Commutators of the Normal-Ordered Hamiltonian with Single-Excitation Unitary Group Generators

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The spin-adapted normal-ordered Hamiltonian for a spin-restricted set of orbitals is

$$\hat{H} = \sum_{pq} f_{pq}\{E_{pq}\} + \frac{1}{2}\sum_{pqrs}\langle pq|rs\rangle\{E_{pr}E_{qs}\}, \tag{1}$$

where p, q, r, and s are spatial orbitals,

$$E_{pq} = a^+_{p_\alpha} a_{q_\alpha} + a^+_{p_\beta} a_{q_\beta} \tag{2}$$

is the singlet unitary-group generator, and

$$f_{pq} = h_{pq} + \sum_i L_{piqi} \tag{3}$$

is the spin-restricted Fock matrix where

$$L_{pqrs} = (2\langle pq|rs\rangle - \langle pq|sr\rangle) \tag{4}$$

Brackets around the unitary group generators imply normal ordering of the component annihilation and creation operators. We choose the convention that i, j, k, $\cdots$ denote occupied orbitals, and a, b, c, $\cdots$ denote unoccupied/virtual orbitals. In addition, permutation operators for two, three, and four pairs of indices are defined by their actions on functions of the indices as, respectively,

$$P_{ij}^{ab} f_{ij}^{ab} = f_{ij}^{ab} + f_{ji}^{ba}, \tag{5}$$

$$P_{ijk}^{abc} f_{ijk}^{abc} = f_{ijk}^{abc} + f_{ikj}^{acb} + f_{jik}^{bac} + f_{jki}^{bca} + f_{kij}^{cab} + f_{kji}^{cba}, \tag{6}$$

and

$$\begin{aligned} P_{ijkl}^{abcd} f_{ijkl}^{abcd} = {} & f_{ijkl}^{abcd} + f_{ijlk}^{abdc} + f_{ikjl}^{acbd} + f_{iklj}^{acdb} + f_{iljk}^{adbc} + f_{ilkj}^{adcb} \\ & + f_{jikl}^{bacd} + f_{jilk}^{badc} + f_{jkil}^{bcad} + f_{jkli}^{bcda} + f_{jlik}^{bdac} + f_{jlki}^{bdca} \\ & + f_{kijl}^{cabd} + f_{kilj}^{cadb} + f_{kjil}^{cbad} + f_{kjli}^{cbda} + f_{klij}^{cdab} + f_{klji}^{cdba} \\ & + f_{lijk}^{dabc} + f_{likj}^{dacb} + f_{ljik}^{dbac} + f_{ljki}^{dbca} + f_{lkij}^{dcab} + f_{lkji}^{dcba} \end{aligned} \tag{7}$$

The non-zero commutators of the Hamiltonian with the single-excitation unitary group generators are,

$$\begin{aligned} \left[\hat{H}, \{E_{ai}\}\right] = {} & 2f_{ia} + \sum_p f_{pa}\{E_{pi}\} - \sum_p f_{ip}\{E_{ap}\} + \sum_{pqr}\langle pq|ra\rangle\{E_{pr}E_{qi}\} \\ & - \sum_{prs}\langle pi|rs\rangle\{E_{pr}E_{as}\} + \sum_{pr} L_{pira}\{E_{pr}\}, \end{aligned} \tag{8}$$

$$\left[\left[\hat{H},\{E_{ai}\}\right],\{E_{bj}\}\right] = P_{ij}^{ab}\left[L_{ijab} - f_{ja}\{E_{bi}\} - \sum_{p} L_{ijap}\{E_{bp}\} + \sum_{p} L_{pjab}\{E_{pi}\}\right.$$
$$- \sum_{pr}\left(\langle jp|ra\rangle\{E_{br}E_{pi}\} + \langle pj|ra\rangle\{E_{pr}E_{bi}\}\right)$$
$$\left. + \frac{1}{2}\sum_{pq}\left(\langle pq|ab\rangle\{E_{pi}E_{qj}\} + \langle ij|pq\rangle\{E_{ap}E_{bq}\}\right)\right], \tag{9}$$

$$\left[\left[\left[\hat{H},\{E_{ai}\}\right],\{E_{bj}\}\right],\{E_{ck}\}\right] = P_{ijk}^{abc}\left[-L_{ijac}\{E_{bk}\} - \sum_{p}\langle kp|ab\rangle\{E_{pj}E_{ci}\} + \sum_{p}\langle kj|ap\rangle\{E_{bp}E_{ci}\}\right], \tag{10}$$

and

$$\left[\left[\left[\left[\hat{H},\{E_{ai}\}\right],\{E_{bj}\}\right],\{E_{ck}\}\right],\{E_{dl}\}\right] = \frac{1}{2}P_{ijkl}^{abcd}\left[\langle kl|ab\rangle\{E_{dj}E_{ci}\}\right] \tag{11}$$

If the reference determinant built from the occupied spin-restricted orbitals is denoted $|0\rangle$, the action of the above commutators on this determinant may be written as

$$\left[\hat{H},\{E_{ai}\}\right]|0\rangle = \left(2f_{ia} + \sum_{b} f_{ba}\{E_{bi}\} - \sum_{j} f_{ij}\{E_{aj}\} + \sum_{bj} L_{bija}\{E_{bj}\}\right.$$
$$\left. + \sum_{cbj}\langle cb|ja\rangle\{E_{cj}E_{bi}\} - \sum_{bkj}\langle bi|kj\rangle\{E_{bk}E_{aj}\}\right)|0\rangle, \tag{12}$$

$$\left[\left[\hat{H},\{E_{ai}\}\right],\{E_{bj}\}\right]|0\rangle = P_{ij}^{ab}\left[L_{ijab} - f_{ja}\{E_{bi}\} - \sum_{k} L_{ijak}\{E_{bk}\} + \sum_{c} L_{cjab}\{E_{ci}\}\right.$$
$$- \sum_{ck}\left(\langle jc|ka\rangle\{E_{bk}E_{ci}\} + \langle cj|ka\rangle\{E_{ck}E_{bi}\}\right)$$
$$\left. + \frac{1}{2}\sum_{cd}\langle cd|ab\rangle\{E_{ci}E_{dj}\} + \frac{1}{2}\sum_{kl}\langle ij|kl\rangle\{E_{ak}E_{bl}\}\right]|0\rangle, \tag{13}$$

$$\left[\left[\left[\hat{H},\{E_{ai}\}\right],\{E_{bj}\}\right],\{E_{ck}\}\right]|0\rangle = P_{ijk}^{abc}\left[-L_{ijac}\{E_{bk}\} - \sum_{d}\langle kd|ab\rangle\{E_{dj}E_{ci}\} + \sum_{l}\langle kj|al\rangle\{E_{bl}E_{ci}\}\right]|0\rangle, \tag{14}$$

and

$$\left[\left[\left[\left[\hat{H},\{E_{ai}\}\right],\{E_{bj}\}\right],\{E_{ck}\}\right],\{E_{dl}\}\right]|0\rangle = \frac{1}{2}P_{ijkl}^{abcd}\left[\langle kl|ab\rangle\{E_{dj}E_{ci}\}\right]|0\rangle. \tag{15}$$