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# EOM-fpCCSD: An Accurate Alternative to EOM-CCSD for Doubly Excited and Charge-Transfer States

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**Electronic Supplementary Information**

## S1 EOM-fpCC and EOM-ptCC working equations

In the spin-free picture, the excitation operator for electronic excitation energies  $\hat{R}^{EE}(k)$  can be written as

$$\begin{aligned}\hat{R}^{EE}(k) &= r_0 + \sum_{i,a} r_i^a(k) \hat{E}_a^i + \frac{1}{2} \sum_{ij} \sum_{ab} r_{ij}^{ab}(k) \hat{E}_a^i \hat{E}_b^j + \dots \\ &= \hat{R}_0(k) + \hat{R}_S(k) + \hat{R}_D(k) \dots,\end{aligned}\quad (1)$$

where  $\hat{E}_a^i$  is the singlet excitation operator

$$\hat{E}_a^i = \hat{a}_a^\dagger \hat{a}_i + \hat{a}_a^\dagger \hat{a}_{\bar{i}} \quad (2)$$

and we have the symmetry relations  $r_{ij}^{ab} = r_{ji}^{ba}$  for each state  $k$ . In the following, we restrict the EOM and CC ansatz to at most double excitations. The configurational subspace during diagonalization is, then, spanned by  $\hat{E}_a^i |\Phi_0\rangle = |\Phi_i^a\rangle$  and  $\hat{E}_a^i \hat{E}_b^j |\Phi_0\rangle = |\Phi_{ij}^{ab}\rangle$ . The working equations (that is, the matrix-vector multiplication performed during the Davidson diagonalization procedure) for the various EE-EOM flavors mentioned here bear similarities to the conventional EE-EOM-CC equations and read as follows (for each  $\hat{R}$  block)

$$(\bar{H}\hat{R})_i^a = I_{ik}R_k^a + I_{ac}R_i^c + (-2I_{iakc} + I_{jakc}[i, a, k, c])R_k^c + 2I_{kc}R_{ik}^{ac} - I_{kc}R_{ki}^{ac} + I_{ilkc}R_{lk}^{ac} + I_{adkc}R_{ik}^{dc} \quad (3)$$

$$\begin{aligned}(\bar{H}\hat{R})_{ij}^{ab} &= P_{ij}^{ab} \left[ \right. \\ &I_{iabd}R_j^d + I_{ijbl}R_l^a + I_{ilkc}t_{lj}^{ab}R_k^c + I_{adkc}t_{ij}^{db}R_k^c + I_{ac}R_{ij}^{cb} + I_{ik}R_{kj}^{ab} + I_{ijkl}R_{kl}^{ab} + I_{abcd}R_{ij}^{cd} \\ &+ I_{iakc}(R_{jk}^{cb} - 2R_{kj}^{cb}) + I_{jakc}[i, a, k, c]R_{kj}^{cb} + I_{jakc}R_{ik}^{cb} \\ &- (\langle kl||cd\rangle + \langle kl|cd\rangle)t_{il}^{ab}R_{jk}^{dc} - (\langle kl||cd\rangle + \langle kl|cd\rangle)t_{ij}^{ad}R_{kl}^{cb} \\ &\left. \right] \quad (4)\end{aligned}$$

with spin-free amplitudes ( $t_{ij}^{ab} = t_{ij}^{a\bar{b}}$ ) and intermediates (all integrals are represented in the restricted orbital basis, that is,  $\langle pq|rs\rangle = \langle p\bar{q}|r\bar{s}\rangle = \langle p\bar{q}|\bar{r}s\rangle = \langle p\bar{q}|\bar{r}\bar{s}\rangle$  using Physicist's notation; summation over repeated indices is implied)

$$\begin{aligned}I_{ik}(i, k) &= -f_{ik} - f_{kd}t_i^d - (\langle kl||id\rangle + \langle kl|id\rangle)t_l^d \\ &\quad - (\langle kl||cd\rangle + \langle kl|cd\rangle)t_{il}^{cd} \\ &\quad - (\langle kl||cd\rangle + \langle kl|cd\rangle)t_i^c t_l^d\end{aligned}\quad (5)$$

$$(6)$$

$$\begin{aligned}
I_{ac} &= f_{ac} - f_{kc}t_k^a + (\langle ka||dc \rangle + \langle ka|dc \rangle) t_k^d \\
&\quad - (\langle kl||cd \rangle + \langle kl|cd \rangle) t_{kl}^{ad} \\
&\quad - (\langle kl||cd \rangle + \langle kl|cd \rangle) t_k^a t_l^d
\end{aligned} \tag{7}$$

$$I_{kc} = f_{kc} + (\langle mk||dc \rangle + \langle mk|dc \rangle) t_m^d \tag{8}$$

$$I_{iakc} = -\langle ka|ci \rangle - (\langle kl||cd \rangle + \langle kl|cd \rangle) t_{il}^{ad} + \langle kl|cd \rangle t_{il}^{da} + \langle kl|cd \rangle t_i^d t_l^a - \langle ka|cd \rangle t_i^d + \langle kl|ci \rangle t_l^a \tag{9}$$

$$I_{jakc}[j, a, k, c] = -\langle ka|jc \rangle + \langle kl|dc \rangle t_j^{da} + \langle kl|dc \rangle t_j^d t_l^a - \langle ak|cd \rangle t_j^d + \langle lk|cj \rangle t_l^a \tag{10}$$

$$I_{ilkc} = -(\langle kl||ci \rangle + \langle kl|ci \rangle) - (\langle kl||cd \rangle + \langle kl|cd \rangle) t_i^d \tag{11}$$

$$I_{adkc} = (\langle ka||cd \rangle + \langle ka|cd \rangle) - (\langle kl||cd \rangle + \langle kl|cd \rangle) t_l^a \tag{12}$$

$$\begin{aligned}
I_{iabd} &= \langle ab|id \rangle - \langle al|id \rangle t_l^b - \langle bl|di \rangle t_l^a + \langle ab|cd \rangle t_i^c \\
&\quad - f_{kd}t_{ik}^{ab} + (\langle kb||cd \rangle + \langle kb|cd \rangle) t_{ik}^{ac} - \langle kb|cd \rangle t_{ik}^{ca} - \langle ak|cd \rangle t_{ik}^{cb} + \langle kl|id \rangle t_{kl}^{ab} \\
&\quad - (\langle kl||cd \rangle + \langle kl|cd \rangle) t_k^c t_{il}^{ab} - (\langle kl||cd \rangle + \langle kl|cd \rangle) t_l^b t_{ik}^{ac} + \langle kl|cd \rangle t_l^b t_{ik}^{ca} + \langle kl|cd \rangle t_k^a t_{il}^{cb} + \langle kl|cd \rangle t_i^c t_{kl}^{ab} \\
&\quad - \langle kb|cd \rangle t_i^c t_k^a - \langle ak|cd \rangle t_i^c t_k^b + \langle kl|di \rangle t_l^a t_k^b + \langle kl|cd \rangle t_k^c t_l^b t_i^c
\end{aligned} \tag{13}$$

$$\begin{aligned}
I_{ijbl} &= -\langle bl|ji \rangle + \langle kl|ji \rangle t_k^b - \langle bl|jc \rangle t_i^c - \langle bl|ci \rangle t_j^c \\
&\quad - f_{lc}t_{ij}^{cb} - (\langle kl||ci \rangle + \langle kl|ci \rangle) t_{kj}^{cb} + \langle kl|ci \rangle t_{jk}^{cb} + \langle kl|jc \rangle t_{ik}^{cb} - \langle lb|cd \rangle t_{ij}^{cd} \\
&\quad - (\langle kl||cd \rangle + \langle kl|cd \rangle) t_k^c t_{ij}^{db} - (\langle kl||cd \rangle + \langle kl|cd \rangle) t_i^d t_{kj}^{cb} + \langle kl|cd \rangle t_i^d t_{jk}^{cb} + \langle kl|dc \rangle t_j^d t_{ik}^{cb} + \langle kl|cd \rangle t_k^b t_{ij}^{dc} \\
&\quad + \langle kl|ci \rangle t_k^b t_j^c + \langle kl|jc \rangle t_k^b t_i^c - \langle lb|cd \rangle t_i^c t_j^d + \langle lk|cd \rangle t_i^c t_j^d t_k^b
\end{aligned} \tag{14}$$

$$I_{ijkl} = \frac{1}{2} \langle ij|kl \rangle + \langle kl|cj \rangle t_i^c + \frac{1}{2} \langle kl|cd \rangle t_{ij}^{cd} + \frac{1}{2} \langle kl|cd \rangle t_i^c t_j^d \tag{15}$$

$$I_{abcd} = \frac{1}{2} \langle ab|cd \rangle - \langle kb|cd \rangle t_k^a + \frac{1}{2} \langle kl|cd \rangle t_{kl}^{ab} + \frac{1}{2} \langle kl|cd \rangle t_k^a t_l^b \quad (16)$$

For the linearized version of fpCCSD, we approximate the disconnected  $\hat{T}_1 \hat{T}_2$  term with  $\hat{T}_1 \hat{T}_p$ , while all remaining disconnected terms are neglected. We also store both pair and broken-pair amplitudes in the  $\hat{T}_2$  tensor, that is,  $\hat{T}_2 = \hat{T}'_2 + \hat{T}_p$ . Thus, we obtain the following modified set of intermediates (using the spin-free amplitudes and integrals represented in the spatial orbital basis)

$$\begin{aligned} I_{iabd}^{\text{fpLCCSD}} &= \langle ab|id \rangle - \langle al|id \rangle t_l^b - \langle bl|di \rangle t_l^a + \langle ab|cd \rangle t_i^c \\ &\quad - f_{kd} t_{ik}^{ab} + (\langle kb||cd \rangle + \langle kb|cd \rangle) t_{ik}^{ac} - \langle kb|cd \rangle t_{ik}^{ca} - \langle ak|cd \rangle t_{ik}^{cb} + \langle kl|id \rangle t_{kl}^{ab} \\ &\quad - (\langle ki||cd \rangle + \langle ki|cd \rangle) t_k^c t_{ii}^{aa} \delta_{ab} - (\langle il||ad \rangle + \langle il|ad \rangle) t_l^b t_{ii}^{aa} \\ &\quad + \langle il|ad \rangle t_l^b t_{ii}^{aa} + \langle ki|bd \rangle t_k^a t_{ii}^{bb} + \langle kk|cd \rangle t_i^c t_{kk}^{aa} \delta_{ab} \end{aligned} \quad (17)$$

$$\begin{aligned} I_{ijbl}^{\text{fpLCCSD}} &= -\langle bl|ji \rangle + \langle kl|ji \rangle t_k^b - \langle bl|jc \rangle t_i^c - \langle bl|ci \rangle t_j^c \\ &\quad - f_{ic} t_{ij}^{cb} - (\langle kl||ci \rangle + \langle kl|ci \rangle) t_{kj}^{cb} + \langle kl|ci \rangle t_{jk}^{cb} + \langle kl|jc \rangle t_{ik}^{cb} - \langle lb|cd \rangle t_{ij}^{cd} \\ &\quad - (\langle kl||cb \rangle + \langle kl|cb \rangle) t_k^c t_{ii}^{bb} \delta_{ij} - (\langle jl||bd \rangle + \langle jl|bd \rangle) t_i^d t_{jj}^{bb} \\ &\quad + \langle jl|bd \rangle t_i^d t_{jj}^{bb} + \langle il|db \rangle t_j^d t_{ii}^{bb} + \langle kl|cc \rangle t_k^b t_{ii}^{cc} \delta_{ij} \end{aligned} \quad (18)$$

Furthermore, in the  $R_D$  equations, we need to modify the following two terms to account for proper treatment of the  $\hat{T}_1 \hat{T}_2$

$$I_{ilkc}^{\text{fpLCCSD}} t_{lj}^{ab} R_k^c \rightarrow - \left[ \left( \langle kl||ci \rangle + \langle kl|ci \rangle \right) t_{ij}^{ab} + \left( \langle kj||cd \rangle + \langle kj|cd \rangle \right) t_i^d t_{jj}^{aa} \delta_{ab} \right] R_k^c \quad (19)$$

$$I_{adkc}^{\text{fpLCCSD}} t_{ij}^{db} R_k^c \rightarrow \left[ \left( \langle ka||cd \rangle + \langle ka|cd \rangle \right) t_{ij}^{db} + \left( \langle kl||cb \rangle + \langle kl|cb \rangle \right) t_l^a t_{ii}^{bb} \delta_{ij} \right] R_k^c \quad (20)$$

## S1.1 Additional terms for EOM-ptCC

In EOM-ptCC, we need to evaluate the additional terms arising from  $\langle P | \hat{\mathcal{H}}_N^{(\text{fpCC})} | 0 \rangle$  and add them to the solution vector of  $R_P$ , that is,

$$\begin{aligned}
(\hat{\mathcal{H}}_N^{\text{(fpCC)}} \hat{R})_{ii}^{aa} = & (\bar{H} \hat{R})_{ii}^{aa} + R_0 \left[ \right. \\
& + 2 \langle ic|aa \rangle t_i^c + \langle cd|aa \rangle t_i^c t_i^d \\
& - 2 \langle ic|ak \rangle t_i^c t_k^a - 2 \langle ia|kc \rangle t_i^c t_k^a - 2 \langle ka|cd \rangle t_i^c t_i^d t_k^a + 2 \langle ik|md \rangle t_m^a t_i^d t_k^a + \langle mk|cd \rangle t_i^c t_m^a t_i^d t_k^a \\
& - 2 \langle ka|ii \rangle t_k^a + \langle km|ii \rangle t_m^a t_k^a \\
& + 2f_{ac} t_{ii}^{ac} - 2f_{kc} t_k^a t_{ii}^{ac} + 2L_{kacd} t_k^c t_{ii}^{ad} - 2L_{kmcd} t_{km}^{ca} t_{ii}^{ad} - 2L_{kmcd} t_k^c t_m^a t_{ii}^{ad} \\
& - 2f_{ik} t_{ik}^{aa} - 2f_{kc} t_i^c t_{ik}^{aa} - 2L_{ickm} t_m^c t_{ik}^{aa} - 2L_{lkdc} t_l^{dc} t_{ik}^{aa} - 2L_{lkdc} t_l^d t_i^c t_{ik}^{aa} \\
& + \langle cd|aa \rangle t_{ii}^{cd} - 2 \langle ka|cd \rangle t_{ii}^{cd} t_k^a + \langle km|cd \rangle t_m^a t_{ii}^{cd} t_k^a \\
& + \langle km|ii \rangle t_{km}^{aa} + 2 \langle ik|mc \rangle t_i^c t_{km}^{aa} + \langle km|cd \rangle t_i^d t_i^c t_{km}^{aa} + \langle km|cd \rangle t_{ii}^{cd} t_{km}^{aa} \\
& + 2L_{icak} t_{ik}^{ac} - 2L_{lkic} t_l^a t_{ik}^{ac} + 2L_{kacd} t_i^d t_{ik}^{ac} + (2L_{klcd} t_{il}^{ad} - 2L_{klcd} t_{il}^{da}) t_{ik}^{ac} \\
& - 2L_{klcd} t_i^d t_l^a t_{ik}^{ac} + (-2 \langle ik|ac \rangle - 2 \langle ia|kc \rangle) t_{ki}^{ac} + (2 \langle im|kc \rangle + 2 \langle ik|mc \rangle) t_m^a t_{ki}^{ac} \\
& + (-2 \langle ka|cd \rangle - 2 \langle ka|dc \rangle) t_i^d t_{ki}^{ac} + (2 \langle lk|cd \rangle + 2 \langle lk|dc \rangle) t_i^d t_l^a t_{ki}^{ac} \\
& + (\langle km|cd \rangle + \langle km|dc \rangle) t_{im}^{da} t_{ki}^{ac} \\
& \left. \right] \tag{21}
\end{aligned}$$

## S1.2 Modified terms for EOM-fpCC

In EOM-fpCC, pair-excitations are treated at the pCCD level and we need to evaluate different terms arising from  $\langle P | \hat{\mathcal{H}}_N^{\text{(pCCD)}} | S \rangle$ ,  $\langle P | \hat{\mathcal{H}}_N^{\text{(pCCD)}} | P \rangle$ , and  $\langle P | \hat{\mathcal{H}}_N^{\text{(pCCD)}} | D \rangle$ . Thus, the pair-contributions of the EOM-fpCC diagonalization problem reduces to

$$\begin{aligned}
(\hat{\mathcal{H}}_N^{\text{(pCCD)}} \hat{R})_{ii}^{aa} = & 2 \left[ \right. \\
& I_{iak}^{\text{fp}} r_k^a + I_{iac}^{\text{fp}} r_i^c + L_{kaca} t_{ii}^{aa} r_k^c - L_{kici} t_{ii}^{aa} r_k^c \\
& + I_{ik}^{\text{fp}} r_{ik}^{aa} + I_{ac}^{\text{fp}} r_{ii}^{ac} + I_{acd}^{\text{fp}} r_{ii}^{cd} + I_{ikl}^{\text{fp}} r_{kl}^{aa} - L_{klca} t_{ii}^{aa} r_{kl}^{ca} - L_{ikdc} t_{ii}^{aa} r_{ki}^{cd} + I_{iac}^{\text{fp}} r_{ik}^{ac} + I_{iack}^{\text{fp}} r_{ik}^{ca} \\
& \left. \right] \tag{22}
\end{aligned}$$

with intermediates

$$I_{iak}^{\text{fp}} = - \langle ak|ii \rangle - f_{ak} t_{ii}^{aa} - \langle ak|ee \rangle t_{ii}^{ee} + L_{aiki} t_{ii}^{aa} \tag{23}$$

$$I_{iac}^{\text{fp}} = \langle ci|aa \rangle - f_{ci} t_{ii}^{aa} + \langle ci|ll \rangle t_{ll}^{aa} - L_{caia} t_{ii}^{aa} \tag{24}$$

$$I_{iakc}^{\text{fp}} = L_{icak} + L_{kica} t_{ii}^{aa} \quad (25)$$

$$I_{iacb}^{\text{fp}} = -\langle ic|ak\rangle - \langle ia|kc\rangle + L_{ikca} t_{ii}^{aa} \quad (26)$$

$$I_{ikl}^{\text{fp}} = \frac{1}{2} \langle kl|ii\rangle + \frac{1}{2} \langle kl|ee\rangle t_{ii}^{ee} \quad (27)$$

$$I_{acd}^{\text{fp}} = \frac{1}{2} \langle ac|dd\rangle + \frac{1}{2} \langle cd|mm\rangle t_{mm}^{aa} \quad (28)$$

$$I_{ik}^{\text{fp}} = -f_{ik} - \langle ik|ee\rangle t_{ii}^{ee} \quad (29)$$

$$I_{ac}^{\text{fp}} = f_{ac} - \langle ac|mm\rangle t_{mm}^{aa} \quad (30)$$