-Fock Orbitals for a Multiconfigurational Perturbation Theory?

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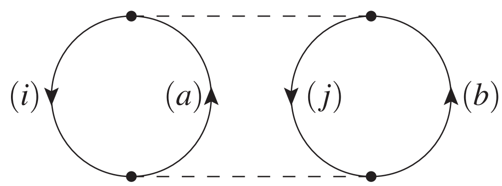
1 Second-Order Diagrams



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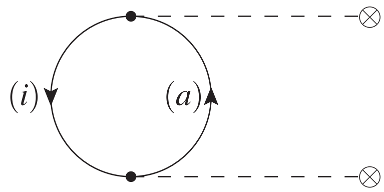

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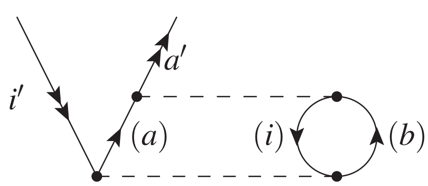

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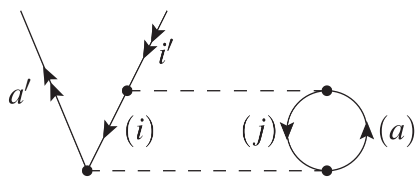

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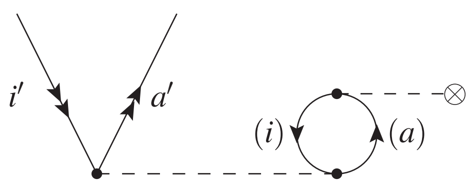

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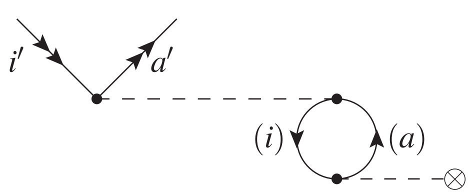

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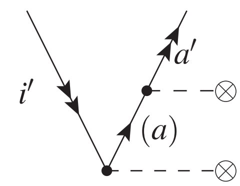

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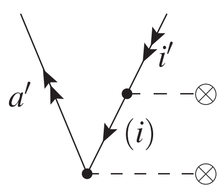

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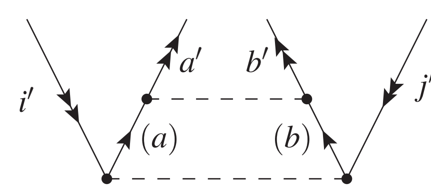

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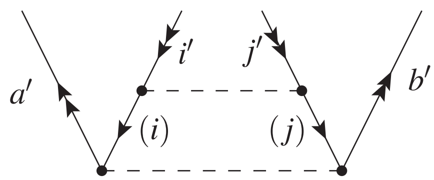

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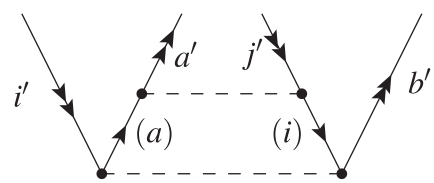

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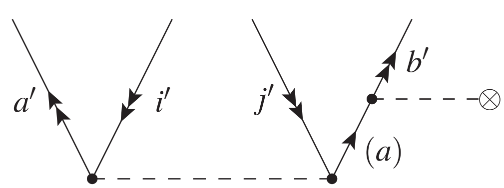

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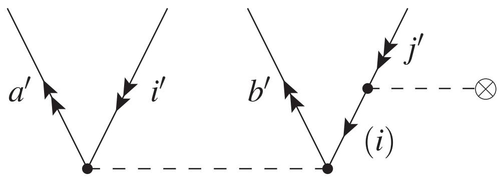

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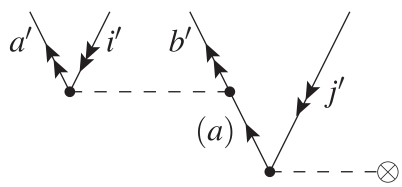

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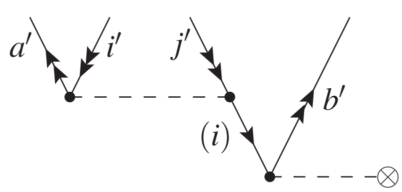

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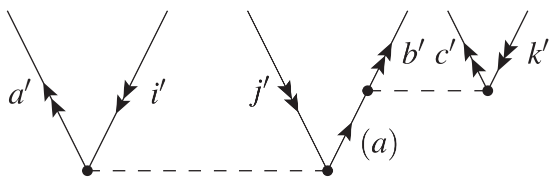

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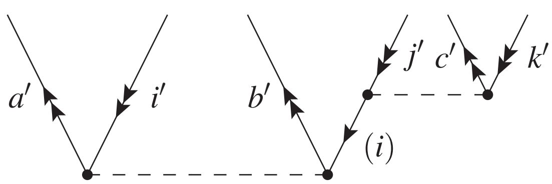

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2 Spin-Unrestricted HK Approach

2.1 QDPT Fock Matrix

2.1.1 Core Fock Matrix

$$ {}^{c}f_{pq}^{\alpha} = h_{pq}^{\alpha} + \sum_{Q}^{N_{aux}} b_{pq}^{Q} J^{Q} - \sum_{Q}^{N_{aux}} \sum_{m''}^{occ} b_{pm''}^{Q} b_{qm''}^{Q} \tag{1} $$

$$ {}^{c}f_{pq}^{\beta} = h_{pq}^{\beta} + \sum_{Q}^{N_{aux}} b_{\bar{p}\bar{q}}^{Q} J^{Q} - \sum_{Q}^{N_{aux}} \sum_{\bar{m}''}^{occ} b_{\bar{p}\bar{m}''}^{Q} b_{\bar{p}\bar{m}''}^{Q} \tag{2} $$

where

$$ J^{Q} = \sum_{m''}^{occ} b_{m''m''}^{Q} + \sum_{\bar{m}}^{occ} b_{\bar{m}''\bar{m}''}^{Q} \tag{3} $$

2.2 One-Electron Interaction

With DF approach:

$$ g_{pq}^{\alpha} = (1-\delta_{pq})\,{}^{c}f_{pq}^{\alpha} + \sum_{Q}^{N_{aux}} b_{pq}^{Q} \tilde{J}^{Q} - \sum_{Q}^{N_{aux}} \sum_{m'}^{occ} b_{pm'}^{Q} b_{qm'}^{Q} \tag{4} $$

$$ g_{pq}^{\beta} = (1-\delta_{pq})\,{}^{c}f_{pq}^{\beta} + \sum_{Q}^{N_{aux}} b_{\bar{p}\bar{q}}^{Q} \tilde{J}^{Q} - \sum_{Q}^{N_{aux}} \sum_{\bar{m}'}^{occ} b_{\bar{p}\bar{m}'}^{Q} b_{\bar{p}\bar{m}'}^{Q} \tag{5} $$

where

$$ \tilde{J}^{Q} = \sum_{m'}^{occ} b_{m'm'}^{Q} + \sum_{\bar{m}}^{occ} b_{\bar{m}'\bar{m}'}^{Q} \tag{6} $$

2.3 The Reference Energy

$$\begin{aligned} E_{ref} &= \sum_I \left(\varepsilon_I + g_{II}\right) + \sum_i \left(\varepsilon_i + g_{ii}\right) \\ &- \frac{1}{2}\sum_{I,J}\langle IJ||IJ\rangle_{DF} - \frac{1}{2}\sum_{i,j}\langle ij||ij\rangle_{DF} - \sum_{I,j}\langle Ij|Ij\rangle_{DF} \end{aligned} \tag{7}$$

2.4 First-Order Diagrams

The modified operator $\hat{W}'^{(1)}$; it has no diagonal contribution here because

$$\langle 0|\hat{W}'^{(1)}|0\rangle = 0 \tag{8}$$

The off-diagonal part of the first-order level-shift operator is represented by the two diagrams. The first diagram represents a single replacement for the final (bra) state relative to the initial (ket) state, with matrix element

$$\widetilde{W}_{I'}^{A'} = g_{A'I'} \tag{9}$$

$$\widetilde{W}_{i'}^{a'} = g_{a'i'} \tag{10}$$

The second diagram represents a double replacement, with matrix element

$$\widetilde{W}_{I'J'}^{A'B'} = \langle I'J'||A'B'\rangle_{DF} \tag{11}$$

$$\widetilde{W}_{i'j'}^{a'b'} = \langle a'b'||i'j'\rangle_{DF} \tag{12}$$

$$\widetilde{W}_{I'j'}^{A'b'} = \langle I'j'|A'b'\rangle_{DF} \tag{13}$$

2.5 First-Order Amplitudes

Let us define

$$t_I^A D_I^A = g_{AI} \quad (14)$$

$$t_i^a D_i^a = g_{ai} \quad (15)$$

and

$$t_{IJ}^{AB} D_{IJ}^{AB} = \langle IJ||AB\rangle_{DF} \quad (16)$$

$$t_{ij}^{ab} D_{ij}^{ab} = \langle ij||ab\rangle_{DF} \quad (17)$$

$$t_{Ij}^{Ab} D_{Ij}^{Ab} = \langle Ij|Ab\rangle_{DF} \quad (18)$$

where

$$D_I^A = f_{II} - f_{AA} \quad (19)$$

$$D_i^a = f_{ii} - f_{aa} \quad (20)$$

$$D_{IJ}^{AB} = f_{II} + f_{JJ} - f_{AA} - f_{BB} \quad (21)$$

$$D_{ij}^{ab} = f_{ii} + f_{jj} - f_{aa} - f_{bb} \quad (22)$$

$$D_{Ij}^{Ab} = f_{II} + f_{jj} - f_{AA} - f_{bb} \quad (23)$$

2.6 Second-Order Diagrams

2.6.1 The Diagonal Term

$$
\begin{aligned}
E_2 &= \sum_{IA} t_I^A g_{IA} + \sum_{ia} t_i^a g_{ia} \\
&+ \frac{1}{4} \sum_{I,J}^{occ} \sum_{A,B}^{vir} t_{IJ}^{AB} \langle IJ || AB \rangle_{DF} \\
&+ \frac{1}{4} \sum_{i,j}^{occ} \sum_{a,b}^{vir} t_{ij}^{ab} \langle ij || ab \rangle_{DF} \\
&+ \sum_{I,j}^{occ} \sum_{A,b}^{vir} t_{Ij}^{Ab} \langle Ij | Ab \rangle_{DF}
\end{aligned} \tag{24}
$$

2.6.2 Single Replacements

α-Block:

$$
\begin{aligned}
W_{I'}^{A'} &= \frac{1}{2} \sum_{IAB} t_{I'I}^{AB} \langle A'I || AB \rangle_{DF} + \sum_{iAb} t_{I'i}^{Ab} \langle A'i | Ab \rangle_{DF} \\
&- \frac{1}{2} \sum_{IJA} t_{IJ}^{A'A} \langle IJ || I'A \rangle_{DF} - \sum_{Ija} t_{Ij}^{A'a} \langle Ij | I'a \rangle_{DF} \\
&+ \sum_{IA} t_{I'I}^{A'A} g_{IA} + \sum_{ia} t_{I'i}^{A'a} g_{ia} \\
&+ \sum_{IA} t_I^A \langle A'I || I'A \rangle_{DF} + \sum_{ia} t_i^a \langle A'i | I'a \rangle_{DF} \\
&+ \sum_{A} t_{I'}^{A} g_{A'A} \\
&- \sum_{I} t_{I}^{A'} g_{II'}
\end{aligned} \tag{25}
$$

β-Block:

$$
\begin{aligned}
W_{i'}^{a'} \;=\;& \frac{1}{2}\sum_{iab} t_{i'i}^{ab}\langle a'i||ab\rangle_{DF} + \sum_{IAb} t_{Ii'}^{Ab}\langle Ia'|Ab\rangle_{DF} \\
-\;& \frac{1}{2}\sum_{ija} t_{ij}^{a'a}\langle ij||i'a\rangle_{DF} - \sum_{IjA} t_{Ij}^{Aa'}\langle Ij|Ai'\rangle_{DF} \\
+\;& \sum_{ia} t_{i'i}^{a'a} g_{ia} + \sum_{IA} t_{Ii'}^{Aa'} g_{IA} \\
+\;& \sum_{ia} t_{i}^{a}\langle a'i||i'a\rangle_{DF} + \sum_{IA} t_{I}^{A}\langle Ia'|Ai'\rangle_{DF} \\
+\;& \sum_{a} t_{i'}^{a} g_{a'a} \\
-\;& \sum_{i} t_{i}^{a'} g_{ii'}
\end{aligned}
\tag{26}
$$

2.6.3 Double Replacements

$\alpha\alpha$-Block:

$$
\begin{aligned}
W_{I'J'}^{A'B'} \;=\;& \frac{1}{2}\sum_{AB} t_{I'J'}^{AB}\langle A'B'||AB\rangle_{DF} \\
+\;& \frac{1}{2}\sum_{IJ} t_{IJ}^{A'B'}\langle IJ||I'J'\rangle_{DF} \\
+\;& P_{-}(I'J')P_{-}(A'B')\left\{\sum_{IA} t_{I'I}^{B'A}\langle A'I||AJ'\rangle_{DF} - \sum_{ia} t_{I'i}^{B'a}\langle A'i|J'a\rangle_{DF}\right\} \\
+\;& P_{-}(A'B')\sum_{A} t_{I'J'}^{A'A} g_{B'A} \\
-\;& P_{-}(I'J')\sum_{I} t_{I'I}^{A'B'} g_{IJ'} \\
+\;& P_{-}(I'J')\sum_{A} t_{J'}^{A}\langle A'B'||I'A\rangle_{DF} \\
-\;& P_{-}(A'B')\sum_{I} t_{I}^{B'}\langle A'I||I'J'\rangle_{DF}
\end{aligned}
\tag{27}
$$

$\beta\beta$-Block:

$$
\begin{aligned}
W_{i'j'}^{a'b'} &= \frac{1}{2}\sum_{ab} t_{i'j'}^{ab}\langle a'b'||ab\rangle_{DF} \\
&+ \frac{1}{2}\sum_{ij} t_{ij}^{a'b'}\langle ij||i'j'\rangle_{DF} \\
&+ P_{-}(i'j')P_{-}(a'b')\left\{\sum_{ia} t_{i'i}^{b'a}\langle a'i||aj'\rangle_{DF} - \sum_{IA} t_{Ii'}^{Ab'}\langle Ia'|Aj'\rangle_{DF}\right\} \\
&+ P_{-}(a'b')\sum_{a} t_{i'j'}^{a'a} g_{b'a} \\
&- P_{-}(i'j')\sum_{i} t_{i'i}^{a'b'} g_{ij'} \\
&+ P_{-}(i'j')\sum_{a} t_{j'}^{a}\langle a'b'||i'a\rangle_{DF} \\
&- P_{-}(a'b')\sum_{i} t_{i}^{b'}\langle a'i||i'j'\rangle_{DF}
\end{aligned} \tag{28}
$$

$\alpha\beta$-Block:

$$
\begin{aligned}
W_{I'j'}^{A'b'} &= \sum_{Ab} t_{I'j'}^{Ab}\langle A'b'|Ab\rangle_{DF} \\
&+ \sum_{Ij} t_{Ij}^{A'b'}\langle Ij|I'j'\rangle_{DF} \\
&- \sum_{iA} t_{I'i}^{Ab'}\langle A'i|Aj'\rangle_{DF} - \sum_{IA} t_{Ij'}^{Ab'}\langle A'I||AI'\rangle_{DF} + \sum_{ia} t_{j'i}^{b'a}\langle A'i|I'a\rangle_{DF} \\
&- \sum_{ia} t_{I'i}^{A'a}\langle b'i||aj'\rangle_{DF} + \sum_{IA} t_{I'I}^{A'A}\langle Ib'|Aj'\rangle_{DF} - \sum_{Ia} t_{Ij'}^{A'a}\langle Ib'|I'a\rangle_{DF} \\
&+ \sum_{a} t_{I'j'}^{A'a} g_{b'a} + \sum_{A} t_{I'j'}^{Ab'} g_{A'A} \\
&- \sum_{i} t_{I'i}^{A'b'} g_{ij'} - \sum_{I} t_{Ij'}^{A'b'} g_{II'} \\
&+ \sum_{a} t_{j'}^{a}\langle A'b'|I'a\rangle_{DF} + \sum_{A} t_{I'}^{A}\langle A'b'|Aj'\rangle_{DF} \\
&- \sum_{i} t_{i}^{b'}\langle A'i|I'j'\rangle_{DF} - \sum_{I} t_{I}^{A'}\langle Ib'|I'j'\rangle_{DF}
\end{aligned} \tag{29}
$$

2.6.4 Triple Replacements

$\alpha\alpha\alpha$-Block:

$$\begin{aligned} W_{I'J'K'}^{A'B'C'} &= P(I'J'/K')P(A'/B'C')\sum_{A} t_{I'J'}^{A'A}\langle B'C'||AK'\rangle_{DF} \\ &- P(I'/J'K')P(A'B'/C')\sum_{I} t_{I'I}^{A'B'}\langle IC'||J'K'\rangle_{DF} \end{aligned} \tag{30}$$

$\beta\beta\beta$-Block:

$$\begin{aligned} W_{i'j'k'}^{a'b'c'} &= P(i'j'/k')P(a'/b'c')\sum_{a} t_{i'j'}^{a'a}\langle b'c'||ak'\rangle_{DF} \\ &- P(i'/j'k')P(a'b'/c')\sum_{i} t_{i'i}^{a'b'}\langle ic'||j'k'\rangle_{DF} \end{aligned} \tag{31}$$

$\alpha\alpha\beta$-Block:

$$\begin{aligned} W_{I'J'k'}^{A'B'c'} &= P\_(A'B')\sum_{A} t_{I'J'}^{A'A}\langle B'c'|Ak'\rangle_{DF} \\ &+ P\_(A'B')\sum_{I} t_{Ik'}^{A'c'}\langle IB'||J'I'\rangle_{DF} \\ &+ P\_(I'J')\sum_{A} t_{J'k'}^{Ac'}\langle B'A'||AI'\rangle_{DF} \\ &+ P\_(I'J')\sum_{I} t_{J'I}^{A'B'}\langle Ic'|I'k'\rangle_{DF} \\ &+ P\_(I'J')P\_(A'B')\sum_{a} t_{I'k'}^{A'a}\langle B'c'|J'a\rangle_{DF} \\ &+ P\_(I'J')P\_(A'B')\sum_{i} t_{I'i}^{B'c'}\langle A'i|J'k'\rangle_{DF} \end{aligned} \tag{32}$$

$\alpha\beta\beta$-Block:

$$\begin{aligned}
W^{A'b'c'}_{I'j'k'} &= P_{-}(j'k')\sum_{a} t^{A'a}_{I'j'}\langle b'c'||ak'\rangle_{DF} \\
&+ P_{-}(j'k')\sum_{i} t^{c'b'}_{j'i}\langle A'i|I'k'\rangle_{DF} \\
&+ P_{-}(b'c')\sum_{i} t^{A'c'}_{I'i}\langle ib'||j'k'\rangle_{DF} \\
&+ P_{-}(b'c')\sum_{a} t^{c'a}_{k'j'}\langle A'b'|I'a\rangle_{DF} \\
&+ P_{-}(j'k')P_{-}(b'c')\sum_{A} t^{Ab'}_{I'j'}\langle A'c'|Ak'\rangle_{DF} \\
&+ P_{-}(j'k')P_{-}(b'c')\sum_{I} t^{A'b'}_{Ik'}\langle Ic'|I'j'\rangle_{DF} \qquad (33)
\end{aligned}$$

where

$$P_{-}(ij) = 1-\mathscr{P}(ij) \qquad (34)$$

$$P(ij/k) = 1-\mathscr{P}(ik)-\mathscr{P}(jk) \qquad (35)$$

$$P(i/jk) = 1-\mathscr{P}(ij)-\mathscr{P}(ik) \qquad (36)$$

where $\mathscr{P}(ij)$ acts to permute the indices i, j.

2.7 QDPT2 Sigma

$$H^{eff(2)}_{\beta\alpha} = E_{ref}\delta_{\alpha\beta}+W'^{(1)}_{\beta\alpha}+W^{(2)}_{\beta\alpha} \qquad (37)$$

QDPT2 σ defined as follows,

$$\sigma_{\alpha} = \sum_{\beta} H^{eff(2)}_{\beta\alpha}c_{\beta} \qquad (38)$$

Hence

$$\sigma_\alpha = E_{ref} c_\alpha + \sum_\beta W'^{(1)}_{\beta\alpha} c_\beta + \sum_\beta W^{(2)}_{\beta\alpha} c_\beta \tag{39}$$

$$\sigma_\alpha = E_{mp2} c_\alpha + \sum_{\beta \neq \alpha} W'^{(1)}_{\beta\alpha} c_\beta + \sum_{\beta \neq \alpha} W^{(2)}_{\beta\alpha} c_\beta \tag{40}$$