Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information - Analytic gradient, geometry optimization and excited state potential energy surfaces from pairing matrix fluctuations and the particle-particle random phase approximation

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The details of the derivation for the analytic gradient formula is provided here.

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I. DERIVATION DETAILS OF THE EXCITATION ENERGY DERIVATIVE FROM THE PP-RPA

The matrix equation for ppRPA is given by[1]

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^\dagger & \mathbf{C} \end{pmatrix} \begin{pmatrix} \mathbf{X}^n \\ \mathbf{Y}^n \end{pmatrix} = \omega_n \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X}^n \\ \mathbf{Y}^n \end{pmatrix} \tag{1}$$

with

$$A_{ab,cd} = \langle ab||cd\rangle + \delta_{ac}\delta_{bd}(\varepsilon_a + \varepsilon_b), \tag{2}$$

$$B_{ab,hi} = \langle ab||hi\rangle, \tag{3}$$

$$C_{hi,jk} = \langle hi||jk\rangle - \delta_{hj}\delta_{ik}(\varepsilon_h + \varepsilon_i). \tag{4}$$

By virtue of Hellmann-Feynman theorem,

$$\frac{\partial \omega_n}{\partial \lambda} = \begin{pmatrix} (\mathbf{X}^n)^\dagger & (\mathbf{Y}^n)^\dagger \end{pmatrix} \left[\frac{\partial}{\partial \lambda} \begin{pmatrix} \mathbf{A}(\lambda) & \mathbf{B}(\lambda) \\ \mathbf{B}^\dagger(\lambda) & \mathbf{C}(\lambda) \end{pmatrix} \Bigg|_{\lambda=0} \right] \begin{pmatrix} \mathbf{X}^n \\ \mathbf{Y}^n \end{pmatrix}, \tag{5}$$

where the normalization

$$(\mathbf{X}^n)^\dagger \mathbf{X}^n - (\mathbf{Y}^n)^\dagger \mathbf{Y}^n = 1 \tag{6}$$

is assumed.

The first derivative **A** matrix elements are given by (note that the perturbed orbitals do not diagonalize H_s)

$$\frac{\partial}{\partial\lambda}A(\lambda)_{ab,cd} \tag{7}$$

$$= \frac{\partial}{\partial\lambda}\langle a(\lambda)b(\lambda)||c(\lambda)d(\lambda)\rangle + \frac{\partial}{\partial\lambda}\left(\delta_{bd}\left(H_s\right)_{a(\lambda)c(\lambda)} + \delta_{ac}\left(H_s\right)_{b(\lambda)d(\lambda)} - \delta_{ad}\left(H_s\right)_{b(\lambda)c(\lambda)} - \delta_{bc}\left(H_s\right)_{a(\lambda)d(\lambda)}\right) \tag{8}$$

$$= \sum_p \left(u^\lambda_{pa}\langle pb||cd\rangle + u^\lambda_{pb}\langle ap||cd\rangle + u^\lambda_{pc}\langle ab||pd\rangle + u^\lambda_{pd}\langle ab||cp\rangle\right) \tag{9}$$

$$+ \sum_p \left(\delta_{bd}u^\lambda_{pa}\langle p|H_s|c\rangle + \delta_{bd}u^\lambda_{pc}\langle a|H_s|p\rangle\right) \tag{10}$$

$$+ \sum_p \left(\delta_{ac}u^\lambda_{pb}\langle p|H_s|d\rangle + \delta_{ac}u^\lambda_{pd}\langle b|H_s|p\rangle\right) \tag{11}$$

$$- \sum_p \left(\delta_{ad}u^\lambda_{pb}\langle p|H_s|c\rangle + \delta_{ad}u^\lambda_{pc}\langle b|H_s|p\rangle\right) \tag{12}$$

$$- \sum_p \left(\delta_{bc}u^\lambda_{pa}\langle p|H_s|d\rangle + \delta_{bc}u^\lambda_{pd}\langle a|H_s|p\rangle\right) \tag{13}$$

$$+ \delta_{bd}\langle a|G^\lambda|c\rangle + \delta_{ac}\langle b|G^\lambda|d\rangle - \delta_{ad}\langle b|G^\lambda|c\rangle - \delta_{bc}\langle a|G^\lambda|d\rangle \tag{14}$$

$$+ \frac{\partial}{\partial\lambda}\langle ab||cd\rangle \tag{15}$$

$$+ \frac{\partial}{\partial\lambda}\left(\delta_{bd}\langle a|H_s|c\rangle + \delta_{ac}\langle b|H_s|d\rangle - \delta_{ad}\langle b|H_s|c\rangle - \delta_{bc}\langle a|H_s|d\rangle\right), \tag{16}$$

where (9) results from the MO derivatives in the ERI; (10) to (13) come from the direct MO derivatives in the 1-particle part; (14) comes from the induced contribution of the MO derivatives in the 1-particle part. (15) is from the nuclear shift of basis functions in the ERI; and (16) results from the nuclear shift of basis functions in the 1-particle part. Also H_s is the HF or DFT effective one-electron operator operator.

For the ERI MO derivative contribution,

$$\sum_p \left(u_{pa}^\lambda \langle pb||cd\rangle + u_{pb}^\lambda \langle ap||cd\rangle + u_{pc}^\lambda \langle ab||pd\rangle + u_{pd}^\lambda \langle ab||cp\rangle\right) \tag{17}$$

$$=\sum_e \left(u_{ea}^\lambda \langle eb||cd\rangle + u_{eb}^\lambda \langle ae||cd\rangle + u_{ec}^\lambda \langle ab||ed\rangle + u_{ed}^\lambda \langle ab||ce\rangle\right) \tag{18}$$

$$+\sum_m u_{ma}^\lambda \langle mb||cd\rangle + u_{mb}^\lambda \langle am||cd\rangle + u_{mc}^\lambda \langle ab||md\rangle + u_{md}^\lambda \langle ab||cm\rangle \tag{19}$$

$$=-\frac{1}{2}\sum_e \left(O_{ea}^\lambda \langle eb||cd\rangle + O_{eb}^\lambda \langle ae||cd\rangle + O_{ec}^\lambda \langle ab||ed\rangle + O_{ed}^\lambda \langle ab||ce\rangle\right) \tag{20}$$

$$-\sum_m \left[O_{am}^\lambda \langle mb||cd\rangle + O_{bm}^\lambda \langle am||cd\rangle + O_{cm}^\lambda \langle ab||md\rangle + O_{dm}^\lambda \langle ab||cm\rangle\right] \tag{21}$$

$$-\sum_m \left[u_{am}^\lambda \langle mb||cd\rangle + u_{bm}^\lambda \langle am||cd\rangle + u_{cm}^\lambda \langle ab||md\rangle + u_{dm}^\lambda \langle ab||cm\rangle\right], \tag{22}$$

only Line (22) involves the MO derivative coefficients u_{ai}^λ. Also, a, b, c, d, e are virtual orbitals and h, i, j, k, l, m, n designate occupied ones throughout the rest of the paper.

The direct 1-particle MO derivative contribution is

$$\sum_p \left(\delta_{bd} u_{pa}^\lambda \langle p|H_s|c\rangle + \delta_{bd} u_{pc}^\lambda \langle a|H_s|p\rangle + \delta_{ac} u_{pb}^\lambda \langle p|H_s|d\rangle + \delta_{ac} u_{pd}^\lambda \langle b|H_s|p\rangle\right) \tag{23}$$

$$-\sum_p \left(\delta_{ad} u_{pb}^\lambda \langle p|H_s|c\rangle + \delta_{ad} u_{pc}^\lambda \langle b|H_s|p\rangle + \delta_{bc} u_{pa}^\lambda \langle p|H_s|d\rangle + \delta_{bc} u_{pd}^\lambda \langle a|H_s|p\rangle\right) \tag{24}$$

$$=\delta_{bd} u_{ca}^\lambda \varepsilon_c + \delta_{bd} u_{ac}^\lambda \varepsilon_a + \delta_{ac} u_{db}^\lambda \varepsilon_d + \delta_{ac} u_{bd}^\lambda \varepsilon_b - \delta_{ad} u_{cb}^\lambda \varepsilon_c - \delta_{ad} u_{bc}^\lambda \varepsilon_b - \delta_{bc} u_{da}^\lambda \varepsilon_d - \delta_{bc} u_{ad}^\lambda \varepsilon_a \tag{25}$$

$$=-\frac{1}{2}\left[O_{ac}^\lambda \delta_{bd}(\varepsilon_a+\varepsilon_c) + O_{bd}^\lambda \delta_{ac}(\varepsilon_b+\varepsilon_d) - O_{bc}^\lambda \delta_{ad}(\varepsilon_b+\varepsilon_c) - O_{ad}^\lambda \delta_{bc}(\varepsilon_a+\varepsilon_d)\right] \tag{26}$$

which does not involve the MO derivatives.

Now the matrix element with the HF/DFT reference is

$$\langle a|G^\lambda|c\rangle \tag{27}$$

$$=\frac{\partial}{\partial\lambda}\sum_m \langle am(\lambda)|cm(\lambda)\rangle + \langle a|\frac{\partial v_{xc}}{\partial\lambda}|c\rangle \tag{28}$$

$$=\sum_p u_{pm}^\lambda \left[\langle ap|cm\rangle + \langle am|cp\rangle\right] \tag{29}$$

$$+\sum_p u_{pm}^\lambda \left(\langle ap|f_{xc}|cm\rangle + \langle am|f_{xc}|cp\rangle\right). \tag{30}$$

Thus, the induced 1-particle MO derivative contribution is

$$\delta_{bd}\langle a|G^{\lambda}|c\rangle + \delta_{ac}\langle b|G^{\lambda}|d\rangle - \delta_{ad}\langle b|G^{\lambda}|c\rangle - \delta_{bc}\langle a|G^{\lambda}|d\rangle \tag{31}$$

$$=\delta_{bd}\left\{\frac{\partial}{\partial\lambda}\sum_m \langle am(\lambda)|cm(\lambda)\rangle + \langle a|\frac{\partial v_{xc}}{\partial\lambda}|c\rangle\right\} \tag{32}$$

$$+\delta_{ac}\left\{\frac{\partial}{\partial\lambda}\sum_m \langle bm(\lambda)|dm(\lambda)\rangle + \langle b|\frac{\partial v_{xc}}{\partial\lambda}|d\rangle\right\} \tag{33}$$

$$-\delta_{ad}\left\{\frac{\partial}{\partial\lambda}\sum_m \langle bm(\lambda)|cm(\lambda)\rangle + \langle b|\frac{\partial v_{xc}}{\partial\lambda}|c\rangle\right\} \tag{34}$$

$$-\delta_{bc}\left\{\frac{\partial}{\partial\lambda}\sum_m \langle am(\lambda)|dm(\lambda)\rangle + \langle a|\frac{\partial v_{xc}}{\partial\lambda}|d\rangle\right\} \tag{35}$$

$$=\delta_{bd}\sum_p u^{\lambda}_{pm}\left[\langle ap|cm\rangle + \langle am|cp\rangle + \langle ap|f_{xc}|cm\rangle + \langle am|f_{xc}|cp\rangle\right] \tag{36}$$

$$+\delta_{ac}\sum_p u^{\lambda}_{pm}\left[\langle bp|dm\rangle + \langle bm|dp\rangle + \langle bp|f_{xc}|dm\rangle + \langle bm|f_{xc}|dp\rangle\right] \tag{37}$$

$$-\delta_{ad}\sum_p u^{\lambda}_{pm}\left[\langle bp|cm\rangle + \langle bm|cp\rangle + \langle bp|f_{xc}|cm\rangle + \langle bm|f_{xc}|cp\rangle\right] \tag{38}$$

$$-\delta_{bc}\sum_p u^{\lambda}_{pm}\left[\langle ap|dm\rangle + \langle am|dp\rangle + \langle ap|f_{xc}|dm\rangle + \langle am|f_{xc}|dp\rangle\right] \tag{39}$$

$$=-\frac{1}{2}\sum_{nm} O^{\lambda}_{nm} \tag{40}$$

$$\Big[\delta_{bd}\left(\langle an|cm\rangle + \langle am|cn\rangle + \langle an|f_{xc}|cm\rangle + \langle am|f_{xc}|cn\rangle\right) \tag{41}$$

$$+\delta_{ac}\left(\langle bn|dm\rangle + \langle bm|dn\rangle + \langle bn|f_{xc}|dm\rangle + \langle bm|f_{xc}|dn\rangle\right) \tag{42}$$

$$-\delta_{ad}\left(\langle bn|cm\rangle + \langle bm|cn\rangle + \langle bn|f_{xc}|cm\rangle + \langle bm|f_{xc}|cn\rangle\right) \tag{43}$$

$$-\delta_{bc}\left(\langle an|dm\rangle + \langle am|dn\rangle + \langle an|f_{xc}|dm\rangle + \langle am|f_{xc}|dn\rangle\right)\Big] \tag{44}$$

$$+\sum_e u^{\lambda}_{em} \tag{45}$$

$$\Big[\delta_{bd}\left(\langle ae|cm\rangle + \langle am|ce\rangle + \langle ae|f_{xc}|cm\rangle + \langle am|f_{xc}|ce\rangle\right) \tag{46}$$

$$+\delta_{ac}\left(\langle be|dm\rangle + \langle bm|de\rangle + \langle be|f_{xc}|dm\rangle + \langle bm|f_{xc}|de\rangle\right) \tag{47}$$

$$-\delta_{ad}\left(\langle be|cm\rangle + \langle bm|ce\rangle + \langle be|f_{xc}|cm\rangle + \langle bm|f_{xc}|ce\rangle\right) \tag{48}$$

$$-\delta_{bc}\left(\langle ae|dm\rangle + \langle am|de\rangle + \langle ae|f_{xc}|dm\rangle + \langle am|f_{xc}|de\rangle\right)\Big]. \tag{49}$$

The nuclear shift contribution to the ERI $\frac{\partial}{\partial\lambda}\langle ab||cd\rangle$ is not related to the MO derivatives either. Finally the nuclear shift contribution to the 1-particle part is

$$\frac{\partial}{\partial\lambda}\left(\delta_{bd}\langle a|H_s|c\rangle + \delta_{ac}\langle b|H_s|d\rangle - \delta_{ad}\langle b|H_s|c\rangle - \delta_{bc}\langle a|H_s|d\rangle\right) \tag{50}$$

$$=\frac{\partial}{\partial\lambda}\left(\langle\delta_{bd}\langle a|H^{core}|c\rangle + \delta_{ac}\langle b|H^{core}|d\rangle - \delta_{ad}\langle b|H^{core}|c\rangle - \delta_{bc}\langle a|H^{core}|d\rangle\right) \tag{51}$$

$$+\frac{\partial}{\partial\lambda}\delta_{bd}\left[\sum_m\langle am|cm\rangle + \langle a|v_{xc}|c\rangle\right] \tag{52}$$

$$+\frac{\partial}{\partial\lambda}\delta_{ac}\left[\sum_m\langle bm|dm\rangle + \langle b|v_{xc}|d\rangle\right] \tag{53}$$

$$-\frac{\partial}{\partial\lambda}\delta_{ad}\left[\sum_m\langle bm|cm\rangle + \langle b|v_{xc}|c\rangle\right] \tag{54}$$

$$-\frac{\partial}{\partial\lambda}\delta_{bc}\left[\sum_m\langle am|dm\rangle + \langle a|v_{xc}|d\rangle\right], \tag{55}$$

where

$$\frac{\partial}{\partial\lambda}\langle a|v_{xc}|c\rangle = \langle\frac{\partial}{\partial\lambda}a|v_{xc}|c\rangle + \langle a|v_{xc}|\frac{\partial}{\partial\lambda}c\rangle + \sum_m(ac|f_{xc}|\frac{\partial}{\partial\lambda}mm) \tag{56}$$

and H^{core} stands for the core Hamiltonian $-\frac{1}{2}\nabla^2_{\mathbf{r}} + v(\mathbf{r})$.

Now the first derivative of the $\mathbf{C}$ matrix elements are

$$\frac{\partial}{\partial\lambda}C(\lambda)_{hi,jk} \tag{57}$$

$$=\frac{\partial}{\partial\lambda}\langle h(\lambda)i(\lambda)||j(\lambda)k(\lambda)\rangle - \frac{\partial}{\partial\lambda}\left(\delta_{ik}\left(H_s\right)_{h(\lambda)j(\lambda)} + \delta_{hj}\left(H_s\right)_{i(\lambda)k(\lambda)} - \delta_{hk}\left(H_s\right)_{i(\lambda)j(\lambda)} - \delta_{ij}\left(H_s\right)_{h(\lambda)k(\lambda)}\right) \tag{58}$$

$$=\sum_p\left(u^\lambda_{ph}\langle pi||jk\rangle + u^\lambda_{pi}\langle hp||jk\rangle + u^\lambda_{pj}\langle hi||pk\rangle + u^\lambda_{pk}\langle hi||jp\rangle\right) \tag{59}$$

$$-\sum_p\Big[\delta_{ik}\left(u^\lambda_{ph}\langle p|H_s|j\rangle + u^\lambda_{pj}\langle h|H_s|p\rangle\right) + \delta_{hj}\left(u^\lambda_{pi}\langle p|H_s|k\rangle + u^\lambda_{pk}\langle i|H_s|p\rangle\right) \tag{60}$$

$$-\delta_{hk}\left(u^\lambda_{pi}\langle p|H_s|j\rangle + u^\lambda_{pj}\langle i|H_s|p\rangle\right) - \delta_{ij}\left(u^\lambda_{ph}\langle p|H_s|k\rangle + u^\lambda_{pk}\langle h|H_s|p\rangle\right)\Big] \tag{61}$$

$$-\left(\delta_{ik}\langle h|G^\lambda|j\rangle + \delta_{hj}\langle i|G^\lambda|k\rangle - \delta_{hk}\langle i|G^\lambda|j\rangle - \delta_{ij}\langle h|G^\lambda|k\rangle\right) \tag{62}$$

$$+\frac{\partial}{\partial\lambda}\langle hi||jk\rangle \tag{63}$$

$$-\frac{\partial}{\partial\lambda}\left(\delta_{ik}\langle h|H_s|j\rangle + \delta_{hj}\langle i|H_s|k\rangle - \delta_{hk}\langle i|H_s|j\rangle - \delta_{ij}\langle h|H_s|k\rangle\right). \tag{64}$$

Now the contribution of ERI MO derivatives is

$$\sum_p \left(u^\lambda_{ph} \langle pi||jk\rangle + u^\lambda_{pi} \langle hp||jk\rangle + u^\lambda_{pj} \langle hi||pk\rangle + u^\lambda_{pk} \langle hi||jp\rangle \right) \tag{65}$$

$$= \sum_e \left(u^\lambda_{eh} \langle ei||jk\rangle + u^\lambda_{ei} \langle he||jk\rangle + u^\lambda_{ej} \langle hi||ek\rangle + u^\lambda_{ek} \langle hi||je\rangle \right) \tag{66}$$

$$-\frac{1}{2} \sum_m \left(O^\lambda_{mh} \langle mi||jk\rangle + O^\lambda_{mi} \langle hm||jk\rangle + O^\lambda_{mj} \langle hi||mk\rangle + O^\lambda_{mk} \langle hi||jm\rangle \right) . \tag{67}$$

The direct contribution of the 1-particle MO derivatives is

$$-\sum_p \Big[\delta_{ik} \left(u^\lambda_{ph} \langle p|H_s|j\rangle + u^\lambda_{pj} \langle h|H_s|p\rangle \right) + \delta_{hj} \left(u^\lambda_{pi} \langle p|H_s|k\rangle + u^\lambda_{pk} \langle i|H_s|p\rangle \right) \tag{68}$$

$$- \delta_{hk} \left(u^\lambda_{pi} \langle p|H_s|j\rangle + u^\lambda_{pj} \langle i|H_s|p\rangle \right) - \delta_{ij} \left(u^\lambda_{ph} \langle p|H_s|k\rangle + u^\lambda_{pk} \langle h|H_s|p\rangle \right) \Big] \tag{69}$$

$$= - \left[\delta_{ik} \left(u^\lambda_{jh} \varepsilon_j + u^\lambda_{hj} \varepsilon_h \right) + \delta_{hj} \left(u^\lambda_{ki} \varepsilon_k + u^\lambda_{ik} \varepsilon_i \right) - \delta_{hk} \left(u^\lambda_{ji} \varepsilon_j + u^\lambda_{ij} \varepsilon_i \right) - \delta_{ij} \left(u^\lambda_{kh} \varepsilon_k + u^\lambda_{hk} \varepsilon_h \right) \right] \tag{70}$$

$$= \frac{1}{2} \left[\delta_{ik} O^\lambda_{jh} \left(\varepsilon_j + \varepsilon_h \right) + \delta_{hj} O^\lambda_{ik} \left(\varepsilon_k + \varepsilon_i \right) - \delta_{hk} O^\lambda_{ij} \left(\varepsilon_i + \varepsilon_j \right) - \delta_{ij} O^\lambda_{hk} \left(\varepsilon_k + \varepsilon_h \right) \right] , \tag{71}$$

which again is MO derivative independent. The induced contribution of the 1-particle MO derivatives is

$$-\left(\delta_{ik}\langle h|G^{\lambda}|j\rangle + \delta_{hj}\langle i|G^{\lambda}|k\rangle - \delta_{hk}\langle i|G^{\lambda}|j\rangle - \delta_{ij}\langle h|G^{\lambda}|k\rangle\right) \tag{72}$$

$$= -\delta_{ik}\left\{\frac{\partial}{\partial\lambda}\sum_{m}\left(\langle hm(\lambda)|jm(\lambda)\rangle + \langle hm(\lambda)|f_{xc}|jm(\lambda)\rangle\right)\right\} \tag{73}$$

$$-\delta_{hj}\left\{\frac{\partial}{\partial\lambda}\sum_{m}\left(\langle im(\lambda)|km(\lambda)\rangle + \langle im(\lambda)|f_{xc}|km(\lambda)\rangle\right)\right\} \tag{74}$$

$$+\delta_{hk}\left\{\frac{\partial}{\partial\lambda}\sum_{m}\left(\langle im(\lambda)|jm(\lambda)\rangle + \langle im(\lambda)|f_{xc}|jm(\lambda)\rangle\right)\right\} \tag{75}$$

$$+\delta_{ij}\left\{\frac{\partial}{\partial\lambda}\sum_{m}\left(\langle hm(\lambda)|km(\lambda)\rangle + \langle hm(\lambda)|f_{xc}|km(\lambda)\rangle\right)\right\} \tag{76}$$

$$= -\delta_{ik}\sum_{pm}u^{\lambda}_{pm}\left[\langle hp|jm\rangle + \langle hm|jp\rangle + \langle hp|f_{xc}|jm\rangle + \langle hm|f_{xc}|jp\rangle\right] \tag{77}$$

$$-\delta_{hj}\sum_{pm}u^{\lambda}_{pm}\left[\langle ip|km\rangle + \langle im|kp\rangle + \langle ip|f_{xc}|km\rangle + \langle im|f_{xc}|kp\rangle\right] \tag{78}$$

$$+\delta_{hk}\sum_{pm}u^{\lambda}_{pm}\left[\langle ip|jm\rangle + \langle im|jp\rangle + \langle ip|f_{xc}|jm\rangle + \langle im|f_{xc}|jp\rangle\right] \tag{79}$$

$$+\delta_{ij}\sum_{pm}u^{\lambda}_{pm}\left[\langle hp|km\rangle + \langle hm|kp\rangle + \langle hp|f_{xc}|km\rangle + \langle hm|f_{xc}|kp\rangle\right] \tag{80}$$

$$=\frac{1}{2}\delta_{ik}\sum_{nm}O^{\lambda}_{nm}\left[\langle hn|jm\rangle + \langle hm|jn\rangle + \langle hn|f_{xc}|jm\rangle + \langle hm|f_{xc}|jn\rangle\right] \tag{81}$$

$$+\frac{1}{2}\delta_{hj}\sum_{nm}O^{\lambda}_{nm}\left[\langle in|km\rangle + \langle im|kn\rangle + \langle in|f_{xc}|km\rangle + \langle im|f_{xc}|kn\rangle\right] \tag{82}$$

$$-\frac{1}{2}\delta_{hk}\sum_{nm}O^{\lambda}_{nm}\left[\langle in|jm\rangle + \langle im|jn\rangle + \langle in|f_{xc}|jm\rangle + \langle im|f_{xc}|jn\rangle\right] \tag{83}$$

$$-\frac{1}{2}\delta_{ij}\sum_{nm}O^{\lambda}_{nm}\left[\langle hn|km\rangle + \langle hm|kn\rangle + \langle hn|f_{xc}|km\rangle + \langle hm|f_{xc}|kn\rangle\right] \tag{84}$$

$$-\delta_{ik}\sum_{em}u^{\lambda}_{em}\left[\langle he|jm\rangle + \langle hm|je\rangle + \langle he|f_{xc}|jm\rangle + \langle hm|f_{xc}|je\rangle\right] \tag{85}$$

$$-\delta_{hj}\sum_{em}u^{\lambda}_{em}\left[\langle ie|km\rangle + \langle im|ke\rangle + \langle ie|f_{xc}|km\rangle + \langle im|f_{xc}|ke\rangle\right] \tag{86}$$

$$+\delta_{hk}\sum_{em}u^{\lambda}_{em}\left[\langle ie|jm\rangle + \langle im|je\rangle + \langle ie|f_{xc}|jm\rangle + \langle im|f_{xc}|je\rangle\right] \tag{87}$$

$$+\delta_{ij}\sum_{em}u^{\lambda}_{em}\left[\langle he|km\rangle + \langle hm|ke\rangle + \langle he|f_{xc}|km\rangle + \langle hm|f_{xc}|ke\rangle\right]. \tag{88}$$

The ERI nuclear shift contribution $\frac{\partial}{\partial\lambda}\langle hi||jk\rangle$ is MO derivative independent again. Finally the nuclear shift contribution to the 1-particle part

$$-\frac{\partial}{\partial\lambda}\left(\delta_{ik}\langle h|H_s|j\rangle + \delta_{hj}\langle i|H_s|k\rangle - \delta_{hk}\langle i|H_s|j\rangle - \delta_{ij}\langle h|H_s|k\rangle\right) \tag{89}$$

$$= -\frac{\partial}{\partial\lambda}\left(\delta_{ik}\langle h|H^{core}|j\rangle + \delta_{hj}\langle i|H^{core}|k\rangle - \delta_{hk}\langle i|H^{core}|j\rangle - \delta_{ij}\langle h|H^{core}|k\rangle\right) \tag{90}$$

$$-\delta_{ik}\frac{\partial}{\partial\lambda}\left[\sum_m \langle hm|jm\rangle + \langle h|v_{xc}|j\rangle\right] \tag{91}$$

$$-\delta_{hj}\frac{\partial}{\partial\lambda}\left[\sum_m \langle im|km\rangle + \langle i|v_{xc}|k\rangle\right] \tag{92}$$

$$+\delta_{hk}\frac{\partial}{\partial\lambda}\left[\sum_m \langle im|jm\rangle + \langle i|v_{xc}|j\rangle\right] \tag{93}$$

$$+\delta_{ij}\frac{\partial}{\partial\lambda}\left[\sum_m \langle hm|km\rangle + \langle h|v_{xc}|k\rangle\right], \tag{94}$$

where

$$\frac{\partial}{\partial\lambda}\langle h|v_{xc}|j\rangle = \langle\frac{\partial}{\partial\lambda}h|v_{xc}|j\rangle + \langle h|v_{xc}|\frac{\partial}{\partial\lambda}j\rangle + \sum_j (hj|f_{xc}|\frac{\partial}{\partial\lambda}mm). \tag{95}$$

is also MO derivative independent.

Now the first derivative of the **B** matrix elements are

$$\frac{\partial}{\partial\lambda}B(\lambda)_{ab,hi} = \frac{\partial}{\partial\lambda}\langle a(\lambda)b(\lambda)||h(\lambda)i(\lambda)\rangle \tag{96}$$

$$= \sum_p \left(u^\lambda_{pa}\langle pb||hi\rangle + u^\lambda_{pb}\langle ap||hi\rangle + u^\lambda_{ph}\langle ab||pi\rangle + u^\lambda_{pi}\langle ab||hp\rangle\right) \tag{97}$$

$$+\frac{\partial}{\partial\lambda}\langle ab||hi\rangle \tag{98}$$

$$= \sum_e \left(-\frac{1}{2}O^\lambda_{ea}\langle eb||hi\rangle - \frac{1}{2}O^\lambda_{eb}\langle ae||hi\rangle + u^\lambda_{eh}\langle ab||ei\rangle + u^\lambda_{ei}\langle ab||he\rangle\right) \tag{99}$$

$$-\sum_m \left(\left(u^\lambda_{am} + O^\lambda_{am}\right)\langle mb||hi\rangle + \left(u^\lambda_{bm} + O^\lambda_{bm}\right)\langle am||hi\rangle + \frac{1}{2}O^\lambda_{mh}\langle ab||mi\rangle + \frac{1}{2}O^\lambda_{mi}\langle ab||hm\rangle\right) \tag{100}$$

$$+\frac{\partial}{\partial\lambda}\langle ab||hi\rangle \tag{101}$$

Coming back to the expression of the eigenvalue first derivative,

$$\frac{\partial\omega_n}{\partial\lambda} = (\mathbf{X}^n)^\dagger\mathbf{A}^\lambda\mathbf{X}^n + (\mathbf{X}^n)^\dagger\mathbf{B}^\lambda\mathbf{Y}^n + (\mathbf{Y}^n)^\dagger\mathbf{B}^{\dagger\lambda}\mathbf{X}^n + (\mathbf{Y}^n)^\dagger\mathbf{C}^\lambda\mathbf{Y}^n, \tag{102}$$

of which the first term is given by

$$(\mathbf{X}^n)^\dagger \mathbf{A}^\lambda \mathbf{X}^n \tag{103}$$

$$= \sum_{a<b,c<d} X^n_{ab} \frac{\partial}{\partial\lambda} A(\lambda)_{ab,cd} X^n_{cd} \tag{104}$$

$$= \sum_{a<b,c<d} X^n_{ab} X^n_{cd} \tag{105}$$

$$\Bigg\{ -\frac{1}{2}\sum_e \left(O^\lambda_{ea}\langle eb||cd\rangle + O^\lambda_{eb}\langle ae||cd\rangle + O^\lambda_{ec}\langle ab||ed\rangle + O^\lambda_{ed}\langle ab||ce\rangle\right) \tag{106}$$

$$-\sum_m \left[O^\lambda_{am}\langle mb||cd\rangle + O^\lambda_{bm}\langle am||cd\rangle + O^\lambda_{cm}\langle ab||md\rangle + O^\lambda_{dm}\langle ab||cm\rangle\right] \tag{107}$$

$$-\sum_m \left[u^\lambda_{am}\langle mb||cd\rangle + u^\lambda_{bm}\langle am||cd\rangle + u^\lambda_{cm}\langle ab||md\rangle + u^\lambda_{dm}\langle ab||cm\rangle\right] \tag{108}$$

$$-\frac{1}{2}\left[O^\lambda_{ac}\delta_{bd}(\varepsilon_a+\varepsilon_c) + O^\lambda_{bd}\delta_{ac}(\varepsilon_b+\varepsilon_d) - O^\lambda_{bc}\delta_{ad}(\varepsilon_b+\varepsilon_c) - O^\lambda_{ad}\delta_{bc}(\varepsilon_a+\varepsilon_d)\right] \tag{109}$$

$$-\sum_{nm} O^\lambda_{nm} \tag{110}$$

$$\Bigg[\delta_{bd}\left(\langle an|cm\rangle + \langle an|f_{xc}|cm\rangle\right) + \delta_{ac}\left(\langle bn|dm\rangle + \langle bn|f_{xc}|dm\rangle\right) \tag{111}$$

$$-\delta_{ad}\left(\langle bn|cm\rangle + \langle bn|f_{xc}|cm\rangle\right) - \delta_{bc}\left(\langle an|dm\rangle + \langle an|f_{xc}|dm\rangle\right)\Bigg] \tag{112}$$

$$+\sum_e u^\lambda_{em} \tag{113}$$

$$\Bigg[\delta_{bd}\left(\langle ae|cm\rangle + \langle am|ce\rangle + \langle ae|f_{xc}|cm\rangle + \langle am|f_{xc}|ce\rangle\right) \tag{114}$$

$$+\delta_{ac}\left(\langle be|dm\rangle + \langle bm|de\rangle + \langle be|f_{xc}|dm\rangle + \langle bm|f_{xc}|de\rangle\right) \tag{115}$$

$$-\delta_{ad}\left(\langle be|cm\rangle + \langle bm|ce\rangle + \langle be|f_{xc}|cm\rangle + \langle bm|f_{xc}|ce\rangle\right) \tag{116}$$

$$-\delta_{bc}\left(\langle ae|dm\rangle + \langle am|de\rangle + \langle ae|f_{xc}|dm\rangle + \langle am|f_{xc}|de\rangle\right)\Bigg] \tag{117}$$

$$+\frac{\partial}{\partial\lambda}\langle ab||cd\rangle + \frac{\partial}{\partial\lambda}\left(\langle\delta_{bd}\langle a|H^{core}|c\rangle + \delta_{ac}\langle b|H^{core}|d\rangle - \delta_{ad}\langle b|H^{core}|c\rangle - \delta_{bc}\langle a|H^{core}|d\rangle\right) \tag{118}$$

$$+\frac{\partial}{\partial\lambda}\delta_{bd}\left[\sum_m \langle am|cm\rangle + \langle a|v_{xc}|c\rangle\right] \tag{119}$$

$$+\frac{\partial}{\partial\lambda}\delta_{ac}\left[\sum_m \langle bm|dm\rangle + \langle b|v_{xc}|d\rangle\right] \tag{120}$$

$$-\frac{\partial}{\partial\lambda}\delta_{ad}\left[\sum_m \langle bm|cm\rangle + \langle b|v_{xc}|c\rangle\right] \tag{121}$$

$$-\frac{\partial}{\partial\lambda}\delta_{bc}\left[\sum_m \langle am|dm\rangle + \langle a|v_{xc}|d\rangle\right]\Bigg\}, \tag{122}$$

the second and third terms are

$$2(\mathbf{X}^n)^\dagger \mathbf{B}^\lambda \mathbf{Y}^n \tag{123}$$

$$=2\sum_{a<b,h<i} X^n_{ab}\frac{\partial}{\partial\lambda}B(\lambda)_{ab,hi}Y^n_{hi} \tag{124}$$

$$=2\sum_{a<b,h<i} X^n_{ab}Y^n_{hi}\Bigg\{\sum_e\left(-\frac{1}{2}O^\lambda_{ea}\langle eb||hi\rangle-\frac{1}{2}O^\lambda_{eb}\langle ae||hi\rangle+u^\lambda_{eh}\langle ab||ei\rangle+u^\lambda_{ei}\langle ab||he\rangle\right) \tag{125}$$

$$-\sum_m\left(\left(u^\lambda_{am}+O^\lambda_{am}\right)\langle mb||hi\rangle+\left(u^\lambda_{bm}+O^\lambda_{bm}\right)\langle am||hi\rangle+\frac{1}{2}O^\lambda_{mh}\langle ab||mi\rangle+\frac{1}{2}O^\lambda_{mi}\langle ab||hm\rangle\right)+\frac{\partial}{\partial\lambda}\langle ab||hi\rangle\Bigg\}, \tag{126}$$

and finally the fourth term is

$$(\mathbf{Y}^n)^\dagger \mathbf{C}^\lambda \mathbf{Y}^n \tag{127}$$

$$= \sum_{h<i,j<k} Y^n_{hi} \frac{\partial}{\partial\lambda} C(\lambda)_{hi,jk} Y^n_{jk} \tag{128}$$

$$= \sum_{h<i,j<k} Y^n_{hi} Y^n_{jk} \tag{129}$$

$$\Bigg\{ \sum_e \left(u^\lambda_{eh}\langle ei||jk\rangle + u^\lambda_{ei}\langle he||jk\rangle + u^\lambda_{ej}\langle hi||ek\rangle + u^\lambda_{ek}\langle hi||je\rangle \right) \tag{130}$$

$$- \frac{1}{2}\sum_m \left(O^\lambda_{mh}\langle mi||jk\rangle + O^\lambda_{mi}\langle hm||jk\rangle + O^\lambda_{mj}\langle hi||mk\rangle + O^\lambda_{mk}\langle hi||jm\rangle \right) \tag{131}$$

$$+ \frac{1}{2}\left[\delta_{ik} O^\lambda_{jh}\left(\varepsilon_j + \varepsilon_h\right) + \delta_{hj} O^\lambda_{ik}\left(\varepsilon_k + \varepsilon_i\right) - \delta_{hk} O^\lambda_{ij}\left(\varepsilon_i + \varepsilon_j\right) - \delta_{ij} O^\lambda_{hk}\left(\varepsilon_k + \varepsilon_h\right) \right] \tag{132}$$

$$+ \sum_{nm} O^\lambda_{nm} \tag{133}$$

$$\Bigg[\delta_{ik}\left(\langle hn|jm\rangle + \langle hn|f_{xc}|jm\rangle\right) + \delta_{hj}\left(\langle in|km\rangle + \langle in|f_{xc}|km\rangle\right) \tag{134}$$

$$- \delta_{hk}\left(\langle in|jm\rangle + \langle in|f_{xc}|jm\rangle\right) - \delta_{ij}\left(\langle hn|km\rangle + \langle hn|f_{xc}|km\rangle\right) \Bigg] \tag{135}$$

$$- \sum_{em} u^\lambda_{em} \tag{136}$$

$$\Bigg[\delta_{ik}\left(\langle he|jm\rangle + \langle hm|je\rangle + \langle he|f_{xc}|jm\rangle + \langle hm|f_{xc}|je\rangle\right) \tag{137}$$

$$+ \delta_{hj}\left(\langle ie|km\rangle + \langle im|ke\rangle + \langle ie|f_{xc}|km\rangle + \langle im|f_{xc}|ke\rangle\right) \tag{138}$$

$$- \delta_{hk}\left(\langle ie|jm\rangle + \langle im|je\rangle + \langle ie|f_{xc}|jm\rangle + \langle im|f_{xc}|je\rangle\right) \tag{139}$$

$$- \delta_{ij}\left(\langle he|km\rangle + \langle hm|ke\rangle + \langle he|f_{xc}|km\rangle + \langle hm|f_{xc}|ke\rangle\right) \Bigg] \tag{140}$$

$$+ \frac{\partial}{\partial\lambda}\langle hi||jk\rangle - \frac{\partial}{\partial\lambda}\left(\delta_{ik}\langle h|H^{core}|j\rangle + \delta_{hj}\langle i|H^{core}|k\rangle - \delta_{hk}\langle i|H^{core}|j\rangle - \delta_{ij}\langle h|H^{core}|k\rangle \right) \tag{141}$$

$$- \delta_{ik}\frac{\partial}{\partial\lambda}\left[\sum_m \langle hm|jm\rangle + \langle h|v_{xc}|j\rangle \right] \tag{142}$$

$$- \delta_{hj}\frac{\partial}{\partial\lambda}\left[\sum_m \langle im|km\rangle + \langle i|v_{xc}|k\rangle \right] \tag{143}$$

$$+ \delta_{hk}\frac{\partial}{\partial\lambda}\left[\sum_m \langle im|jm\rangle + \langle i|v_{xc}|j\rangle \right] \tag{144}$$

$$+ \delta_{ij}\frac{\partial}{\partial\lambda}\left[\sum_m \langle hm|km\rangle + \langle h|v_{xc}|k\rangle \right] \Bigg\}. \tag{145}$$

First let us separate out those terms which are independent of the MO derivative coefficients

$$\left.\frac{\partial \omega_n}{\partial \lambda}\right|_{indpt} \tag{146}$$

$$= \sum_{a<b,c<d} X^n_{ab} X^n_{cd} \tag{147}$$

$$\Bigg\{ -\frac{1}{2}\sum_e \left(O^\lambda_{ea}\langle eb||cd\rangle + O^\lambda_{eb}\langle ae||cd\rangle + O^\lambda_{ec}\langle ab||ed\rangle + O^\lambda_{ed}\langle ab||ce\rangle\right) \tag{148}$$

$$-\sum_m \left[O^\lambda_{am}\langle mb||cd\rangle + O^\lambda_{bm}\langle am||cd\rangle + O^\lambda_{cm}\langle ab||md\rangle + O^\lambda_{dm}\langle ab||cm\rangle\right] \tag{149}$$

$$-\frac{1}{2}\left[O^\lambda_{ac}\delta_{bd}(\varepsilon_a+\varepsilon_c) + O^\lambda_{bd}\delta_{ac}(\varepsilon_b+\varepsilon_d) - O^\lambda_{bc}\delta_{ad}(\varepsilon_b+\varepsilon_c) - O^\lambda_{ad}\delta_{bc}(\varepsilon_a+\varepsilon_d)\right] \tag{150}$$

$$-\sum_{nm} O^\lambda_{nm}\Bigg[\delta_{bd}\left(\langle an|cm\rangle + \langle an|f_{xc}|cm\rangle\right) + \delta_{ac}\left(\langle bn|dm\rangle + \langle bn|f_{xc}|dm\rangle\right) \tag{151}$$

$$-\delta_{ad}\left(\langle bn|cm\rangle + \langle bn|f_{xc}|cm\rangle\right) - \delta_{bc}\left(\langle an|dm\rangle + \langle an|f_{xc}|dm\rangle\right)\Bigg] \tag{152}$$

$$+\frac{\partial}{\partial\lambda}\langle ab||cd\rangle + \frac{\partial}{\partial\lambda}\left(\delta_{bd}\langle a|H^{core}|c\rangle + \delta_{ac}\langle b|H^{core}|d\rangle - \delta_{ad}\langle b|H^{core}|c\rangle - \delta_{bc}\langle a|H^{core}|d\rangle\right) \tag{153}$$

$$+\frac{\partial}{\partial\lambda}\delta_{bd}\left[\sum_m \langle am|cm\rangle + \langle a|v_{xc}|c\rangle\right] \tag{154}$$

$$+\frac{\partial}{\partial\lambda}\delta_{ac}\left[\sum_m \langle bm|dm\rangle + \langle b|v_{xc}|d\rangle\right] \tag{155}$$

$$-\frac{\partial}{\partial\lambda}\delta_{ad}\left[\sum_m \langle bm|cm\rangle + \langle b|v_{xc}|c\rangle\right] \tag{156}$$

$$-\frac{\partial}{\partial\lambda}\delta_{bc}\left[\sum_m \langle am|dm\rangle + \langle a|v_{xc}|d\rangle\right]\Bigg\} \tag{157}$$

$$-2\sum_{a<b,h<i} X^n_{ab} Y^n_{hi}\Bigg\{\sum_e\left(\frac{1}{2}O^\lambda_{ea}\langle eb||hi\rangle + \frac{1}{2}O^\lambda_{eb}\langle ae||hi\rangle\right) \tag{158}$$

$$+\sum_m\left(O^\lambda_{am}\langle mb||hi\rangle + O^\lambda_{bm}\langle am||hi\rangle + \frac{1}{2}O^\lambda_{mh}\langle ab||mi\rangle + \frac{1}{2}O^\lambda_{mi}\langle ab||hm\rangle\right) - \frac{\partial}{\partial\lambda}\langle ab||hi\rangle\Bigg\} \tag{159}$$

$$+\sum_{h<i,j<k} Y^n_{hi} Y^n_{jk} \tag{160}$$

$$\Bigg\{ -\frac{1}{2}\sum_m \big(O^\lambda_{mh}\langle mi||jk\rangle + O^\lambda_{mi}\langle hm||jk\rangle + O^\lambda_{mj}\langle hi||mk\rangle + O^\lambda_{mk}\langle hi||jm\rangle\big) \tag{161}$$

$$+\frac{1}{2}\big[\delta_{ik}O^\lambda_{jh}\left(\varepsilon_j+\varepsilon_h\right) + \delta_{hj}O^\lambda_{ik}\left(\varepsilon_k+\varepsilon_i\right) - \delta_{hk}O^\lambda_{ij}\left(\varepsilon_i+\varepsilon_j\right) - \delta_{ij}O^\lambda_{hk}\left(\varepsilon_k+\varepsilon_h\right)\big] \tag{162}$$

$$+\sum_{nm} O^\lambda_{nm}\Bigg[\delta_{ik}\left(\langle hn|jm\rangle + \langle hn|f_{xc}|jm\rangle\right) + \delta_{hj}\left(\langle in|km\rangle + \langle in|f_{xc}|km\rangle\right) \tag{163}$$

$$-\delta_{hk}\left(\langle in|jm\rangle + \langle in|f_{xc}|jm\rangle\right) - \delta_{ij}\left(\langle hn|km\rangle + \langle hn|f_{xc}|km\rangle\right)\Bigg] \tag{164}$$

$$+\frac{\partial}{\partial\lambda}\langle hi||jk\rangle - \frac{\partial}{\partial\lambda}\left(\delta_{ik}\langle h|H^{core}|j\rangle + \delta_{hj}\langle i|H^{core}|k\rangle - \delta_{hk}\langle i|H^{core}|j\rangle - \delta_{ij}\langle h|H^{core}|k\rangle\right) \tag{165}$$

$$-\delta_{ik}\frac{\partial}{\partial\lambda}\left[\sum_m \langle hm|jm\rangle + \langle h|v_{xc}|j\rangle\right] \tag{166}$$

$$-\delta_{hj}\frac{\partial}{\partial\lambda}\left[\sum_m \langle im|km\rangle + \langle i|v_{xc}|k\rangle\right] \tag{167}$$

$$+\delta_{hk}\frac{\partial}{\partial\lambda}\left[\sum_m \langle im|jm\rangle + \langle i|v_{xc}|j\rangle\right] \tag{168}$$

$$+\delta_{ij}\frac{\partial}{\partial\lambda}\left[\sum_m \langle hm|km\rangle + \langle h|v_{xc}|k\rangle\right]\Bigg\}, \tag{169}$$

and those that are dependent on the MO coefficients

$$\left.\frac{\partial \omega_n}{\partial \lambda}\right|_{depdt} \tag{170}$$

$$= \sum_{a<b,c<d} X^n_{ab} X^n_{cd} \tag{171}$$

$$\Bigg\{ -\sum_m \left[u^\lambda_{am}\langle mb||cd\rangle + u^\lambda_{bm}\langle am||cd\rangle + u^\lambda_{cm}\langle ab||md\rangle + u^\lambda_{dm}\langle ab||cm\rangle\right] \tag{172}$$

$$+ \sum_e u^\lambda_{em} \tag{173}$$

$$\Bigg[\delta_{bd}\left(\langle ae|cm\rangle + \langle am|ce\rangle + \langle ae|f_{xc}|cm\rangle + \langle am|f_{xc}|ce\rangle\right) \tag{174}$$

$$+ \delta_{ac}\left(\langle be|dm\rangle + \langle bm|de\rangle + \langle be|f_{xc}|dm\rangle + \langle bm|f_{xc}|de\rangle\right) \tag{175}$$

$$- \delta_{ad}\left(\langle be|cm\rangle + \langle bm|ce\rangle + \langle be|f_{xc}|cm\rangle + \langle bm|f_{xc}|ce\rangle\right) \tag{176}$$

$$- \delta_{bc}\left(\langle ae|dm\rangle + \langle am|de\rangle + \langle ae|f_{xc}|dm\rangle + \langle am|f_{xc}|de\rangle\right)\Bigg]\Bigg\} \tag{177}$$

$$+2 \sum_{a<b,h<i} X^n_{ab} Y^n_{hi} \Bigg\{ \sum_e \left(u^\lambda_{eh}\langle ab||ei\rangle + u^\lambda_{ei}\langle ab||he\rangle\right) - \sum_m \left(u^\lambda_{am}\langle mb||hi\rangle + u^\lambda_{bm}\langle am||hi\rangle\right) \Bigg\} \tag{178}$$

$$+ \sum_{h<i,j<k} Y^n_{hi} Y^n_{jk} \tag{179}$$

$$\Bigg\{ \sum_e \left(u^\lambda_{eh}\langle ei||jk\rangle + u^\lambda_{ei}\langle he||jk\rangle + u^\lambda_{ej}\langle hi||ek\rangle + u^\lambda_{ek}\langle hi||je\rangle\right) \tag{180}$$

$$- \sum_{em} u^\lambda_{em} \tag{181}$$

$$\Bigg[\delta_{ik}\left(\langle he|jm\rangle + \langle hm|je\rangle + \langle he|f_{xc}|jm\rangle + \langle hm|f_{xc}|je\rangle\right) \tag{182}$$

$$+ \delta_{hj}\left(\langle ie|km\rangle + \langle im|ke\rangle + \langle ie|f_{xc}|km\rangle + \langle im|f_{xc}|ke\rangle\right) \tag{183}$$

$$- \delta_{hk}\left(\langle ie|jm\rangle + \langle im|je\rangle + \langle ie|f_{xc}|jm\rangle + \langle im|f_{xc}|je\rangle\right) \tag{184}$$

$$- \delta_{ij}\left(\langle he|km\rangle + \langle hm|ke\rangle + \langle he|f_{xc}|km\rangle + \langle hm|f_{xc}|ke\rangle\right)\Bigg]\Bigg\}. \tag{185}$$

Now let us rename the dummy variables in $\frac{\partial \omega_n}{\partial \lambda}\Big|_{depdt}$

$$\left.\frac{\partial \omega_n}{\partial \lambda}\right|_{depdt} \tag{186}$$

$$= -\sum_m \sum_{abcd} X^n_{ab} X^n_{cd} \langle mb||cd\rangle u^\lambda_{am} \tag{187}$$

$$+ 2 \sum_{(b,c)<d} X^n_{bd} X^n_{cd} \sum_{am} u^\lambda_{am} \left(\langle ba|cm\rangle + \langle ba|f_{xc}|cm\rangle\right) \tag{188}$$

$$+ 2 \sum_{d<(b,c)} X^n_{db} X^n_{dc} \sum_{am} u^\lambda_{am} \left(\langle ba|cm\rangle + \langle ba|f_{xc}|cm\rangle\right) \tag{189}$$

$$- 2 \sum_{c<d<b} X^n_{db} X^n_{cd} \sum_{am} u^\lambda_{am} \left(\langle ba|cm\rangle + \langle ba|f_{xc}|cm\rangle\right) \tag{190}$$

$$- 2 \sum_{b<d<c} X^n_{bd} X^n_{dc} \sum_{am} u^\lambda_{am} \left(\langle ba|cm\rangle + \langle ba|f_{xc}|cm\rangle\right) \tag{191}$$

$$+2 \sum_{c<b} \sum_{mi} X^n_{cb} Y^n_{mi} \sum_a \langle cb||ai\rangle u^\lambda_{am} - 2 \sum_{ab} \sum_{h<i} X^n_{ab} Y^n_{hi} \sum_m \langle mb||hi\rangle u^\lambda_{am} \tag{192}$$

$$+ \sum_{mj} \sum_{ih} Y^n_{mj} Y^n_{ih} \sum_a \langle aj||ih\rangle u^\lambda_{am} \tag{193}$$

$$- 2 \sum_{(h,j)<i} Y^n_{hi} Y^n_{ji} \sum_{am} u^\lambda_{am} \left(\langle ha|jm\rangle + \langle ha|f_{xc}|jm\rangle\right) \tag{194}$$

$$- 2 \sum_{i<(h,j)} Y^n_{ih} Y^n_{ij} \sum_{am} u^\lambda_{am} \left(\langle ha|jm\rangle + \langle ha|f_{xc}|jm\rangle\right) \tag{195}$$

$$+ 2 \sum_{j<i<h} Y^n_{ih} Y^n_{ji} \sum_{am} u^\lambda_{am} \left(\langle ha|jm\rangle + \langle ha|f_{xc}|jm\rangle\right) \tag{196}$$

$$+ 2 \sum_{h<i<j} Y^n_{hi} Y^n_{ij} \sum_{am} u^\lambda_{am} \left(\langle ha|jm\rangle + \langle ha|f_{xc}|jm\rangle\right). \tag{197}$$

where we recognize

$$ {}^{n}L_{am} \tag{198}$$

$$ = -2\sum_{b}\sum_{c<d} X^n_{ab}X^n_{cd}\langle mb||cd\rangle \tag{199}$$

$$ +2\left[\sum_{(b,c)<d} X^n_{bd}X^n_{cd} + \sum_{d<(b,c)} X^n_{db}X^n_{dc} - \sum_{c<d<b} X^n_{db}X^n_{cd} - \sum_{b<d<c} X^n_{bd}X^n_{dc}\right] \tag{200}$$

$$ \left(\langle ba|cm\rangle + \langle ba|f_{xc}|cm\rangle\right) \tag{201}$$

$$ -2\sum_{c<b}\sum_{i} X^n_{cb}Y^n_{mi}\langle cb||ia\rangle + 2\sum_{b}\sum_{h<i} X^n_{ab}Y^n_{hi}\langle bm||hi\rangle \tag{202}$$

$$ +2\sum_{j}\sum_{h<i} Y^n_{mj}Y^n_{hi}\langle aj||hi\rangle \tag{203}$$

$$ -2\left[\sum_{(h,j)<i} Y^n_{hi}Y^n_{ji} + \sum_{i<(h,j)} Y^n_{ih}Y^n_{ij} - \sum_{j<i<h} Y^n_{ih}Y^n_{ji} - \sum_{h<i<j} Y^n_{hi}Y^n_{ij}\right] \tag{204}$$

$$ \frac{\partial}{\partial\lambda}\left(\langle ha|jm\rangle + \langle ha|f_{xc}|jm\rangle\right). \tag{205}$$

Now the Z-vector method can be used. Instead of solving

$$ \mathbf{H}^{(1)}\mathbf{u}^{\lambda} = \mathbf{b}^{\lambda} \tag{206}$$

to obtain the individual MO derivatives u^{λ} for each perturbation, one can solve once and for all

$$ \mathbf{H}^{(1)}\mathbf{z}^{n} = {}^{n}\mathbf{L}, \tag{207}$$

where the matrix elements of Equation (206) are given as

$$ H^{(1)}_{ai,bj} = \delta_{ab}\delta_{ij}\left(\varepsilon_a - \varepsilon_i\right) + \sum_{bj}\left[2(ai|bj) + 2(ai|f_{xc}|bj)\right], \tag{208}$$

$$ b^{\lambda}_{ai} \tag{209}$$

$$ = -\left\{\frac{\partial}{\partial\lambda}\langle a|H^{core}|i\rangle + \frac{\partial}{\partial\lambda}\sum_{j}(ai|jj) + \sum_{j}(ai|f_{xc}|\frac{\partial}{\partial\lambda}jj) + \left[\langle\frac{\partial}{\partial\lambda}\phi_a|v_{xc}|\phi_i\rangle + \langle\phi_a|v_{xc}|\frac{\partial}{\partial\lambda}\phi_i\rangle\right]\right\} \tag{210}$$

$$ +\sum_{jk} O^{\lambda}_{jk}\left[(ai|jk) + (ai|f_{xc}|jk)\right] + \varepsilon_i O^{\lambda}_{ai}. \tag{211}$$

Then

$$ \left({}^{n}\mathbf{L}\right)^{\mathrm{T}}\mathbf{u}^{\lambda} = \left(\mathbf{z}^{n}\right)^{\mathrm{T}}\mathbf{b}^{\lambda}. \tag{212}$$

Consider how to make the evaluation of ${}^nL_{am}$'s computationally more affordable. Define the following intermediate quantities

$$ {}^nK_{mb} = \sum_{c<d} X^n_{cd} \langle mb||cd\rangle, \tag{213} $$

$$ {}^nV_{bc} = \sum_{(b,c)<d} X^n_{bd}X^n_{cd} + \sum_{d<(b,c)} X^n_{db}X^n_{dc} - \sum_{c<d<b} X^n_{db}X^n_{cd} - \sum_{b<d<c} X^n_{bd}X^n_{dc}, \tag{214} $$

$$ {}^nG_{aj} = \sum_{h<i} Y^n_{hi} \langle aj||hi\rangle, \tag{215} $$

$$ {}^nU_{hj} = \sum_{(h,j)<i} Y^n_{hi}Y^n_{ji} + \sum_{i<(h,j)} Y^n_{ih}Y^n_{ij} - \sum_{j<i<h} Y^n_{ih}Y^n_{ji} - \sum_{h<i<j} Y^n_{hi}Y^n_{ij}. \tag{216} $$

we then arrive at

$$ {}^nL_{am} = -2\sum_b X^n_{ab}\,{}^nK_{mb} + 2\sum_{bc} {}^nV_{bc}\left(\langle ba|cm\rangle + \langle ba|f_{xc}|cm\rangle\right) \tag{217} $$

$$ -2\sum_i Y^n_{mi}\,{}^nK_{ia} + 2\sum_b X^n_{ab}\,{}^nG_{bm} \tag{218} $$

$$ +2\sum_j Y^n_{mj}\,{}^nG_{aj} - 2\sum_{hj} {}^nU_{hj}\left(\langle ha|jm\rangle + \langle ha|f_{xc}|jm\rangle\right). \tag{219} $$

Thus the computational cost of constructing ${}^n\mathbf{L}$ for each excitation is $O(N^4)$, the same scaling as that of solving the Z-vector equation iteratively.

Coming back to the MO derivative independent contribution, and let us get rid of those antisymmetric restrictions, we arrive at

$$\left.\frac{\partial \omega_n}{\partial \lambda}\right|_{indpt} \tag{220}$$

$$= -\sum_{e}\sum_{ab}\sum_{c<d} X^n_{ab}X^n_{cd}O^\lambda_{ea}\langle eb||cd\rangle - 2\sum_{m}\sum_{ab}\sum_{c<d} X^n_{ab}X^n_{cd}O^\lambda_{am}\langle mb||cd\rangle \tag{221}$$

$$-\left(\sum_{(a,b)<c} X^n_{ac}X^n_{bc} + \sum_{c<(a,b)} X^n_{ca}X^n_{cb} - \sum_{b<c<a} X^n_{ca}X^n_{bc} - \sum_{a<c<b} X^n_{ac}X^n_{cb}\right) O^\lambda_{ab}\varepsilon_a \tag{222}$$

$$-\left(\sum_{(a,b)<c} X^n_{ac}X^n_{bc} + \sum_{c<(b,a)} X^n_{ca}X^n_{cb} - \sum_{a<c<b} X^n_{cb}X^n_{ac} - \sum_{b<c<a} X^n_{bc}X^n_{ca}\right) \tag{223}$$

$$\left[\sum_{nm} O^\lambda_{nm}\left(\langle am|bn\rangle + \langle am|f_{xc}|bn\rangle\right)\right] \tag{224}$$

$$+\sum_{a<b,c<d} X^n_{ab}X^n_{cd}\frac{\partial}{\partial\lambda}\langle ab||cd\rangle \tag{225}$$

$$+\left(\sum_{(a,b)<c} X^n_{ac}X^n_{bc} + \sum_{c<(b,a)} X^n_{ca}X^n_{cb} - \sum_{a<c<b} X^n_{cb}X^n_{ac} - \sum_{b<c<a} X^n_{bc}X^n_{ca}\right) \frac{\partial}{\partial\lambda}\langle a|H^{core}|b\rangle \tag{226}$$

$$+\left(\sum_{(a,b)<c} X^n_{ac}X^n_{bc} + \sum_{c<(b,a)} X^n_{ca}X^n_{cb} - \sum_{a<c<b} X^n_{cb}X^n_{ac} - \sum_{b<c<a} X^n_{bc}X^n_{ca}\right) \tag{227}$$

$$\left[\sum_{m}\frac{\partial}{\partial\lambda}\langle am|bm\rangle + \sum_{m}(ab|f_{xc}|\frac{\partial}{\partial\lambda}mm) + \langle\frac{\partial}{\partial\lambda}a|v_{xc}|b\rangle + \langle a|v_{xc}|\frac{\partial}{\partial\lambda}b\rangle\right] \tag{228}$$

$$-\sum_{ab}\sum_{h<i} X^n_{ab}Y^n_{hi}\sum_{e} O^\lambda_{ea}\langle eb||hi\rangle - 2\sum_{ab}\sum_{h<i} X^n_{ab}Y^n_{hi}\sum_{m} O^\lambda_{am}\langle mb||hi\rangle - \sum_{a<b}\sum_{hi} X^n_{ab}Y^n_{hi}\sum_{m} O^\lambda_{mh}\langle ab||mi\rangle \tag{229}$$

$$+2\sum_{a<b,h<i} X^n_{ab}Y^n_{hi}\frac{\partial}{\partial\lambda}\langle ab||hi\rangle \tag{230}$$

$$-\sum_{hi}\sum_{j<k}\sum_{m} Y^n_{hi}Y^n_{jk}O^\lambda_{mh}\langle mi||jk\rangle \tag{231}$$

$$+\left(\sum_{(h,i)<j} Y^n_{hj}Y^n_{ij} + \sum_{j<(h,i)} Y^n_{jh}Y^n_{ji} - \sum_{i<j<h} Y^n_{jh}Y^n_{ij} - \sum_{h<j<i} Y^n_{hj}Y^n_{ji}\right) O^\lambda_{ih}\varepsilon_h \tag{232}$$

$$+\left(\sum_{(h,i)<j} Y^n_{hj}Y^n_{ij} + \sum_{j<(h,i)} Y^n_{jh}Y^n_{ji} - \sum_{i<j<h} Y^n_{jh}Y^n_{ij} - \sum_{h<j<i} Y^n_{hj}Y^n_{ji}\right) \tag{233}$$

$$\left[\sum_{nm} O^\lambda_{nm}\left(\langle hm|in\rangle + \langle hm|f_{xc}|in\rangle\right)\right] \tag{234}$$

$$+\sum_{h<i,j<k} Y_{hi}^n Y_{jk}^n \frac{\partial}{\partial\lambda}\langle hi||jk\rangle \tag{235}$$

$$-\left(\sum_{(h,i)<j} Y_{hj}^n Y_{ij}^n + \sum_{j<(h,i)} Y_{jh}^n Y_{ji}^n - \sum_{i<j<h} Y_{jh}^n Y_{ij}^n - \sum_{h<j<i} Y_{hj}^n Y_{ji}^n\right) \frac{\partial}{\partial\lambda}\langle h|H^{core}|i\rangle \tag{236}$$

$$-\left(\sum_{(h,i)<j} Y_{hj}^n Y_{ij}^n + \sum_{j<(h,i)} Y_{jh}^n Y_{ji}^n - \sum_{i<j<h} Y_{jh}^n Y_{ij}^n - \sum_{h<j<i} Y_{hj}^n Y_{ji}^n\right) \tag{237}$$

$$\left[\sum_m \frac{\partial}{\partial\lambda}\langle hm|im\rangle + \sum_m (hi|f_{xc}|\frac{\partial}{\partial\lambda}mm) + \langle\frac{\partial}{\partial\lambda}h|v_{xc}|i\rangle + \langle h|v_{xc}|\frac{\partial}{\partial\lambda}i\rangle\right]. \tag{238}$$

With the definitions given by Lines (213) to (216) we obtain

$$\left.\frac{\partial\omega_n}{\partial\lambda}\right|_{indpt} \tag{239}$$

$$= -\sum_e \sum_{ab} X_{ab}{}^n K_{eb} O_{ea}^\lambda - 2\sum_m \sum_{ab} X_{ab}^n{}^n K_{mb} O_{am}^\lambda - \sum_{ab} {}^n V_{ab} O_{ab}^\lambda \varepsilon_a \tag{240}$$

$$-\sum_{ab} {}^n V_{ab} \left[\sum_{nm} O_{nm}^\lambda \left(\langle am|bn\rangle + \langle am|f_{xc}|bn\rangle\right)\right] \tag{241}$$

$$+\sum_{a<b,c<d} X_{ab}^n X_{cd}^n \frac{\partial}{\partial\lambda}\langle ab||cd\rangle + \sum_{ab} {}^n V_{ab} \frac{\partial}{\partial\lambda}\langle a|H^{core}|b\rangle \tag{242}$$

$$+\sum_{ab} {}^n V_{ab} \left[\sum_m \frac{\partial}{\partial\lambda}\langle am|bm\rangle + \sum_m (ab|f_{xc}|\frac{\partial}{\partial\lambda}mm) + \langle\frac{\partial}{\partial\lambda}a|v_{xc}|b\rangle + \langle a|v_{xc}|\frac{\partial}{\partial\lambda}b\rangle\right] \tag{243}$$

$$-\sum_{ab}\sum_e X_{ab}^n{}^n G_{eb} O_{ea}^\lambda + 2\sum_{ab}\sum_m X_{ab}^n{}^n G_{bm} O_{am}^\lambda - \sum_{hi}\sum_m Y_{hi}^{nn} K_{mi} O_{mh}^\lambda + 2\sum_{a<b,h<i} X_{ab}^n Y_{hi}^n \frac{\partial}{\partial\lambda}\langle ab||hi\rangle \tag{244}$$

$$-\sum_{hi}\sum_m Y_{hi}^{nn} G_{mi} O_{mh}^\lambda + \sum_{hi} {}^n U_{hi} O_{ih}^\lambda \varepsilon_h \tag{245}$$

$$+\sum_{hi} {}^n U_{hi} \left[\sum_{nm} O_{nm}^\lambda \left(\langle hm|in\rangle + \langle hm|f_{xc}|in\rangle\right)\right] \tag{246}$$

$$+\sum_{h<i,j<k} Y_{hi}^n Y_{jk}^n \frac{\partial}{\partial\lambda}\langle hi||jk\rangle \sum_{hi} {}^n U_{hi} \frac{\partial}{\partial\lambda}\langle h|H^{core}|i\rangle \tag{247}$$

$$-\sum_{hi} {}^n U_{hi} \left[\sum_m \frac{\partial}{\partial\lambda}\langle hm|im\rangle + \sum_m (hi|f_{xc}|\frac{\partial}{\partial\lambda}mm) + \langle\frac{\partial}{\partial\lambda}h|v_{xc}|i\rangle + \langle h|v_{xc}|\frac{\partial}{\partial\lambda}i\rangle\right]. \tag{248}$$

Thus excitation energy gradient calculation procedure is $O(N^4)$.

II. ALTERNATIVE DERIVATION FROM THE LANGRANGIAN APPROACH

In this part we derive the pp-RPA excitation energy gradient using the Lagrangian formulation by Furche and Ahlrichs[2]. The pp-RPA equation is given by

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^\dagger & \mathbf{C} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}, \tag{249}$$

where

$$A_{ab,cd} = \delta_{ac}\langle b|H_s|d\rangle + \delta_{bd}\langle a|H_s|c\rangle - \delta_{ad}\langle b|H_s|c\rangle - \delta_{bc}\langle a|H_s|d\rangle - 2\mu + \langle ab||cd\rangle, \tag{250}$$

$$B_{ab,ij} = \langle ab||ij\rangle, \tag{251}$$

$$C_{ij,kl} = -\delta_{ik}\langle j|H_s|l\rangle - \delta_{jl}\langle i|H_s|k\rangle + \delta_{il}\langle j|H_s|k\rangle + \delta_{jk}\langle i|H_s|l\rangle + 2\mu + \langle ij||kl\rangle, \tag{252}$$

and we have $i<j$, $a<b$. The normalization

$$\mathbf{X}^\dagger\mathbf{X} - \mathbf{Y}^\dagger\mathbf{Y} = 1 \tag{253}$$

is satisfied. The pp-RPA equation can also be rewritten compactly as

$$\Lambda|X,Y\rangle = \omega\Delta|X,Y\rangle, \tag{254}$$

Now let us define the functional

$$G[X,Y,\omega] = \langle X,Y|\Lambda|X,Y\rangle - \omega\left(\langle X,Y|\Delta|X,Y\rangle - 1\right). \tag{255}$$

The variational principle dictates the following stationary conditions for G,

$$\frac{\delta G}{\delta\langle X,Y|} = \left(\Lambda - \omega\Delta\right)|X,Y\rangle = 0, \tag{256}$$

$$\frac{\delta G}{\delta\omega} = -\left(\langle X,Y|\Delta|X,Y\rangle - 1\right) = 0. \tag{257}$$

The first condition recovers the pp-RPA equation and the second one yields the normalization condition. Therefore

$$\omega^\lambda = G^\lambda[X,Y,\omega] = \langle X,Y|\Lambda^\lambda|X,Y\rangle. \tag{258}$$

The Λ^λ matrix includes both direct contributions due to shifts of the basis functions and indirect contributions due to the relaxation of molecular orbitals. We can choose to proceed with the evaluation of G^λ and afterwards group together the direct and indirect contributions, as in our current implementation. The molecular orbital first derivatives can be eliminated later using the Z-vector technique.

As an alternative, we may choose to avoid the introduction of the molecular orbital derivatives from the very beginning by introducing the following functional,

$$L[X,Y,\omega,c,Z,W] = G[X,Y,\omega] + \sum_{ia} Z_{ia}\left(H_s\right)_{ia} - \sum_{pq,p\leq q} W_{pq}(O_{pq} - \delta_{pq}). \tag{259}$$

The variational principle applied to L with respect to $\langle X,Y|$ and ω yields Equations (256) and (257). The next two conditions give the Brillouin's theorem

$$\frac{\delta L}{\delta Z_{ia}} = \left(H_s\right)_{ia} = 0 \tag{260}$$

and the molecular orbital orthonormality condition

$$\frac{\delta L}{\delta W_{pq}} = -\left(O_{pq} - \delta_{pq}\right) = 0. \tag{261}$$

Now the Lagrange multipliers Z and W are fixed by the stationary condition with respect to the molecular orbital coefficients,

$$\frac{\delta L}{\delta c_{\mu p}} = 0. \tag{262}$$

Thus the derivative of the excitation energies follows as

$$\begin{aligned}\omega^{\lambda} =& L^{\lambda}[X,Y,\omega,c,Z,W] \\ =& G^{(\lambda)}[X,Y,\omega] + \sum_{ia} Z_{ia}\left(H_s\right)_{ia}^{(\lambda)} - \sum_{pq,p\leq q} W_{pq} O_{pq}^{(\lambda)},\end{aligned} \tag{263}$$

where the (λ) indicates that only the direct derivative with respect to the shift of basis functions is taken. Thus we see that the dependence on the MO coefficients has been eliminated using the L functional.

Now we proceed to solve the Lagrange multipliers Z and W from Equation (262). Multiplying $c_{\mu q}$ on both sides and summing over μ, we arrive at

$$Q_{pq} + \sum_{ia} Z_{ia} \sum_{\mu} \frac{\partial\left(H_s\right)_{ia}}{\partial c_{\mu p}} c_{\mu q} = \sum_{rs,r\leq s} W_{rs} \sum_{\mu} \frac{\partial O_{rs}}{\partial c_{\mu p}} c_{\mu q}, \tag{264}$$

where

$$Q_{pq} = \sum_{\mu} \frac{\partial G[X,Y,\omega]}{\partial c_{\mu p}} c_{\mu q}. \tag{265}$$

Let us also mark that

$$\left(H_s\right)_{ia} = \left(H^{core}\right)_{ia} + \sum_{j}\left[(ia|jj) - c_x(ij|ja)\right] + V_{ia}^{xc}, \tag{266}$$

where c_x stands for the amount of HF exchange, which is separated out from the LDA/GGA contributions for the sake of clarity following Furche and Ahrichs' convention.

The right hand side (RHS) is the same as in the particle-hole case, and so is the second term on the left hand side (LHS). The results are give as below.

1. $p = i \leq q = j$

$$\sum_{rs, r\leq s} W_{rs} \sum_{\mu} \frac{\partial O_{rs}}{\partial c_{\mu i}} c_{\mu j} = W_{ij}(1 + \delta_{ij}), \tag{267}$$

$$\sum_{i_1 a_1} Z_{i_1 a_1} \sum_{\mu} \frac{\partial \left(H_s\right)_{i_1 a_1}}{\partial c_{\mu i}} c_{\mu j} = \sum_{i_1 a_1} \left\{ 2(ij|i_1 a_1) + 2 f^{xc}_{ij, i_1 a_1} - c_x \left[(ii_1|ja_1) + (ia_1|ji_1) \right] \right\} Z_{i_1 a_1} \equiv H^+_{ij}[Z], \tag{268}$$

where we also defined $H^+_{pq}[Z]$.

2. $p = i, q = a$

$$\sum_{rs, r\leq s} W_{rs} \sum_{\mu} \frac{\partial O_{rs}}{\partial c_{\mu i}} c_{\mu a} = W_{ia}, \tag{269}$$

$$\sum_{i_1 a_1} Z_{i_1 a_1} \sum_{\mu} \frac{\partial \left(H_s\right)_{i_1 a_1}}{\partial c_{\mu i}} c_{\mu a} \tag{270}$$

$$= Z_{ia}\varepsilon_a + \sum_{i_1 a_1} \left\{ 2(ia|i_1 a_1) + 2 f^{xc}_{ia, i_1 a_1} - c_x \left[(ii_1|aa_1) + (ia_1|ai_1) \right] \right\} Z_{i_1 a_1} \tag{271}$$

$$= Z_{ia}\varepsilon_a + H^+_{ia}[Z]. \tag{272}$$

3. $p = a, q = i$

$$\sum_{rs, r\leq s} W_{rs} \sum_{\mu} \frac{\partial O_{rs}}{\partial c_{\mu a}} c_{\mu i} = W_{ia}, \tag{273}$$

$$\sum_{i_1 a_1} Z_{i_1 a_1} \sum_{\mu} \frac{\partial \left(H_s\right)_{i_1 a_1}}{\partial c_{\mu a}} c_{\mu i} = Z_{ia}\varepsilon_{i\sigma}. \tag{274}$$

4. $p = a \leq q = b$

$$\sum_{rs, r\leq s} W_{rs} \sum_{\mu} \frac{\partial O_{rs}}{\partial c_{\mu a}} c_{\mu b} = W_{ab}(1 + \delta_{ab}), \tag{275}$$

$$\sum_{i_1 a_1} Z_{i_1 a_1} \sum_{\mu} \frac{\partial \left(H_s\right)_{i_1 a_1}}{\partial c_{\mu a}} c_{\mu b} = 0. \tag{276}$$

Thus now we only need to consider the derivatives with respect to

$$G[X, Y, \omega] \tag{277}$$

$$= \langle X, Y|\Lambda|X, Y\rangle - \omega \left(\langle X, Y|\Delta|X, Y\rangle - 1 \right). \tag{278}$$

Now that

$$\frac{\partial\langle X,Y|}{\partial c_{\mu p}}\Lambda|X,Y\rangle-\omega\frac{\partial\langle X,Y|}{\partial c_{\mu p}}\Delta|X,Y\rangle \tag{279}$$

$$=\frac{\partial\langle X,Y|}{\partial c_{\mu p}}\left(\Lambda|X,Y\rangle-\omega\Delta|X,Y\rangle\right)=0 \tag{280}$$

due to Equation (254), we only have to take the derivative with respect to Λ. Assuming that the orbitals are real, we rewrite

$$G[X,Y,\omega] \tag{281}$$

$$=\mathbf{X}^{\mathrm{T}}\mathbf{A}\mathbf{X}+2\mathbf{X}^{\mathrm{T}}\mathbf{B}\mathbf{Y}+\mathbf{Y}^{\mathrm{T}}\mathbf{C}\mathbf{Y}-\omega\left(\mathbf{X}^{\mathrm{T}}\mathbf{X}-\mathbf{Y}^{\mathrm{T}}\mathbf{Y}-1\right) \tag{282}$$

$$=\sum_{a<b}\sum_{c<d}X_{ab}A_{ab,cd}X_{cd}+2\sum_{a<b}\sum_{i<j}X_{ab}B_{ab,ij}Y_{ij}+\sum_{i<j}\sum_{k<l}Y_{ij}C_{ij,kl}Y_{kl} \tag{283}$$

$$-\omega\left(\sum_{a<b}X_{ab}X_{ab}-\sum_{i<j}Y_{ij}Y_{ij}-1\right) \tag{284}$$

Now let us evaluate them case by case.

1. $p=i_1\leq q=j_1$

The derivative in the first term $\mathbf{X}^{\mathrm{T}}\mathbf{A}\mathbf{X}$,

$$\sum_{\mu}\frac{\partial A_{ab,cd}}{\partial c_{\mu i_1}}c_{\mu j_1} \tag{285}$$

$$=\sum_{\mu}\frac{\partial}{\partial c_{\mu i_1}}\left(\delta_{ac}\langle b|H_s|d\rangle+\delta_{bd}\langle a|H_s|c\rangle-\delta_{ad}\langle b|H_s|c\rangle-\delta_{bc}\langle a|H_s|d\rangle-2\mu+(ac|bd)-(ad|bc)\right)c_{\mu j_1}. \tag{286}$$

There are only the implicit contributions from the H_s terms. Now

$$\sum_{\mu}\frac{\partial}{\partial c_{\mu i_1}}\langle b|H_s|d\rangle c_{\mu j_1} \tag{287}$$

$$=\sum_{\mu}\left(\frac{\partial}{\partial c_{\mu i_1}}\sum_{j}\left[(bd|jj)-c_x(bj|jd)\right]+\left.\frac{\partial V^{xc}_{bd}}{\partial c_{\mu i_1}}\right|_{indirect}\right)c_{\mu j_1} \tag{288}$$

$$=(bd|j_1i_1)+(bd|i_1j_1)-c_x\left[(bj_1|i_1d)+(bi_1|j_1d)\right]+f^{xc}_{bd,j_1i_1}+f^{xc}_{bd,i_1j_1} \tag{289}$$

$$=2(i_1j_1|bd)+2f^{xc}_{i_1j_1,bd}-c_x\left[(i_1b|j_1d)+(i_1d|j_1b)\right], \tag{290}$$

$$\sum_{\mu}\frac{\partial}{\partial c_{\mu i_1}}\langle a|H_s|c\rangle c_{\mu j_1} \tag{291}$$

$$=2(i_1j_1|ac)+2f^{xc}_{i_1j_1,ac}-c_x\left[(i_1a|j_1c)+(i_1c|j_1a)\right], \tag{292}$$

$$\sum_{\mu} \frac{\partial}{\partial c_{\mu i_1}} \langle b|H_s|c\rangle c_{\mu j_1} \tag{293}$$

$$=2(i_1 j_1|bc) + 2f^{xc}_{i_1 j_1,bc} - c_x \left[(i_1 b|j_1 c) + (i_1 c|j_1 b)\right], \tag{294}$$

$$\sum_{\mu} \frac{\partial}{\partial c_{\mu i_1}} \langle a|H_s|d\rangle c_{\mu j_1} \tag{295}$$

$$=2(i_1 j_1|ad) + 2f^{xc}_{i_1 j_1,ad} - c_x \left[(i_1 a|j_1 d) + (i_1 d|j_1 a)\right]. \tag{296}$$

Therefore using the antisymmetry relations $X_{ab} = -X_{ba}, Y_{ij} = -Y_{ji}$,

$$\sum_{a<b} \sum_{c<d} X_{ab} \left(\sum_{\mu} \frac{\partial A_{ab,cd}}{\partial c_{\mu i_1}} c_{\mu j_1} \right) X_{cd} \tag{297}$$

$$= \sum_{a<(b,d)} X_{ab} \left(2(i_1 j_1|bd) + 2f^{xc}_{i_1 j_1,bd} - c_x \left[(i_1 b|j_1 d) + (i_1 d|j_1 b)\right]\right) X_{ad} \tag{298}$$

$$+ \sum_{(a,c)<b} X_{ab} \left(2(i_1 j_1|ac) + 2f^{xc}_{i_1 j_1,ac} - c_x \left[(i_1 a|j_1 c) + (i_1 c|j_1 a)\right]\right) X_{cb} \tag{299}$$

$$- \sum_{c<a<b} X_{ab} \left(2(i_1 j_1|bc) + 2f^{xc}_{i_1 j_1,bc} - c_x \left[(i_1 b|j_1 c) + (i_1 c|j_1 b)\right]\right) X_{ca} \tag{300}$$

$$- \sum_{a<b<d} X_{ab} \left(2(i_1 j_1|ad) + 2f^{xc}_{i_1 j_1,ad} - c_x \left[(i_1 a|j_1 d) + (i_1 d|j_1 a)\right]\right) X_{bd} \tag{301}$$

$$= \sum_{a<(b,c)} X_{ab} \left(2(i_1 j_1|bc) + 2f^{xc}_{i_1 j_1,bc} - c_x \left[(i_1 b|j_1 c) + (i_1 c|j_1 b)\right]\right) X_{ac} \tag{302}$$

$$+ \sum_{(b,c)<a} X_{ba} \left(2(i_1 j_1|bc) + 2f^{xc}_{i_1 j_1,bc} - c_x \left[(i_1 b|j_1 c) + (i_1 c|j_1 b)\right]\right) X_{ca} \tag{303}$$

$$- \sum_{c<a<b} X_{ab} \left(2(i_1 j_1|bc) + 2f^{xc}_{i_1 j_1,bc} - c_x \left[(i_1 b|j_1 c) + (i_1 c|j_1 b)\right]\right) X_{ca} \tag{304}$$

$$- \sum_{b<a<c} X_{ba} \left(2(i_1 j_1|bc) + 2f^{xc}_{i_1 j_1,bc} - c_x \left[(i_1 b|j_1 c) + (i_1 c|j_1 b)\right]\right) X_{ac} \tag{305}$$

$$= \sum_{bc} \left(2(i_1 j_1|bc) + 2f^{xc}_{i_1 j_1,bc} - c_x \left[(i_1 b|j_1 c) + (i_1 c|j_1 b)\right]\right) V_{bc} \tag{306}$$

$$=H^{+}_{i_1 j_1}[V], \tag{307}$$

where we defined

$$V_{bc} = \sum_{a<(b,c)} X_{ab} X_{ac} + \sum_{(b,c)<a} X_{ba} X_{ca} - \sum_{c<a<b} X_{ab} X_{ca} - \sum_{b<a<c} X_{ba} X_{ac}. \tag{308}$$

The derivative with respect to the second term $2\mathbf{X}^{\mathrm{T}}\mathbf{B}\mathbf{Y}$,

$$\sum_{\mu} \frac{\partial B_{ab,ij}}{\partial c_{\mu i_1}} c_{\mu j_1} \tag{309}$$

$$= \sum_{\mu} \frac{\partial}{\partial c_{\mu i_1}} \left[(ai|bj) - (aj|bi)\right] c_{\mu j_1} \tag{310}$$

$$= \delta_{i_1 i} \left[(aj_1|bj) - (aj|bj_1)\right] + \delta_{i_1 j} \left[(ai|bj_1) - (aj_1|bi)\right]. \tag{311}$$

Therefore,

$$2 \sum_{a<b} \sum_{i<j} X_{ab} \left(\sum_{\mu} \frac{\partial B_{ab,ij}}{\partial c_{\mu i_1}} c_{\mu j_1} \right) Y_{ij} \tag{312}$$

$$= 2 \sum_{a<b} \sum_{i<j} X_{ab} \left(\delta_{i_1 i} \left[(aj_1|bj) - (aj|bj_1)\right] + \delta_{i_1 j} \left[(ai|bj_1) - (aj_1|bi)\right] \right) Y_{ij} \tag{313}$$

$$= 2 \sum_{a<b} \sum_{i_1<j} X_{ab} \left[(aj_1|bj) - (aj|bj_1)\right] Y_{i_1 j} + 2 \sum_{a<b} \sum_{i<i_1} X_{ab} \left[(ai|bj_1) - (aj_1|bi)\right] Y_{i i_1} \tag{314}$$

$$= 2 \sum_{a<b} \sum_{i_1<i} X_{ab} \left[(aj_1|bi) - (ai|bj_1)\right] Y_{i_1 i} + 2 \sum_{a<b} \sum_{i<i_1} X_{ab} \left[(ai|bj_1) - (aj_1|bi)\right] Y_{i i_1} \tag{315}$$

$$= 2 \sum_{a<b} \sum_{i_1<i} X_{ab} \left[(ib|aj_1) - (ia|bj_1)\right] Y_{i_1 i} + 2 \sum_{a<b} \sum_{i<i_1} X_{ab} \left[(j_1 b|ai) - (j_1 a|bi)\right] Y_{i i_1} \tag{316}$$

$$\equiv 2 \sum_{i_1<i} Y_{i_1 i} H^{-}_{i j_1}[X] + 2 \sum_{i<i_1} H^{-}_{j_1 i}[X] Y_{i i_1}, \tag{317}$$

where we also defined $H^{-}_{pq}[X]$. The derivative with respect to the third term $\mathbf{Y}^{\mathrm{T}}\mathbf{C}\mathbf{Y}$,

$$\sum_{\mu} \frac{\partial C_{ij,kl}}{\partial c_{\mu i_1}} c_{\mu j_1} \tag{318}$$

$$= \sum_{\mu} \frac{\partial}{\partial c_{\mu i_1}} \left[-\delta_{ik} \langle j|H_s|l\rangle - \delta_{jl} \langle i|H_s|k\rangle + \delta_{il} \langle j|H_s|k\rangle + \delta_{jk} \langle i|H_s|l\rangle + 2\mu + \langle ij||kl\rangle \right] c_{\mu j_1}. \tag{319}$$

The contributions with respect to H_s are

$$\sum_{\mu} \frac{\partial \langle j|H_s|l\rangle}{\partial c_{\mu i_1}} c_{\mu j_1} = \left(\delta_{i_1 j}\delta_{j_1 l} + \delta_{i_1 l}\delta_{j_1 j}\right) \varepsilon_{j_1} + 2(i_1 j_1|jl) + 2 f^{xc}_{i_1 j_1, jl} - c_x \left[(i_1 j|j_1 l) + (i_1 l|j_1 j)\right], \tag{320}$$

$$\sum_{\mu} \frac{\partial \langle i|H_s|k\rangle}{\partial c_{\mu i_1}} c_{\mu j_1} = \left(\delta_{i_1 i}\delta_{j_1 k} + \delta_{i_1 k}\delta_{j_1 i}\right) \varepsilon_{j_1} + 2(i_1 j_1|ik) + 2 f^{xc}_{i_1 j_1, ik} - c_x \left[(i_1 i|j_1 k) + (i_1 k|j_1 i)\right], \tag{321}$$

$$\sum_{\mu} \frac{\partial \langle j|H_s|k\rangle}{\partial c_{\mu i_1}} c_{\mu j_1} = \left(\delta_{i_1 j}\delta_{j_1 k} + \delta_{i_1 k}\delta_{j_1 j}\right) \varepsilon_{j_1} + 2(i_1 j_1|jk) + 2 f^{xc}_{i_1 j_1, jk} - c_x \left[(i_1 j|j_1 k) + (i_1 k|j_1 j)\right], \tag{322}$$

$$\sum_{\mu} \frac{\partial \langle i|H_s|l\rangle}{\partial c_{\mu i_1}} c_{\mu j_1} = \left(\delta_{i_1 i}\delta_{j_1 l} + \delta_{i_1 l}\delta_{j_1 i}\right)\varepsilon_{j_1} + 2(i_1 j_1|il) + 2f^{xc}_{i_1 j_1, il} - c_x\left[(i_1 i|j_1 l) + (i_1 l|j_1 i)\right]. \tag{323}$$

The contributions with respect to $\langle ij||kl\rangle$ are

$$\sum_{\mu} \frac{\partial}{\partial c_{\mu i_1}} \langle ij||kl\rangle c_{\mu j_1} \tag{324}$$

$$= \langle j_1 j||kl\rangle\delta_{i_1 i} + \langle ij_1||kl\rangle\delta_{i_1 j} + \langle ij||j_1 l\rangle\delta_{i_1 k} + \langle ij||kj_1\rangle\delta_{i_1 l}. \tag{325}$$

Therefore

$$\sum_{i<j}\sum_{k<l} Y_{ij}\left(\sum_{\mu} \frac{\partial C_{ij,kl}}{\partial c_{\mu i_1}} c_{\mu j_1}\right) Y_{kl} \tag{326}$$

$$= -2U_{i_1 j_1}\varepsilon_{j_1} - H^{+}_{i_1 j_1}[U] \tag{327}$$

$$+ \sum_{i<j}\sum_{k<l} Y_{ij}\left(\langle j_1 j||kl\rangle\delta_{i_1 i}\right) Y_{kl} + \sum_{i<j}\sum_{k<l} Y_{ij}\left(\langle ij_1||kl\rangle\delta_{i_1 j}\right) Y_{kl} \tag{328}$$

$$+ \sum_{i<j}\sum_{k<l} Y_{ij}\left(\langle ij||j_1 l\rangle\delta_{i_1 k}\right) Y_{kl} + \sum_{i<j}\sum_{k<l} Y_{ij}\left(\langle ij||kj_1\rangle\delta_{i_1 l}\right) Y_{kl} \tag{329}$$

$$= -2U_{i_1 j_1}\varepsilon_{j_1} - H^{+}_{i_1 j_1}[U] \tag{330}$$

$$+ \sum_{i_1<j}\sum_{k<l} Y_{i_1 j}\left((jl|kj_1) - (jk|lj_1)\right) Y_{kl} + \sum_{j<i_1}\sum_{k<l} Y_{ji_1}\left((j_1 l|kj) - (j_1 k|lj)\right) Y_{kl} \tag{331}$$

$$+ \sum_{i<j}\sum_{i_1<l} Y_{ij}\left((lj|ij_1) - (li|jj_1)\right) Y_{i_1 l} + \sum_{i<j}\sum_{k<i_1} Y_{ij}\left((j_1 j|ik) - (j_1 i|jk)\right) Y_{ki_1} \tag{332}$$

$$= -2U_{i_1 j_1}\varepsilon_{j_1} - H^{+}_{i_1 j_1}[U] + 2\sum_{i_1<j} Y_{i_1 j} H^{-}_{jj_1}[Y] + 2\sum_{j<i_1} H^{-}_{j_1 j}[Y] Y_{ji_1}. \tag{333}$$

To summarize,

$$Q_{i_1 j_1} = H^{+}_{i_1 j_1}[V] + 2\sum_{i_1<i} Y_{i_1 i} H^{-}_{ij_1}[X] + 2\sum_{i<i_1} H^{-}_{j_1 i}[X] Y_{ii_1} \tag{334}$$

$$-2U_{i_1 j_1}\varepsilon_{j_1} - H^{+}_{i_1 j_1}[U] + 2\sum_{i_1<i} Y_{i_1 i} H^{-}_{ij_1}[Y] + 2\sum_{i<i_1} H^{-}_{j_1 i}[Y] Y_{ii_1}. \tag{335}$$

2. $p = i_1, q = a_1$

The derivative in the first term $\mathbf{X}^{\mathrm{T}}\mathbf{A}\mathbf{X}$,

$$\sum_{\mu} \frac{\partial A_{ab,cd}}{\partial c_{\mu i_1}} c_{\mu a_1} \tag{336}$$

$$= \sum_{\mu} \frac{\partial}{\partial c_{\mu i_1}} \left(\delta_{ac}\langle b|H_s|d\rangle + \delta_{bd}\langle a|H_s|c\rangle - \delta_{ad}\langle b|H_s|c\rangle - \delta_{bc}\langle a|H_s|d\rangle - 2\mu + (ac|bd) - (ad|bc)\right) c_{\mu a_1}. \tag{337}$$

There are only the implicit contributions from the H_s terms. Using previous the result in Equation (307) we arrive at

$$\sum_{a<b}\sum_{c<d} X_{ab}\left(\sum_{\mu}\frac{\partial A_{ab,cd}}{\partial c_{\mu i_1}}c_{\mu a_1}\right)X_{cd} = H^{+}_{i_1a_1}[V]. \tag{338}$$

The contribution from the second term $2\mathbf{X}^{\mathrm{T}}\mathbf{B}\mathbf{Y}$ is given by

$$2\sum_{a<b}\sum_{i<j} X_{ab}\left(\sum_{\mu}\frac{\partial B_{ab,ij}}{\partial c_{\mu i_1}}c_{\mu a_1}\right)Y_{ij} \tag{339}$$

$$=2\sum_{i_1<i} Y_{i_1 i}H^{-}_{ia_1}[X] + 2\sum_{i<i_1} H^{-}_{a_1 i}[X]Y_{ii_1}. \tag{340}$$

Finally the contribution from the third term $\mathbf{Y}^{\mathrm{T}}\mathbf{C}\mathbf{Y}$,

$$\sum_{i<j}\sum_{k<l} Y_{ij}\left(\sum_{\mu}\frac{\partial C_{ij,kl}}{\partial c_{\mu i_1}}c_{\mu a_1}\right)Y_{kl} \tag{341}$$

$$=-H^{+}_{i_1a_1}[U] + 2\sum_{i_1<j} Y_{i_1 j}H^{-}_{ja_1}[Y] + 2\sum_{j<i_1} H^{-}_{a_1 j}[Y]Y_{ji_1}. \tag{342}$$

To summarize

$$Q_{i_1a_1} = H^{+}_{i_1a_1}[V] + 2\sum_{i_1<i} Y_{i_1 i}H^{-}_{ia_1}[X] + 2\sum_{i<i_1} H^{-}_{a_1 i}[X]Y_{ii_1} \tag{343}$$

$$-H^{+}_{i_1a_1}[U] + 2\sum_{i_1<i} Y_{i_1 i}H^{-}_{ia_1}[Y] + 2\sum_{j<i_1} H^{-}_{a_1 i}[Y]Y_{ii_1}. \tag{344}$$

3. $p = a_1 \le q = b_1$

The derivative in the first term $\mathbf{X}^{\mathrm{T}}\mathbf{A}\mathbf{X}$,

$$\sum_{\mu}\frac{\partial A_{ab,cd}}{\partial c_{\mu a_1}}c_{\mu b_1} \tag{345}$$

$$=\sum_{\mu}\frac{\partial}{\partial c_{\mu a_1}}\left(\delta_{ac}\langle b|H_s|d\rangle + \delta_{bd}\langle a|H_s|c\rangle - \delta_{ad}\langle b|H_s|c\rangle - \delta_{bc}\langle a|H_s|d\rangle - 2\mu + \langle ab||cd\rangle\right)c_{\mu b_1} \tag{346}$$

$$=\delta_{ac}\delta_{a_1b}\delta_{b_1d}\varepsilon_{b_1} + \delta_{ac}\delta_{a_1d}\delta_{b_1b}\varepsilon_{b_1} + \delta_{bd}\delta_{a_1a}\delta_{b_1c}\varepsilon_{b_1} + \delta_{bd}\delta_{a_1c}\delta_{b_1a}\varepsilon_{b_1} \tag{347}$$

$$-\delta_{ad}\delta_{a_1b}\delta_{b_1c}\varepsilon_{b_1} - \delta_{ad}\delta_{a_1c}\delta_{b_1b}\varepsilon_{b_1} - \delta_{bc}\delta_{a_1a}\delta_{b_1d}\varepsilon_{b_1} - \delta_{bc}\delta_{a_1d}\delta_{b_1a}\varepsilon_{b_1} \tag{348}$$

$$+\delta_{a_1a}\langle b_1b||cd\rangle + \delta_{a_1b}\langle ab_1||cd\rangle + \delta_{a_1c}\langle ab||b_1d\rangle + \delta_{a_1d}\langle ab||cb_1\rangle. \tag{349}$$

Therefore

$$\sum_{a<b}\sum_{c<d} X_{ab}\left(\sum_{\mu}\frac{\partial A_{ab,cd}}{\partial c_{\mu a_1}}c_{\mu b_1}\right)X_{cd} \tag{350}$$

$$=2V_{a_1b_1}\varepsilon_{b_1} \tag{351}$$

$$+\sum_{a<b}\sum_{c<d} X_{ab}\left(\delta_{a_1a}\langle b_1b||cd\rangle\right)X_{cd}+\sum_{a<b}\sum_{c<d} X_{ab}\left(\delta_{a_1b}\langle ab_1||cd\rangle\right)X_{cd} \tag{352}$$

$$+\sum_{a<b}\sum_{c<d} X_{ab}\left(\delta_{a_1c}\langle ab||b_1d\rangle\right)X_{cd}+\sum_{a<b}\sum_{c<d} X_{ab}\left(\delta_{a_1d}\langle ab||cb_1\rangle\right)X_{cd} \tag{353}$$

$$=2V_{a_1b_1}\varepsilon_{b_1}+2\sum_{a_1<a} X_{a_1a}H^{-}_{ab_1}[X]+2\sum_{a<a_1} H^{-}_{b_1a}[X]X_{aa_1}. \tag{354}$$

The derivative in the second term $2\mathbf{X}^{\mathrm{T}}\mathbf{B}\mathbf{Y}$ is

$$\sum_{\mu}\frac{\partial B_{ab,ij}}{\partial c_{\mu a_1}}c_{\mu b_1} \tag{355}$$

$$=\sum_{\mu}\frac{\partial\langle ab||ij\rangle}{\partial c_{\mu a_1}}c_{\mu b_1} \tag{356}$$

$$=\delta_{a_1a}\langle b_1b||ij\rangle+\delta_{a_1b}\langle ab_1||ij\rangle. \tag{357}$$

Therefore

$$2\sum_{a<b}\sum_{i<j} X_{ab}\left(\sum_{\mu}\frac{\partial B_{ab,ij}}{\partial c_{\mu a_1}}c_{\mu b_1}\right)Y_{ij} \tag{358}$$

$$=2\sum_{a_1<b}\sum_{i<j} X_{a_1b}\left((bj|ib_1)-(bi|jb_1)\right)Y_{ij}+2\sum_{a<a_1}\sum_{i<j} X_{aa_1}\left((b_1j|ia)-(b_1i|ja)\right)Y_{ij} \tag{359}$$

$$=2\sum_{a_1<a} X_{a_1a}H^{-}_{ab_1}[Y]+2\sum_{a<a_1} H^{-}_{b_1a}[Y]X_{aa_1}. \tag{360}$$

Finally the derivative with respect to $\mathbf{Y}^{\mathrm{T}}\mathbf{C}\mathbf{Y}$

$$\sum_{\mu}\frac{\partial C_{ij,kl}}{\partial c_{\mu a_1}}c_{\mu b_1} \tag{361}$$

$$=\sum_{\mu}\frac{\partial}{\partial c_{\mu a_1}}\left[-\delta_{ik}\langle j|H_s|l\rangle-\delta_{jl}\langle i|H_s|k\rangle+\delta_{il}\langle j|H_s|k\rangle+\delta_{jk}\langle i|H_s|l\rangle+2\mu+\langle ij||kl\rangle\right]c_{\mu b_1} \tag{362}$$

$$=0. \tag{363}$$

To summarize

$$Q_{a_1b_1}=2V_{a_1b_1}\varepsilon_{b_1}+2\sum_{a_1<a} X_{a_1a}H^{-}_{ab_1}[X]+2\sum_{a<a_1} H^{-}_{b_1a}[X] \tag{364}$$

$$+2\sum_{a_1<a} X_{a_1a}H^{-}_{ab_1}[Y]+2\sum_{a<a_1} H^{-}_{b_1a}[Y]X_{aa_1}. \tag{365}$$

4. $p = a_1, q = i_1$

The contributions from the first term $\mathbf{X}^{\mathrm{T}}\mathbf{A}\mathbf{X}$,

$$\begin{aligned}&\sum_{a<b}\sum_{c<d} X_{ab}\left(\sum_{\mu}\frac{\partial A_{ab,cd}}{\partial c_{\mu a_1}}c_{\mu i_1}\right)X_{cd}\\ =&2\sum_{a_1<a} X_{a_1a}H^{-}_{ai_1}[X] + 2\sum_{a<a_1} H^{-}_{i_1a}[X]X_{aa_1}.\end{aligned} \tag{366}$$

The contributions from the second term $2\mathbf{X}^{\mathrm{T}}\mathbf{B}\mathbf{Y}$

$$\begin{aligned}&2\sum_{a<b}\sum_{i<j} X_{ab}\left(\sum_{\mu}\frac{\partial B_{ab,ij}}{\partial c_{\mu a_1}}c_{\mu i_1}\right)Y_{ij}\\ =&2\sum_{a_1<a} X_{a_1a}H^{-}_{ai_1}[Y] + 2\sum_{a<a_1} H^{-}_{i_1a}[Y]X_{aa_1}.\end{aligned} \tag{367}$$

And the derivative with respect to $\mathbf{Y}^{\mathrm{T}}\mathbf{C}\mathbf{Y}$ is zero. To summarize

$$Q_{a_1i_1} = 2\sum_{a_1<a} X_{a_1a}H^{-}_{ai_1}[X] + 2\sum_{a<a_1} H^{-}_{i_1a}[X]X_{aa_1} + 2\sum_{a_1<a} X_{a_1a}H^{-}_{ai_1}[Y] + 2\sum_{a<a_1} H^{-}_{i_1a}[Y]X_{aa_1}. \tag{368}$$

Therefore, to sum up, we have obtained the following four equations,

$$Q_{i_1j_1} + H^{+}_{i_1j_1}[Z] = W_{i_1j_1}(1+\delta_{i_1j_1}), \tag{369}$$

$$Q_{i_1a_1} + Z_{i_1a_1}\varepsilon_{a_1} + H^{+}_{i_1a_1}[Z] = W_{i_1a_1}, \tag{370}$$

$$Q_{a_1i_1} + Z_{i_1a_1}\varepsilon_{i_1} = W_{i_1a_1}, \tag{371}$$

$$Q_{a_1b_1} = W_{a_1b_1}(1+\delta_{a_1b_1}). \tag{372}$$

Subtracting Equation (371) from Equation (370) we arrive at

$$\left(\varepsilon_{a_1} - \varepsilon_{i_1}\right)Z_{i_1a_1} + H^{+}_{i_1a_1}[Z] = -\left(Q_{i_1a_1} - Q_{a_1i_1}\right), \tag{373}$$

which is called the Z-vector equation. After the Z-vector equation is solved for Z we then can evaluate W using

$$W_{i_1j_1} = \frac{Q_{i_1j_1} + H^{+}_{i_1j_1}[Z]}{1+\delta_{i_1j_1}}, \tag{374}$$

$$W_{i_1a_1} = Q_{a_1i_1} + Z_{i_1a_1}\varepsilon_{i_1}, \tag{375}$$

$$W_{a_1b_1} = \frac{Q_{a_1b_1}}{1+\delta_{a_1b_1}}. \tag{376}$$

Finally, with both Z and W at hand the excitation energy gradient can be evaluated via (263).

III. SUPPLEMENTAL RESULTS

III.1. Equivalence of CISD and pp-RPA with HF* reference for the hydrogen molecule

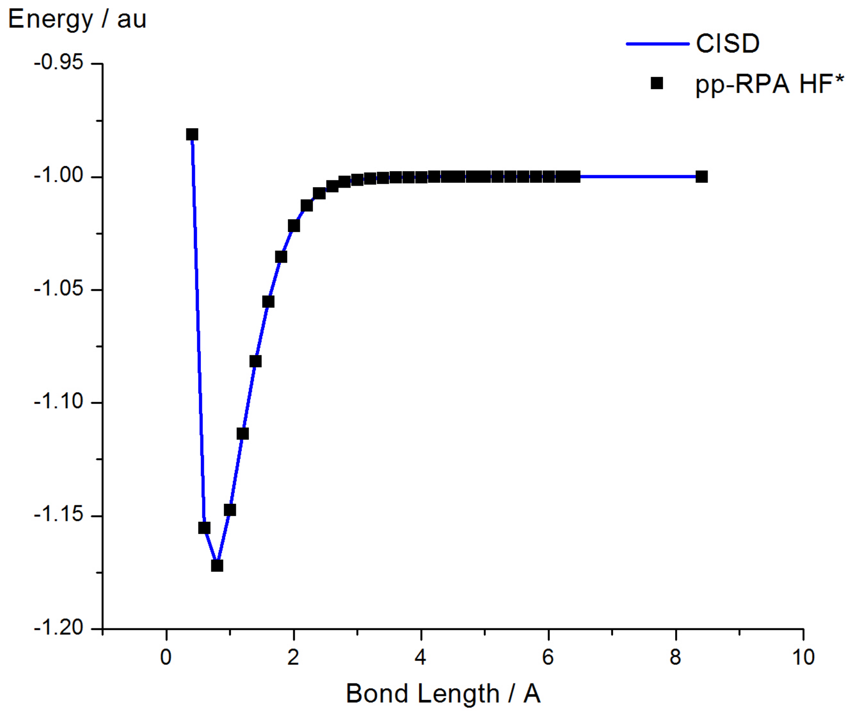


Figure 1. Bond dissociation curves for the hydrogen molecule with CISD and pp-RPA with the HF reference with the Cartesian cc-pVQZ basis set[3]. Their results are identical for this system.

III.2. Equilibrium bond lengths and adiabatic excitation energies of BH and CH^+

Table I. Equilibrium bond lengths and adiabatic excitation energies for the ground state and the lowest three excited states of BH. (Units: Hartree, Å)

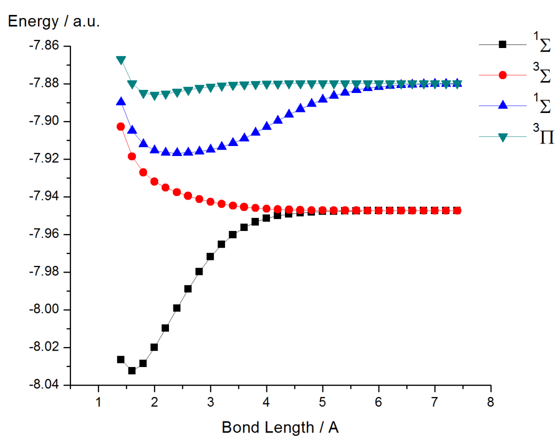
Method	$^1\Sigma$	$^3\Pi$		$^1\Pi$		$^3\Sigma^-$	
	R(B-H)	R(B-H)	Adia. EE	R(B-H)	Adia. EE	R(B-H)	Adia. EE
Full CI	1.238	1.196	0.0477	1.238	0.1110	1.227	0.1723
pp-RPA/B3LYP ref/Plan A	1.244	1.157	0.0467	1.187	0.1228	1.146	0.1843
pp-RPA/B3LYP ref/Plan B	1.240	1.155	0.0466	1.185	0.1226	1.145	0.1841
(TD-)LDA	1.257	1.178	0.0287	1.229	0.0936	-	-

Table II. Equilibrium bond lengths and adiabatic excitation energies for the ground state and the lowest three excited states of CH^+. (Units: Hartree, Å)

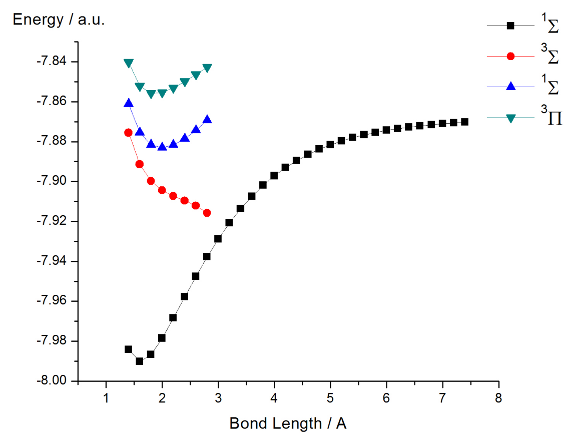
Method	$^1\Sigma$	$^3\Pi$		$^1\Pi$		$^3\Sigma^-$	
	R(C-H)	R(C-H)	Adia. EE	R(C-H)	Adia. EE	R(C-H)	Adia. EE
Full CI	1.136	1.141	0.0420	1.264	0.1128	1.248	0.1742
pp-RPA/B3LYP ref/Plan A	1.098	1.077	0.0395	1.138	0.1199	1.119	0.1873
pp-RPA/B3LYP ref/Plan B	1.140	1.120	0.0405	1.236	0.1166	1.185	0.1858
(TD-)LDA	1.165	1.128	-0.0228	1.257	0.0921	-	-

The Cartesian 6-311++G(d,p)[4–6] basis sets are used. The equilibrium bond lengths of pp-RPA are slightly underestimated for both systems, and the underestimation for the equilibrium bond length for the double excitation $^3\Sigma^-$ is greater compared to single excitations. The (TD-)LDA gives better bond lengths but considerably worse adiabatic excitation energies. The double excitation $^3\Sigma^-$ is absent in TDLDA.

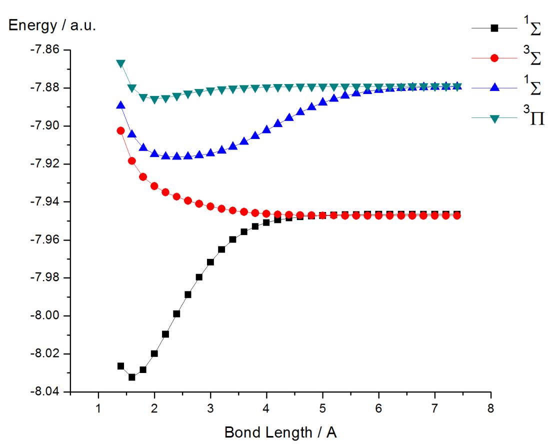
III.3. Dissociation curves for the ground state and excited states of LiH and NaH



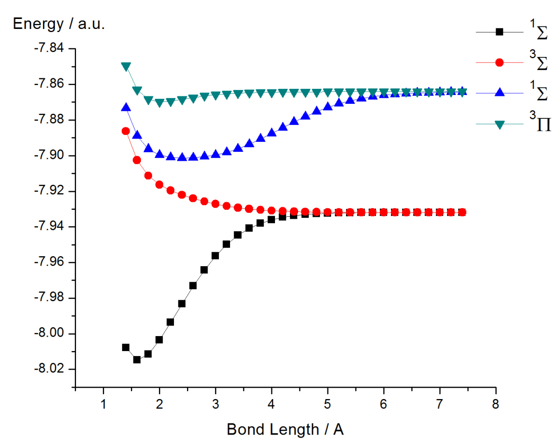
(a) Full CI



(b) (TD-)LDA

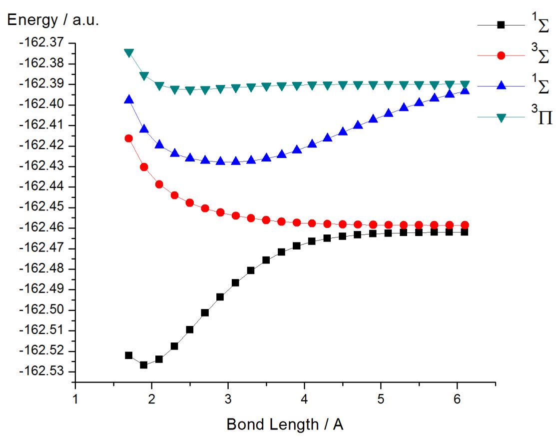


(a) (EOM-)CCSD

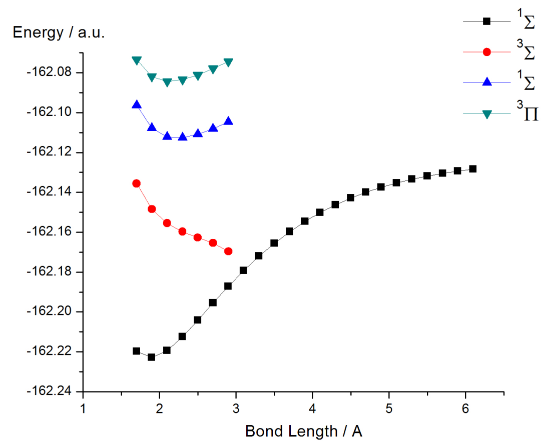


(b) Plan A ppRPA with HF reference

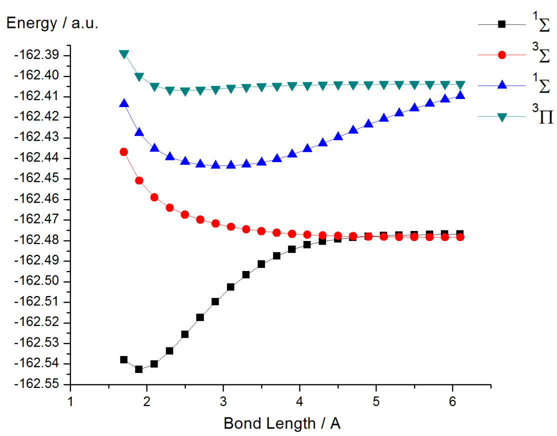
Figure 2. Ground state and excited state bond dissociation curves for the LiH molecule.



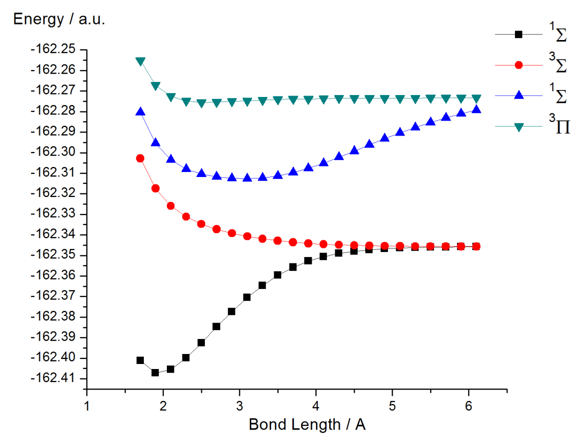
(a) MRCISD(Q)



(b) (TD-)LDA



(a) (EOM-)CCSD



(b) Plan A ppRPA with HF reference

Figure 3. Ground state and excited state bond dissociation curves for the NaH molecule.

The Cartesian 6-311++G(d,p)[4–6] basis sets are used. For both cases (TD-)LDA fails qualitatively for greatly overestimating the ground state energies due to its huge static correlation errors. Even EOM-CCSD in this case predict incorrect energy ordering at large separations. However, pp-RPA with the HF reference reproduces that reference Full CI and MRCISD(Q)[7,8] results very well.

REFERENCES

[1]H. van Aggelen, Y. Yang, and W. Yang, Phys. Rev. A **88**, 030501 (2013).

[2]F. Furche and R. Ahlrichs, J. Chem. Phys. **117**, 7433 (2002).

[3]J. Dunning, Thom H., J. Chem. Phys. **90**, 1007 (1989).

[4]W. J. Hehre, R. Ditchfield, and J. A. Pople, J. Chem. Phys. **56**, 2257 (1972).

[5]J. D. Dill and J. A. Pople, J. Chem. Phys. **62**, 2921 (1975).

[6]C. Hariharan, J. Chem. Phys **77**, 3654 (1982).

[7]S. R. Langhoff and E. R. Davidson, Int. J. Quantum Chem. **8**, 61 (1974).

[8]P. J. Bruna, S. D. Peyerimhoff, and R. J. Buenker, Chem. Phys. Lett. **72**, 278 (1980).