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 $\hat{R}^{\mathrm{EE}}(k)$ can be written as

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

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

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

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 $\hat{E}_a^i\left|\Phi_0\right\rangle = \left|\Phi_i^a\right\rangle$ and $\hat{E}_a^i\hat{E}_b^j\left|\Phi_0\right\rangle = \left|\Phi_{ij}^{ab}\right\rangle$. 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)

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

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

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

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

$$\tag{6}$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

S1.1 Additional terms for EOM-ptCC

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

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

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 $\langle P|\,\hat{\mathcal{H}}_N^{(\mathrm{pCCD})}\,|S\rangle$, $\langle P|\,\hat{\mathcal{H}}_N^{(\mathrm{pCCD})}\,|P\rangle$, and $\langle P|\,\hat{\mathcal{H}}_N^{(\mathrm{pCCD})}\,|D\rangle$. Thus, the pair-contributions of the EOM-fpCC diagonalization problem reduces to

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

with intermediates

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

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

$$I^{\mathrm{fp}}_{iakc} = L_{icak} + L_{kica} t^{aa}_{ii} \tag{25}$$

$$I^{\mathrm{fp}}_{iack} = -\langle ic|ak\rangle - \langle ia|kc\rangle + L_{ikca} t^{aa}_{ii} \tag{26}$$

$$I^{\mathrm{fp}}_{ikl} = \frac{1}{2}\langle kl|ii\rangle + \frac{1}{2}\langle kl|ee\rangle\, t^{ee}_{ii} \tag{27}$$

$$I^{\mathrm{fp}}_{acd} = \frac{1}{2}\langle ac|dd\rangle + \frac{1}{2}\langle cd|mm\rangle\, t^{aa}_{mm} \tag{28}$$

$$I^{\mathrm{fp}}_{ik} = -f_{ik} - \langle ik|ee\rangle\, t^{ee}_{ii} \tag{29}$$

$$I^{\mathrm{fp}}_{ac} = f_{ac} - \langle ac|mm\rangle\, t^{aa}_{mm} \tag{30}$$