## Appendix B: The equivalence of Hellmann-Feynman and direct CIS derivative couplings

The purpose of this supplemental appendix is to demonstrate the equivalence of the Hellmann-Feynman derivative couplings presented in Equations 81–83 with the direct derivative couplings given by Equation A23. As already discussed, this task can be reduced to proving that Equations A24 and A25 are identical. We reproduce them here, as Equations B1 ("HFT," or Hellmann-Feynman term) and B2 ("DDT," or direct-differentation term), respectively:

$$
\begin{aligned}
\mathrm{HFT} = \frac{1}{E_J - E_I} \sum_{\mu\nu} S_{\mu\nu}^{\mathrm{A}[x]} \Bigg\{ & - \sum_{\alpha\beta} \widetilde{P}_{\mu\alpha} \left( B_{\beta\nu}^{IJ} + B_{\nu\beta}^{IJ} \right) F_{\alpha\beta} \\
& - \sum_{\alpha\beta\gamma\delta} \widetilde{P}_{\mu\alpha} \left( R_{\nu\gamma}^{I} R_{\delta\beta}^{J} + R_{\delta\beta}^{I} R_{\nu\gamma}^{J} \right) \Pi_{\alpha\beta\gamma\delta} \\
& - \sum_{\alpha\beta\gamma\delta} \widetilde{P}_{\mu\alpha} \left( R_{\gamma\nu}^{I} R_{\beta\delta}^{J} + R_{\beta\delta}^{I} R_{\gamma\nu}^{J} \right) \Pi_{\alpha\beta\gamma\delta} \\
& + \sum_{\alpha\beta\gamma\delta} \widetilde{P}_{\mu\alpha} P_{\nu\delta} \left( B_{\gamma\beta}^{IJ} + B_{\beta\gamma}^{IJ} \right) \Pi_{\alpha\beta\gamma\delta} \\
& + C_{\mu b} Y_{bi} C_{\nu i} \Bigg\}
\end{aligned}
\tag{B1}
$$

$$
\mathrm{DDT} = - \sum_{\mu\nu} S_{\mu\nu}^{\mathrm{A}[x]} \left( \sum_{iab} C_{\nu a} t_i^{Ia} t_i^{Jb} C_{\mu b} + \sum_{ija} C_{\nu i} t_i^{Ia} t_j^{Ja} C_{\mu j} \right) \tag{B2}
$$

We begin by reverting to the MO representation of Equation B1:

$$\mathrm{HFT} = \frac{1}{E_J - E_I} \sum_{\mu\nu} S^{A[x]}_{\mu\nu} \Bigg\{ - \sum_{iab} t^{Ia}_i t^{Jb}_i \left(\varepsilon_a C_{\mu a} C_{\nu b} + \varepsilon_b C_{\mu b} C_{\nu a}\right) \tag{B3}$$

$$+ \sum_{ija} t^{Ia}_i t^{Ja}_j \left(\varepsilon_i C_{\mu i} C_{\nu j} + \varepsilon_j C_{\mu j} C_{\nu i}\right) \tag{B4}$$

$$- \sum_{ijwab} t^{Ia}_i t^{Jb}_j C_{\mu w} \begin{bmatrix} C_{\nu a}\Pi_{wjib} + C_{\nu j}\Pi_{awib} \\ +C_{\nu i}\Pi_{ajwb} + C_{\nu b}\Pi_{ajiw} \end{bmatrix} \tag{B5}$$

$$- \sum_{imwab} t^{Ia}_i t^{Jb}_i C_{\mu w} C_{\nu m} \left(\Pi_{awbm} + \Pi_{ambw}\right) \tag{B6}$$

$$+ \sum_{ijmwa} t^{Ia}_i t^{Ja}_j C_{\mu w} C_{\nu m} \left(\Pi_{iwjm} + \Pi_{imjw}\right) \tag{B7}$$

$$+ \sum_{ikbc} C_{\mu b} C_{\nu i} \begin{bmatrix} \sum_d \left(t^{Id}_k t^{Jc}_k + t^{Ic}_k t^{Jd}_k\right) \Pi_{cbdi} \\ + \sum_\ell \left(t^{Ib}_\ell t^{Jc}_k + t^{Ic}_k t^{Jb}_\ell\right) \Pi_{\ell cki} \\ - \sum_\ell \left(t^{Ic}_\ell t^{Jc}_k + t^{Ic}_k t^{Jc}_\ell\right) \Pi_{\ell bki} \\ + \sum_d \left(t^{Id}_i t^{Jc}_k + t^{Ic}_k t^{Jd}_i\right) \Pi_{bcdk} \end{bmatrix} \Bigg\} \tag{B8}$$

Terms B3 and B4 come from that in Equation B1 containing the Fock matrix $\mathbf{F}$; Term B5 from that containing $\mathbf{R}^I$ and $\mathbf{R}^J$; Terms B6 and B7 from that containing $\mathbf{B}^{IJ}$; and Term B8 from that containing $\mathbf{Y}$.

Next we isolate the virtual ($w \in \{a, b, c, \dots\}$) portions of the sums in Terms B6 and B7 and swap indices:

$$- \sum_{imabc} t^{Ia}_i t^{Jb}_i C_{\mu c} C_{\nu m} \left(\Pi_{acbm} + \Pi_{bcam}\right) + \sum_{ijmac} t^{Ia}_i t^{Ja}_j C_{\mu c} C_{\nu m} \left(\Pi_{icjm} + \Pi_{jcim}\right) \tag{B9}$$

$$= - \sum_{ikbcd} C_{\mu b} C_{\nu i} \left(t^{Id}_k t^{Jc}_k \Pi_{cbdi} + t^{Ic}_k t^{Jd}_k \Pi_{cbdi}\right) + \sum_{ik\ell bc} C_{\mu b} C_{\nu i} \left(t^{Ic}_\ell t^{Jc}_k \Pi_{\ell bki} + t^{Ic}_k t^{Jc}_\ell \Pi_{\ell bki}\right) \tag{B10}$$

$$= - \sum_{ikbcd} C_{\mu b} C_{\nu i} \left(t^{Id}_k t^{Jc}_k + t^{Ic}_k t^{Jd}_k\right) \Pi_{cbdi} + \sum_{ik\ell bc} C_{\mu b} C_{\nu i} \left(t^{Id}_k t^{Jc}_k + t^{Ic}_k t^{Jd}_k\right) \Pi_{\ell bki} \tag{B11}$$

These sums cancel two of the four pieces of Term B8. The remaining (occupied) sums in Terms B6 and B7, for which $w = k$, are symmetric; they vanish when traced against $\mathbf{S}^{\mathrm{A}[x]}$, per the identity

$$\mathrm{Tr}\left(\mathbf{Z}^{\mathrm{A}}\mathbf{X}\right) = \mathrm{Tr}\left(\mathbf{Z}^{\mathrm{A}}\mathbf{X}^{\mathrm{A}}\right) \tag{B12}$$

We now have

$$\mathrm{HFT} = \frac{1}{E_J - E_I} \sum_{\mu\nu} S_{\mu\nu}^{A[x]} \Bigg\{ -\sum_{iab} t_i^{Ia} t_i^{Jb} \left(\varepsilon_a C_{\mu a} C_{\nu b} + \varepsilon_b C_{\mu b} C_{\nu a}\right) \tag{B13}$$

$$+\sum_{ija} t_i^{Ia} t_j^{Ja} \left(\varepsilon_i C_{\mu i} C_{\nu j} + \varepsilon_j C_{\mu j} C_{\nu i}\right) \tag{B14}$$

$$-\sum_{ijwab} t_i^{Ia} t_j^{Jb} C_{\mu w} \begin{bmatrix} C_{\nu a}\Pi_{wjib} + C_{\nu j}\Pi_{awib} \\ +C_{\nu i}\Pi_{ajwb} + C_{\nu b}\Pi_{ajiw} \end{bmatrix} \tag{B15}$$

$$+\sum_{ikbc} C_{\mu b} C_{\nu i} \begin{bmatrix} \sum_\ell \left(t_\ell^{Ib} t_k^{Jc} + t_k^{Ic} t_\ell^{Jb}\right) \Pi_{\ell cki} \\ +\sum_d \left(t_i^{Id} t_k^{Jc} + t_k^{Ic} t_i^{Jd}\right) \Pi_{bcdk} \end{bmatrix} \Bigg\} \tag{B16}$$

One set of sums — that in Term B15 — still runs over arbitrary molecular orbitals indexed by $w$. Where $w$ takes the place of a virtual in the two-electron integral $\Pi_{ajib}$ (*e.g.*, $\Pi_{wjib}$), we isolate the occupied portion ($w \in \{i, j, k, \dots\}$) of the sum; where $w$ replaces an occupied orbital, we isolate the virtual portion. Then we permute and relabel indices on the two-electron integrals:

$$-\sum_{ijmab} t_i^{Ia} t_j^{Jb} C_{\mu m} C_{\nu a} \Pi_{mjib} - \sum_{ijmab} t_i^{Ia} t_j^{Jb} C_{\mu m} C_{\nu b} \Pi_{ajim} \tag{B17}$$
$$-\sum_{ijabc} t_i^{Ia} t_j^{Jb} C_{\mu c} C_{\nu j} \Pi_{acib} - \sum_{ijabc} t_i^{Ia} t_j^{Jb} C_{\mu c} C_{\nu i} \Pi_{ajcb}$$

$$= \sum_{ijmab} t_i^{Ia} t_j^{Jb} C_{\mu m} C_{\nu a} \Pi_{ibjm} + \sum_{ijmab} t_i^{Ia} t_j^{Jb} C_{\mu m} C_{\nu b} \Pi_{jaim} \tag{B18}$$
$$-\sum_{ijabc} t_i^{Ia} t_j^{Jb} C_{\mu c} C_{\nu j} \Pi_{cabi} - \sum_{ijabc} t_i^{Ia} t_j^{Jb} C_{\mu c} C_{\nu i} \Pi_{cbaj}$$

$$= \sum_{ik\ell bc} C_{\mu i} C_{\nu b} t_\ell^{Ib} t_k^{Jc} \Pi_{\ell cki} + \sum_{ik\ell bc} C_{\mu i} C_{\nu b} t_k^{Ic} t_\ell^{Jb} \Pi_{\ell cki} \tag{B19}$$
$$-\sum_{ikbcd} C_{\mu b} C_{\nu i} t_k^{Ic} t_i^{Jd} \Pi_{bcdk} - \sum_{ikbcd} C_{\mu b} C_{\nu i} t_i^{Id} t_k^{Jc} \Pi_{bcdk}$$

$$= \sum_{ik\ell bc} C_{\mu i} C_{\nu b} \left(t_\ell^{Ib} t_k^{Jc} + t_k^{Ic} t_\ell^{Jb}\right) \Pi_{\ell cki} \tag{B20}$$
$$-\sum_{ikbcd} C_{\mu b} C_{\nu i} \left(t_k^{Ic} t_i^{Jd} + t_i^{Id} t_k^{Jc}\right) \Pi_{bcdk}$$

Adding this piece of Term B15 to Term B16, we find that one sum cancels, leaving

$$\sum_{ik\ell bc} C_{\mu b} C_{\nu i} \left(t_\ell^{Ib} t_k^{Jc} + t_k^{Ic} t_\ell^{Jb}\right) \Pi_{\ell cki} + \sum_{ik\ell bc} C_{\mu i} C_{\nu b} \left(t_\ell^{Ib} t_k^{Jc} + t_k^{Ic} t_\ell^{Jb}\right) \Pi_{\ell cki} \tag{B21}$$

$$= \sum_{ik\ell bc} \left(C_{\mu b} C_{\nu i} + C_{\mu i} C_{\nu b}\right) \left(t_\ell^{Ib} t_k^{Jc} + t_k^{Ic} t_\ell^{Jb}\right) \Pi_{\ell cki} \tag{B22}$$

which is clearly symmetric and, thus, can be discarded. We are left with the orbital energy Terms B13 and B14 and the remaining sums from Term B15:

$$\mathrm{HFT} = \frac{1}{E_J - E_I} \sum_{\mu\nu} S_{\mu\nu}^{A[x]} \Bigg\{ -\sum_{iab} t_i^{Ia} t_i^{Jb} \left( \varepsilon_a C_{\mu a} C_{\nu b} + \varepsilon_b C_{\mu b} C_{\nu a} \right) \tag{B23}$$

$$+ \sum_{ija} t_i^{Ia} t_j^{Ja} \left( \varepsilon_i C_{\mu i} C_{\nu j} + \varepsilon_j C_{\mu j} C_{\nu i} \right) \tag{B24}$$

$$- \sum_{ijabc} t_i^{Ia} t_j^{Jb} C_{\mu c} \left( C_{\nu a} \Pi_{cjib} + C_{\nu b} \Pi_{ajic} \right) \tag{B25}$$

$$- \sum_{ijmab} t_i^{Ia} t_j^{Jb} C_{\mu m} \left( C_{\nu j} \Pi_{amib} + C_{\nu i} \Pi_{ajmb} \right) \Bigg\} \tag{B26}$$

Recall that we have the following relationship (Equation A18) between two-electron integrals and CIS energies:

$$\sum_{jb} \Pi_{ajib} t_j^{Ib} = \left( E_I + \varepsilon_i - \varepsilon_a - E_{\mathrm{HF}} \right) t_i^{Ia} \tag{B27}$$

Applying it to Terms B25 and B26, we obtain

$$\begin{aligned}
& - \sum_{iac} t_i^{Ia} t_i^{Jc} C_{\mu c} C_{\nu a} \left( E_J + \varepsilon_i - \varepsilon_c - E_{\mathrm{HF}} \right) && \text{(B28)} \\
& - \sum_{jbc} t_j^{Ic} t_j^{Jb} C_{\mu c} C_{\nu b} \left( E_I + \varepsilon_j - \varepsilon_c - E_{\mathrm{HF}} \right) \\
& - \sum_{jmb} t_m^{Ib} t_j^{Jb} C_{\mu m} C_{\nu j} \left( E_I + \varepsilon_m - \varepsilon_b - E_{\mathrm{HF}} \right) \\
& - \sum_{ima} t_i^{Ia} t_m^{Ja} C_{\mu m} C_{\nu i} \left( E_J + \varepsilon_m - \varepsilon_a - E_{\mathrm{HF}} \right) \\
= & - \sum_{iab} t_i^{Ia} t_i^{Jb} C_{\mu b} C_{\nu a} \left( E_J + \varepsilon_i - \varepsilon_b - E_{\mathrm{HF}} \right) && \text{(B29)} \\
& - \sum_{iab} t_i^{Ia} t_i^{Jb} C_{\mu a} C_{\nu b} \left( E_I + \varepsilon_i - \varepsilon_a - E_{\mathrm{HF}} \right) \\
& - \sum_{ija} t_i^{Ia} t_j^{Ja} C_{\mu i} C_{\nu j} \left( E_I + \varepsilon_i - \varepsilon_a - E_{\mathrm{HF}} \right) \\
& - \sum_{ija} t_i^{Ia} t_j^{Ja} C_{\mu j} C_{\nu i} \left( E_J + \varepsilon_j - \varepsilon_a - E_{\mathrm{HF}} \right)
\end{aligned}$$

The virtual orbital energies from the first two terms in Equation B29 cancel from Term B23, and the occupied orbital energies from the last two terms cancel from Term B24, such that we are finally left with

$$\text{HFT} = \frac{1}{E_J - E_I} \sum_{\mu\nu} S^{A[x]}_{\mu\nu} \Bigg\{ - \sum_{iab} t_i^{Ia} t_i^{Jb} C_{\mu b} C_{\nu a} \left( E_J + \varepsilon_i - E_{\text{HF}} \right) \\ - \sum_{iab} t_i^{Ia} t_i^{Jb} C_{\mu a} C_{\nu b} \left( E_I + \varepsilon_i - E_{\text{HF}} \right) \\ - \sum_{ija} t_i^{Ia} t_j^{Ja} C_{\mu i} C_{\nu j} \left( E_I - \varepsilon_a - E_{\text{HF}} \right) \\ - \sum_{ija} t_i^{Ia} t_j^{Ja} C_{\mu j} C_{\nu i} \left( E_J - \varepsilon_a - E_{\text{HF}} \right) \Bigg\} \tag{B30}$$

We can rewrite each of these terms as half the sum of its symmetrized and antisymmetrized versions — the former of which vanishes in the trace (*cf.* Equation B12). So we have

$$\text{HFT} = \frac{1}{2\left(E_J - E_I\right)} \sum_{\mu\nu} S^{A[x]}_{\mu\nu} \Bigg\{ - \sum_{iab} t_i^{Ia} t_i^{Jb} \left( C_{\mu b} C_{\nu a} - C_{\mu a} C_{\nu b} \right) \left( E_J + \varepsilon_i - E_{\text{HF}} \right) \\ - \sum_{iab} t_i^{Ia} t_i^{Jb} \left( C_{\mu a} C_{\nu b} - C_{\mu b} C_{\nu a} \right) \left( E_I + \varepsilon_i - E_{\text{HF}} \right) \\ - \sum_{ija} t_i^{Ia} t_j^{Ja} \left( C_{\mu i} C_{\nu j} - C_{\mu j} C_{\nu i} \right) \left( E_I - \varepsilon_a - E_{\text{HF}} \right) \\ - \sum_{ija} t_i^{Ia} t_j^{Ja} \left( C_{\mu j} C_{\nu i} - C_{\mu i} C_{\nu j} \right) \left( E_J - \varepsilon_a - E_{\text{HF}} \right) \Bigg\} \tag{B31}$$

$$= \frac{1}{2\left(E_J - E_I\right)} \sum_{\mu\nu} S^{A[x]}_{\mu\nu} \Bigg\{ - \sum_{iab} t_i^{Ia} t_i^{Jb} \left( C_{\mu b} C_{\nu a} - C_{\mu a} C_{\nu b} \right) \left( E_J - E_I \right) \\ - \sum_{ija} t_i^{Ia} t_j^{Ja} \left( C_{\mu j} C_{\nu i} - C_{\mu i} C_{\nu j} \right) \left( E_J - E_I \right) \Bigg\} \tag{B32}$$

$$= -\frac{1}{2} \sum_{\mu\nu} S^{A[x]}_{\mu\nu} \Bigg\{ \sum_{iab} t_i^{Ia} t_i^{Jb} \left( C_{\mu b} C_{\nu a} - C_{\mu a} C_{\nu b} \right) \\ + \sum_{ija} t_i^{Ia} t_j^{Ja} \left( C_{\mu j} C_{\nu i} - C_{\mu i} C_{\nu j} \right) \Bigg\} \tag{B33}$$

And we use Equation B12 once again — this time "in reverse," replacing an antisymmetric object with its asymmetric equivalent — to obtain

$$\text{HFT} = -\sum_{\mu\nu} S^{A[x]}_{\mu\nu} \left( \sum_{iab} C_{\nu a} t_i^{Ia} t_i^{Jb} C_{\mu b} + \sum_{ija} C_{\nu i} t_i^{Ia} t_j^{Ja} C_{\mu j} \right) = \text{DDT} \tag{B34}$$

which is exactly what we wanted. We have proven that Equations A24/B1 and A25/B2 are equivalent — and, thus, that the derivative-coupling methods given by Equations 81–83 and Equation A23 are, too.