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Gradient of the ZAPT2 energy

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Abstract. An explicit expression for the analytical first derivative of the Z-averaged perturbation theory taken to second order energy, due to Lee and Jayatilaka, is presented for application to high-spin systems described by a restricted open-shell Hartree–Fock wavefunction. The use of frozen core orbitals is incorporated into the derivation.

Key words: Analytical derivative – Møller–Plesset perturbation theory – High-spin state

1 Introduction

Open-shell perturbation theories based on the unrestricted Hartree–Fock reference wavefunction (unrestricted Møller–Plesset, or UMP) [1–4] frequently suffer from poor performance and slow convergence attributable mainly to the effects of spin contamination [5–8]. Several solutions [9–13] based on the restricted open-shell Hartree–Fock (ROHF) wavefunction for a system of highest spin include measures for avoiding spin contamination (at least at second order), while attempting to retain the important property of size extensivity and the relative efficiency and simplicity characteristic of closed-shell Møller–Plesset second-order perturbation (MP2) theory [1]. ROHF perturbation theories fall into two categories, those that use a configuration state function basis [9, 10] and those that use a spin-orbital determinant basis [11–16]. The first category contains the OPT1 and OPT2 methods [9] and the method of Hubac and Cársky [10], while the second includes the RMP [11, 12], ROMP [13], and Z-averaged perturbation theory (ZAPT) [14–16] methods.

In a comparative study [17], OPT2 was found to perform well but includes a term which causes the energy to be noninvariant to rotations amongst degenerate open-shell orbitals, and may therefore be undifferentiable in certain situations. OPT1 yields the lowest energies but is the least reliable method for other predictions as well as having the least convergent series. RMP and ROMP both require different spatial orbitals for the α and β spins, and therefore their computational cost at second order is about 3 times that of a comparable closed-shell MP2 calculation and is worse at higher orders [18].

The ZAPT correlation correction, on the other hand, is consistently the smallest in magnitude – though this fact is strongly suggestive of good series convergence [19]. ZAPT incurs less spin contamination at higher orders than RMP or ROMP, requires a single set of orbitals, and therefore performs well without being disproportionately expensive. Moreover, the physically appealing model of open-shell spin orbitals that are simply averaged over the Z component of spin forms the basis of the theory. Overall, ZAPT would appear to be the method of choice for open-shell systems. To take full advantage of these qualities it is desirable to have expressions for the analytical derivatives of the second-order energy (ZAPT2). The derivation of these derivative expressions is the subject of this work. It should be emphasized that the present method is not adaptable to the low-spin cases of a system with unpaired electrons.

2 Derivation

While it is impractical to present a complete derivation of the gradient, the purpose of this section is to provide an outline of the main steps, while the following section clarifies some rearrangements that have been made to simplify the final expression. Like most post-Hartree–Fock analyses, the ZAPT2 energy correction is expressed in the molecular orbital (MO) basis. Here, it is customary for i, j, k to index doubly occupied active MOs (hereafter referred to as DOCC), a, b, c to index virtual MOs (VIRT), w, x, y, z to index singly occupied MOs (SOCC), p, q, r, s, t index general MOs, and $\mu, \nu, \lambda, \sigma$ index the basis set of atom-centered orbitals (AO). In addition, m, n index doubly occupied frozen-core MOs (CORE). Occasionally, upper-case indices refer to the corresponding MO shell.

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The ZAPT2 energy correction consists of seven terms. It is convenient to define each term as being a sum over two-electron integrals times an "amplitude" factor,

$$E^{(2)}_{\mathrm{ZAPT}} = \sum_{i,j,a,b} (ia|jb) T^{ab}_{ij} + \sum_{i,j,x,a} (ix|ja) T^{xa}_{ij} + \frac{1}{2} \sum_{i,j,x,y} (ix|jy) T^{xy}_{ij}$$
$$+ \sum_{i,x,a,b} (ia|xb) T^{ab}_{ix} + \frac{1}{2} \sum_{x,y,a,b} (xa|yb) T^{ab}_{xy}$$
$$+ \sum_{i,x,y,a} (ix|ya) T^{xa}_{iy} + \frac{1}{2} \sum_{i,x,y,a} (ix|xa) T^{ya}_{iy} \quad . \tag{1}$$

The integrals in Eq. (1) are transformed into the MO basis. In general,

$$(pq|rs) = \sum_{\mu,\nu,\lambda,\sigma} C_{\mu p} C_{\nu q} C_{\lambda r} C_{\sigma s} (\mu\nu|\lambda\sigma) \quad , \tag{2}$$

where $C_{\mu \mathrm{p}}$ are the MO coefficients and the four-index symbol, $(\mu\nu|\lambda\sigma)$, denotes a regular two-electron repulsion integral over AOs in Mulliken notation. In Eq. (1), the amplitudes, T^{qs}_{pr}, have a numerator containing two-electron integrals and a denominator containing orbital energies,

$$\begin{aligned}
T^{ab}_{ij} &= [2(ia|jb) - (ib|ja)]/D^{ab}_{ij}, \\
T^{xa}_{ij} &= [2(ix|ja) - (ia|jx)]/D^{xa}_{ij}, \\
T^{xy}_{ij} &= [(ix|jy) - (iy|jx)]/D^{xy}_{ij}, \\
T^{ab}_{ix} &= [2(ia|xb) - (ib|xa)]/D^{ab}_{ix}, \\
T^{ab}_{xy} &= [(xa|yb) - (xb|ya)]/D^{ab}_{xy}, \\
T^{xa}_{iy} &= (ix|ya)/D^{xa}_{iy}, \\
T^{ya}_{iy} &= (iy|ya)/D^{a}_{i} \quad ,
\end{aligned} \tag{3}$$

where

$$D^{rs}_{pq} = \varepsilon_p + \varepsilon_q - \varepsilon'_r - \varepsilon'_s \quad , \tag{4}$$

and a two-index denominator is also used for clarity,

$$D^{q}_{p} = \frac{1}{2} D^{qq}_{pp} = \varepsilon_p - \varepsilon'_q \quad . \tag{5}$$

The orbital energies in Eqs. (4) and (5) are defined using the "averaged" Fock operator [20, 21],

$$\hat{F}^{\mathrm{av}} = \hat{h} + \sum_{p}^{\mathrm{all}} f_p \left(2\hat{J} - \hat{K}\right) \quad , \tag{6}$$

where f_{p} is the occupation number of the pth shell. $\hat{h}, \hat{J}$, and $\hat{K}$ are the usual core-Hamiltonian, Coulomb, and exchange operators, respectively. The summation limit "all" is used to clarify a sum over CORE, DOCC, SOCC, and VIRT indices. The matrix elements of Eq. (6),

$$\varepsilon_{\tilde{p}\tilde{q}} = h_{\tilde{p}\tilde{q}} + \sum_{r}^{\mathrm{all}} f_r [2(\tilde{p}\tilde{q}|rr) - (\tilde{p}r|\tilde{q}r)] \quad , \tag{7}$$

involve uncanonicalized orbitals (~) at convergence. Thus, the orbital energies in Eqs. (4) and (5) have the form

$$\varepsilon_{pp} = h_{pp} + \sum_{q}^{\mathrm{all}} f_q [2(pp|qq) - (pq|pq)] \tag{8}$$

after diagonalizing the unique-shell blocks of the matrix (Eq. 7). It is convenient to define SOCC energies to have an additional "integral component" consisting of a sum of exchange integrals over the open-shell orbitals,

$$\begin{aligned}
\varepsilon_p &= \varepsilon_{pp} - \frac{1}{2} \sum_{y} (py|py), \qquad \text{for } p \in \{X\}, \\
\varepsilon'_p &= \varepsilon_{pp} + \frac{1}{2} \sum_{y} (py|py), \qquad \text{for } p \in \{X\}, \\
\varepsilon'_p &= \varepsilon_p = \varepsilon_{pp}, \qquad \text{for } p \notin \{X\} \quad ,
\end{aligned} \tag{9}$$

where $\{X\}$ symbolizes the set of SOCC indices, and a prime is used in Eqs(4), (5), and (9) to indicate the change of sign of the exchange integral term. The label symmetries in terms 2 and 4 of Eq. (1) can be exploited to give

$$E^{(2)}_{\mathrm{ZAPT}} = \frac{1}{2} \sum_{ijab} (ia|jb) T^{ab}_{ij} + \frac{1}{2} \sum_{ijxa} (ix|ja) T^{xa}_{ij}$$
$$+ \frac{1}{2} \sum_{ijxa} (ia|jx) T^{ax}_{ij} + \frac{1}{2} \sum_{ijxy} (ix|jy) T^{xy}_{ij}$$
$$+ \frac{1}{2} \sum_{ijab} (ia|jb) T^{ab}_{ij} + \frac{1}{2} \sum_{ixab} (ia|xb) T^{ab}_{ix}$$
$$+ \frac{1}{2} \sum_{ixab} (xa|ib) T^{ab}_{xi} + \frac{1}{2} \sum_{xyab} (xa|yb) T^{ab}_{xy}$$
$$+ \sum_{ixya} (ix|ya) T^{xa}_{iy} + \frac{1}{2} \sum_{ixya} (ix|xa) T^{ya}_{iy} \quad . \tag{10}$$

Equation (10) is equivalent to the sum of two "closed-shell-type" terms and the two remaining terms as follows,

$$E^{(2)}_{\mathrm{ZAPT}} = \frac{1}{2} \sum_{i,j} \sum_{p,q}^{\mathrm{s.v.}} (ip|jq) \left[C_{pq} (ip|jq) - (iq|jp) \right] / D^{pq}_{ij}$$
$$+ \frac{1}{2} \sum_{p,q}^{\mathrm{d.s.}} \sum_{a,b} (pa|qb) \left[C_{pq} (pa|qb) - (pb|qa) \right] / D^{ab}_{pq}$$
$$+ \sum_{ixya} (ix|ya) T^{xa}_{iy} + \frac{1}{2} \sum_{ixya} (ix|xa) T^{ya}_{iy} \quad , \tag{11}$$

where

$$\begin{aligned}
C_{pq} &= 1, \qquad \text{for both } p \in \{X\} \text{and } q \in \{X\}, \\
C_{pq} &= 2, \qquad \text{otherwise} \quad .
\end{aligned} \tag{12}$$

In Eq. (11), a summation range that extends over both SOCC and VIRT indices is indicated by "s.v.", likewise, one extending over DOCC and SOCC indices is denoted "d.s.". Thus, in the first term of Eq. (11), SOCC indices appear to be included in the VIRT list, while in the second term they appear to be in the DOCC list. The advantage of Eq. (11) is that much of the derivative analysis is now similar to the closed-shell case. In general, each ZAPT2 term is differentiated with respect to a perturbation, γ,

$$\left(E^{(2)}_{\mathrm{ZAPT}}\right)^{\gamma} = \left[\sum_{p,q,r,s} (pr|qs)T^{rs}_{pq}\right]^{\gamma} + \cdots \ . \tag{13}$$

As described earlier, the amplitudes (Eq. 3) involve a numerator and a denominator factor,

$$T^{rs}_{pq} = \frac{N^{rs}_{pq}}{D^{rs}_{pq}} \ . \tag{14}$$

Since each ZAPT2 term contains at least one pair of like summation indices the derivatives of the integral and of the amplitude numerator are the same,

$$\left[\sum_{p,q,r,s} (pr|qs)T^{rs}_{pq}\right]^{\gamma} = \sum_{p,q,r,s}\left[2(pr|qs)^{(\gamma)}T^{rs}_{pq} - \frac{(pr|qs)N^{rs}_{pq}}{\left(D^{rs}_{pq}\right)^2}\left[D^{rs}_{pq}\right]^{\gamma}\right] \ . \tag{15}$$

Hence, each ZAPT2 term yields a "numerator" derivative and a "denominator" derivative. In the former, the derivative of a two-electron integral is well known,

$$\begin{aligned}(pq|rs)^{(\gamma)} ={}&(pq|rs)^{\gamma} + \sum_t U^{\gamma}_{tp}(tq|rs) + \sum_t U^{\gamma}_{tq}(pt|rs)\\ &+ \sum_t U^{\gamma}_{tr}(pq|ts) + \sum_t U^{\gamma}_{ts}(pq|rt) \ .\end{aligned} \tag{16}$$

Note that Eq. (16) involves a transformed pure "integral" derivative term,

$$(pq|rs)^{\gamma} = \sum_{\mu,\nu,\lambda,\sigma} C_{\mu p}C_{\nu q}C_{\lambda r}C_{\sigma s}(\mu\nu|\lambda\sigma)^{\gamma} \ , \tag{17}$$

and terms in which the four original MOs are replaced by a rotation of the MOs in response to the perturbation. Note that, since the U^{γ}_{tp} are elements of a rotation matrix, in general,

$$U^{\gamma}_{tp} \neq U^{\gamma}_{pt} \ . \tag{18}$$

They are, however, related by the orthogonality condition [22],

$$U^{\gamma}_{pq} + U^{\gamma}_{qp} + S^{\gamma}_{pq} = 0 \ , \tag{19}$$

upon which much of analytical derivative theory is based. In Eq. (19), the S^{γ}_{pq} are transformed derivative overlap integrals,

$$S^{\gamma}_{pq} = \sum_{\mu\nu} C_{\mu p}C_{\nu q}S^{\gamma}_{\mu\nu} \ , \tag{20}$$

by analogy with Eq. (17). When the sums over t are subdivided into their unique shell terms, different classes of response can be identified. Substitution of Eq. (16) into Eq. (15) leads to terms such as

$$\left[\sum_{p,q}\sum_{r,s}(pr|qs)T^{rs}_{pq}\right]^{\gamma} = \sum_{t,p}U^{\gamma}_{tp}\sum_{q,r,s}(tr|qs)T^{rs}_{pq} + \cdots \ . \tag{21}$$

If t,p belong to the same shell, the U^{γ}_{tp} are the so-called "non-independent" or "dependent-pair" (DP) responses. These are rotations which do not affect the total energy, in contrast to the "independent-pair" (IP) responses in which t,p belong to different shells. At this point, a definition for the DP responses is required. The choice of canonicalization (Eqs. 6, 7, 8) yields a definition of the form (see Eq. 11.39 of Ref. [20])

$$U^{\gamma}_{tp} = \frac{Q^{\gamma}_{tp}}{\left(\varepsilon_p - \varepsilon_t\right)} \ . \tag{22}$$

The right-hand side of Eq. (22) has six terms,

$$\begin{aligned}Q^{\gamma}_{pq} ={}&\varepsilon^{\gamma}_{pq} - S^{\gamma}_{pq}\varepsilon_q + \sum_{r\in R}^{\neq P}\left(U^{\gamma}_{rp}\varepsilon_{rq} + U^{\gamma}_{rq}\varepsilon_{rp}\right)\\ &+\sum_{r>s}^{\mathrm{IP}}(f_r - f_s)U^{\gamma}_{rs}G_{pqrs} - \sum_{r>s}^{\mathrm{occ}} f_r S^{\gamma}_{rs}G_{pqrs}\\ &-\frac{1}{2}\sum_{r}^{\mathrm{occ}} f_r S^{\gamma}_{rr}G_{pqrr} \ ,\end{aligned} \tag{23}$$

where

$$\varepsilon^{\gamma}_{pq} = h^{\gamma}_{pq} + \sum_r f_r[2(pq|rr)^{\gamma} - (pr|qr)^{\gamma}] \ , \tag{24}$$

$$G_{pqrs} = 4(pq|rs) - (pr|qs) - (ps|qr) \ . \tag{25}$$

In Eq. (24), the core-Hamiltonian derivative integral is defined analogously to Eq. (20). In Eq. (23) the summation limit "occ" is used to mean CORE, DOCC, and SOCC indices, and the IP summation spans SOCC, doubly occupied (CORE and DOCC) index pairs, then VIRT, doubly occupied (CORE and DOCC) pairs, then the VIRT, SOCC pairings. The summation range of the third term of Eq. (23) spans all shells, R, that are not the DP (P or Q) shell. Thus, Eq. (23) defines the DP responses in terms of the IP responses. However, the orbital energy difference in the denominator of Eq. (22) can give rise to instabilities if near-degeneracies between orbitals occur, and it is worthwhile to remove these wherever possible. From Eq. (19), the substitution

$$U^{\gamma}_{pp} = -\frac{1}{2}S^{\gamma}_{pp} \tag{26}$$

is made for the diagonal orbital responses in the first term of Eq. (21), with the off-diagonal response terms combined as follows,

$$\begin{aligned}&\sum_{t>p}\left[U^{\gamma}_{tp}\sum_{q,r,s}(tr|qs)T^{rs}_{pq} + U^{\gamma}_{pt}\sum_{q,r,s}(pr|qs)T^{rs}_{tq}\right]\\ &\quad-\frac{1}{2}\sum_p S^{\gamma}_{pp}\sum_{q,r,s}(pr|qs)T^{rs}_{pq} \ .\end{aligned} \tag{27}$$

Equation (19) is used again to substitute half the responses in Eq. (27) to give

$$= \sum_{t>p} U^{\gamma}_{tp} \left[\sum_{q,r,s} (tr|qs) T^{rs}_{pq} - \sum_{q,r,s} (pr|qs) T^{rs}_{tq} \right] - \sum_{t>p} S^{\gamma}_{tp} \sum_{q,r,s} (pr|qs) T^{rs}_{tq} - \frac{1}{2} \sum_{p} S^{\gamma}_{pp} \sum_{q,r,s} (pr|qs) T^{rs}_{pq} - \frac{1}{2} \sum_{p} S^{\gamma}_{pp} \sum_{q,r,s} (pr|qs) T^{rs}_{pq} \quad . \tag{28}$$

The second and third terms of Eq. (28) may be combined, while the factors in brackets, involving the difference of off-diagonal response multipliers, can be cross-multiplied to equate their denominators,

$$= \sum_{t>p} U^{\gamma}_{tp} \sum_{q,r,s} \left[\frac{(tr|qs) N^{rs}_{pq}}{D^{rs}_{pq} D^{rs}_{tq}} D^{rs}_{tq} - \frac{(pr|qs) N^{rs}_{tq}}{D^{rs}_{pq} D^{rs}_{tq}} D^{rs}_{pq} \right] - \frac{1}{2} \sum_{t,p} S^{\gamma}_{tp} \sum_{q,r,s} (tr|qs) T^{rs}_{pq} \quad . \tag{29}$$

Since the first term of Eq. (29) is symmetric in the *p*, *q* and *r*, *s* indices, the numerators are also equal, leaving the difference of the two "denominator" factors,

$$= \sum_{t>p} U^{\gamma}_{tp} \sum_{q,r,s} \frac{(tr|qs) N^{rs}_{pq}}{D^{rs}_{pq} D^{rs}_{tq}} \left(D^{rs}_{tq} - D^{rs}_{pq} \right) + \cdots \quad , \tag{30}$$

which is equivalent to just the difference of the two orbital energies,

$$= - \sum_{t>p} U^{\gamma}_{tp} (\varepsilon_p - \varepsilon_t) \sum_{q,r,s} \frac{(tr|qs) N^{rs}_{pq}}{D^{rs}_{pq} D^{rs}_{tq}} \equiv \sum_{t>p} U^{\gamma}_{tp} (\varepsilon_p - \varepsilon_t) P^{(2)}_{tp} \quad . \tag{31}$$

In Eq. (31), factors multiplying the orbital responses have been identified as elements of the "response-density" matrix, $\mathbf{P}^{(2)}$, while those multiplying overlap derivative integrals in Eq. (29) contribute to the "energy-weighted" response density, $\mathbf{W}^{(2)}$. The orbital energy difference in the denominator of Eq. (22) now cancels,

$$\sum_{t>p} U^{\gamma}_{tp} (\varepsilon_p - \varepsilon_t) P^{(2)}_{tp} = \sum_{t>p} Q^{\gamma}_{tp} P^{(2)}_{tp} \quad . \tag{32}$$

Terms similar to the right-hand side of Eq. (32), but for which $t = p$, arise from the associated denominator derivative of Eq. (15), which contains derivatives of orbital energies,

$$\varepsilon^{\gamma}_{p} = Q^{\gamma}_{pp} \quad , \tag{33}$$

where Q^{γ}_{pp} has the same form as it does in Eq. (23). In all the ZAPT2 terms, the occurrence of eigenvalue derivatives matches that of the off-diagonal response substitutions so, overall, we may write

$$\left(E^{(2)}_{\mathrm{ZAPT}} \right)^{\gamma} = \sum_{t,p} Q^{\gamma}_{tp} P^{(2)}_{tp} + \cdots \tag{34}$$

where *t*,*p* belong to the same shell. Indeed, when the denominator derivative lacks matching eigenvalue derivatives, the corresponding orbital rotation terms can be made to cancel. For instance, in the fourth term of Eq. (11) open-shell DP indices occur twice in the numerator derivative but not in the denominator derivative. Gathering the former terms together leads to an expression of the form

$$\sum_{x,y} U^{\gamma}_{xy} \left[\sum_{i,z,a} (ix|ya)(iz|za)/D^{a}_{i} + \sum_{i,z,a} (iy|xa)(iz|za)/D^{a}_{i} \right] \equiv \sum_{x,y} U^{\gamma}_{xy} M_{xy} \quad , \tag{35}$$

where the response multiplier is symmetric,

$$M_{xy} = M_{yx} \quad . \tag{36}$$

Following the same approach taken in Eqs. (26), (27), and (28), the response term

$$\sum_{x>y} U^{\gamma}_{xy} (M_{xy} - M_{yx}) - \sum_{x>y} S^{\gamma}_{yx} M_{yx} - \frac{1}{2} \sum_{x} S^{\gamma}_{xx} M_{xx} \tag{37}$$

vanishes, leaving a combined overlap-derivative term,

$$= - \sum_{x,y} S^{\gamma}_{xy} \sum_{i,z,a} (ix|ya)(iz|za)/D^{a}_{i} \quad . \tag{38}$$

For responses involving CORE indices, the strategy (Eqs. 26, 27, 28, 29, 30, 31) cannot be employed because *t* and *p* cannot both be CORE indices. However, the orbital energy difference in Eq. (22) will be perfectly stable if the COREs and DOCCs are chosen sensibly.

Following the procedures described so far, and gathering together like responses, the second-order ZAPT derivative will have the intermediate form

$$\left(E^{2}_{\mathrm{ZAPT}} \right)^{\gamma} = \sum_{p,q}^{\mathrm{DP}} U^{\gamma}_{pq} (\varepsilon_q - \varepsilon_p) P^{(2)}_{pq} + \sum_{p,q}^{\mathrm{IP}} U^{\gamma}_{pq} \{ L_{pq} \} + \sum_{p,q}^{\mathrm{DP}} S^{\gamma}_{pq} \left\{ W^{(2)}_{pq} \right\} + \sum_{p,q}^{\mathrm{IP}} S^{\gamma}_{pq} \left\{ W^{(2)}_{pq} \right\} + \sum_{p,q,r,s} (pq|rs)^{\gamma} \left[\Gamma^{\mathrm{NS}}_{pqrs} + \left\{ \Gamma^{\mathrm{S}}_{pqrs} \right\} \right] \quad , \tag{39}$$

where the DP summation spans all pairs of doubly occupied (CORE and DOCC) indices, then all SOCC index pairs, followed by all VIRT index pairs. In the second term of Eq. (39), the factor multiplying IP responses, *L*, is identified with the so-called MP2 (or "ZAPT2") Lagrangian. The two-particle terms of Eq. (39) arise when Eq. (16) is substituted into expressions such as Eq. (15). The first term of Eq. (16) yields the so-called "non-separable" two-particle density, Γ^{NS}, by a reordering of summations (recalling Eq. 17),

$$\sum_{p,q,r,s} (pr|qs)^{\gamma} T^{rs}_{pq} = \sum_{\mu,\nu,\lambda,\sigma} (\mu\nu|\lambda\sigma)^{\gamma} \left[\sum_{p,q,r,s} C_{\mu p} C_{\nu r} C_{\lambda q} C_{\sigma s} T^{rs}_{pq} \right] \equiv \sum_{\mu,\nu,\lambda,\sigma} (\mu\nu|\lambda\sigma)^{\gamma} \Gamma^{\mathrm{NS}}_{\mu\nu\lambda\sigma} \quad . \tag{40}$$

The so-called “separable” two-particle terms of Eq. (39), Γ^{S}, are described in detail later. Together, these two terms contribute to the ZAPT2 two-particle density matrix elements,

$$\Gamma^{(2)}_{pqrs} = \Gamma^{\mathrm{NS}}_{pqrs} + \Gamma^{\mathrm{S}}_{pqrs} \ . \tag{41}$$

The curly brackets in Eq. (39) are used to indicate incomplete quantities since further terms of the $\mathbf{L}$, $\mathbf{W}^{(2)}$, and Γ^{S} matrices are generated by making the substitution (Eq. 32) for the first term of Eq. (39),

$$\left(E^2_{\mathrm{ZAPT}}\right)^{\gamma} = \sum_{p,q}^{\mathrm{DP}} Q^{\gamma}_{pq} P^{(2)}_{pq} + \cdots \ , \tag{42}$$

leaving only the IP responses to be determined,

$$\begin{aligned}\left(E^2_{\mathrm{ZAPT}}\right)^{\gamma} &= \sum_{p,q}^{\mathrm{DP}} h^{\gamma}_{pq} P^{(2)}_{pq} + \sum_{p,q}^{\mathrm{IP}} U^{\gamma}_{pq} L_{pq} + \sum_{p,q}^{\mathrm{DP}} S^{\gamma}_{pq} \left\{ W^{(2)}_{pq} \right\} \\ &\quad + \sum_{p,q}^{\mathrm{IP}} S^{\gamma}_{pq} \left\{ W^{(2)}_{pq} \right\} + \sum_{p,q,r,s} (pq|rs)^{\gamma} \left[\Gamma^{\mathrm{NS}}_{pqrs} + \left\{ \Gamma^{\mathrm{S}}_{pqrs} \right\} \right] \ .\end{aligned} \tag{43}$$

The second term of Eq. (43) can be constructed following solution of the coupled perturbed ROHF equations [20],

$$\sum_{p>q}^{\mathrm{IP}} A_{pqrs} U^{\gamma}_{pq} = B^{\gamma}_{rs} \ , \tag{44}$$

since the Fock matrix (Eq. 7) is symmetric at convergence. In Eq. (44),

$$\begin{aligned} A_{pqrs} &= \tau^{pq}_{rs} - \tau^{qp}_{rs} + \delta_{pr}\left(\xi^{p}_{qs} - \zeta_{qs}\right) - \delta_{qr}\left(\xi^{q}_{ps} - \zeta_{ps}\right) \\ &\quad - \delta_{ps}\left(\xi^{p}_{qr} - \zeta_{qr}\right) + \delta_{qs}\left(\xi^{q}_{pr} - \zeta_{pr}\right) \end{aligned} \tag{45}$$

is often referred to as the “orbital Hessian”, where

$$\begin{aligned}\tau^{pq}_{rs} &= 2\left(\alpha_{rp} - \alpha_{sp}\right)(pq|rs) + \left(\beta_{rp} - \beta_{sp}\right)[(pr|qs) \\ &\quad + (ps|qr)] \ ,\end{aligned} \tag{46}$$

$$\xi^{r}_{pq} = f_r h_{pq} + \sum_{s}^{\mathrm{occ}} \left[\alpha_{rs}(pq|ss) + \beta_{rs}(ps|qs)\right] \ , \tag{47}$$

$$\zeta_{pq} = f_p h_{pq} + \sum_{s}^{\mathrm{occ}} \left[\alpha_{ps}(pq|ss) + \beta_{ps}(ps|qs)\right] \ , \tag{48}$$

and δ_{pq} is the regular “Kronecker delta”,

$$\begin{aligned} \delta_{pq} &= 1, \quad \text{for } p = q \ , \\ \delta_{pq} &= 0, \quad \text{for } p \neq q \ , \end{aligned} \tag{49}$$

In Eqs. (46), (47), and (48), α_{pq} and β_{pq} are, respectively, the Coulomb and exchange coupling constants in the high-spin case, with the following values when p,q index doubly occupied (D), singly occupied (S), or virtual (V) MOs,

$$\begin{array}{cccc} \alpha_{pq} & D & S & V \\ D & 2 & 1 & 0 \\ S & 1 & \frac{1}{2} & 0 \\ V & 0 & 0 & 0 \end{array} \qquad \begin{array}{cccc} \beta_{pq} & D & S & V \\ D & -1 & -\frac{1}{2} & 0 \\ S & -\frac{1}{2} & -\frac{1}{2} & 0 \\ V & 0 & 0 & 0 \end{array} \tag{50}$$

Note that, formally,

$$\begin{aligned} &\tau^{pq}_{rs} \neq \tau^{qp}_{rs}, \\ &\tau^{pq}_{rs} = -\tau^{pq}_{sr}, \\ &\xi^{r}_{pq} = \xi^{r}_{qp}, \\ &\zeta_{pq} \neq \zeta_{qp} \ . \end{aligned}$$

The right-hand-side of Eq. (44) has five terms,

$$\begin{aligned} B^{\gamma}_{rs} &= \zeta^{\gamma}_{rs} - \zeta^{\gamma}_{sr} - \frac{1}{2}\sum_{p}^{\mathrm{occ}} S^{\gamma}_{pp}\tau^{pp}_{rs} - \sum_{p>}^{\mathrm{all}}\sum_{q}^{\mathrm{occ}} S^{\gamma}_{pq}\tau^{pq}_{rs} \\ &\quad - \sum_{p>}^{\mathrm{all}}\sum_{q}^{\mathrm{occ}} S^{\gamma}_{pq}\left[\delta_{pr}\left(\xi^{r}_{qs} - \zeta_{qs}\right) - \delta_{ps}\left(\xi^{s}_{qr} - \zeta_{qr}\right)\right] \ , \end{aligned} \tag{51}$$

where

$$\zeta^{\gamma}_{pq} = f_p h^{\gamma}_{pq} + \sum_{s}^{\mathrm{occ}} \left[\alpha_{ps}(pq|ss)^{\gamma} + \beta_{ps}(ps|qs)^{\gamma}\right] \ . \tag{52}$$

Normally, it would be necessary to solve Eq. (44) for each perturbation; however, the “Z-vector” substitution [23],

$$\sum_{p,q}^{\mathrm{IP}} U^{\gamma}_{pq} L_{pq} = \sum_{p,q}^{\mathrm{IP}} B^{\gamma}_{pq} Z_{pq} \ , \tag{53}$$

may be applied, where Z is the solution to the linear equation

$$\sum_{p,q}^{\mathrm{IP}} A_{pqrs} Z_{pq} = L_{rs} \ , \tag{54}$$

which is independent of the perturbation. Substituting Eq. (53) into Eq. (43) as follows

$$\begin{aligned}\left(E^2_{\mathrm{ZAPT}}\right)^{\gamma} &= \sum_{p,q}^{\mathrm{DP}} h^{\gamma}_{pq} P^{(2)}_{pq} + \sum_{p,q}^{\mathrm{IP}} Z_{pq} B^{\gamma}_{pq} + \sum_{p,q}^{\mathrm{DP}} S^{\gamma}_{pq} \left\{ W^{(2)}_{pq} \right\} \\ &\quad + \sum_{p,q}^{\mathrm{IP}} S^{\gamma}_{pq} \left\{ W^{(2)}_{pq} \right\} + \sum_{p,q,r,s} (pq|rs)^{\gamma} \left[\Gamma^{\mathrm{NS}}_{pqrs} + \left\{ \Gamma^{\mathrm{S}}_{pqrs} \right\} \right] \end{aligned} \tag{55}$$

yields final terms of $\mathbf{W}^{(2)}$ and Γ^{S}, and defines the IP block of $\mathbf{P}^{(2)}$, giving an expression for the derivative of the ZAPT2 energy of the form

$$\left(E^2_{\mathrm{ZAPT}}\right)^{\gamma} = \sum_{p,q} h^{\gamma}_{pq} P^{(2)}_{pq} + \sum_{p,q} S^{\gamma}_{pq} W^{(2)}_{pq} + \sum_{p,q,r,s} (pq|rs)^{\gamma} \Gamma^{(2)}_{pqrs} \ . \tag{56}$$

For the derivative of the total energy (ROHF energy plus the ZAPT2 correction), the response densities are added to their ROHF counterparts [24],

$$\begin{aligned} P_{pq} &= P_{pq}^{\mathrm{HF}} + P_{pq}^{(2)}, \\ W_{pq} &= W_{pq}^{\mathrm{HF}} + W_{pq}^{(2)}, \\ \Gamma_{pqrs} &= \Gamma_{pqrs}^{\mathrm{HF}} + \Gamma_{pqrs}^{(2)} \ . \end{aligned} \tag{57}$$

It is usually convenient to back-transform the densities (Eq. 57) so they may be combined directly with the derivative integrals in the AO basis,

$$\begin{aligned} P_{\mu\nu} &= \sum_{p,q} C_{\mu p} C_{\nu q} P_{pq}, \\ W_{\mu\nu} &= \sum_{p,q} C_{\mu p} C_{\nu q} W_{pq}, \\ \Gamma_{\mu\nu\lambda\sigma} &= \sum_{p,q,r,s} C_{\mu p} C_{\nu q} C_{\lambda r} C_{\sigma s} \Gamma_{pqrs} \ . \end{aligned} \tag{58}$$

As described earlier, all but one term of the two-particle response density are separable in terms of two-index quantities, so only the four-index back-transformation (Eq. 40) is needed in Eq. (58). The final derivative expression then has the standard form

$$E^{\gamma} = \sum_{\mu,\nu} h_{\mu\nu}^{\gamma} P_{\mu\nu} + \sum_{\mu,\nu} S_{\mu\nu}^{\gamma} W_{\mu\nu} + \sum_{\mu,\nu,\lambda,\sigma} (\mu\nu|\lambda\sigma)^{\gamma} \Gamma_{\mu\nu\lambda\sigma} \ . \tag{59}$$

Note that, frequently, the derivative analysis leads to the definition only of a lower- or upper-triangular block of a given density-like matrix (Eq. 57), although it is often convenient to symmetrize such matrices in practice.

3 Rearrangements

Rearrangements of various terms appearing in Eqs. (9), (23), (41), and (51) will be presented to illustrate the derivation of the final quantities $\mathbf{P}^{(2)}$, $\mathbf{W}^{(2)}$, $\mathbf{L}$, and Γ^{S} needed to evaluate the gradient formula (Eq. 56). We begin with the manipulation of the six terms of Eq. (23). The first term yields a straightforward core-Hamiltonian derivative term and a separable two-particle density term, to be described later, while the second term leads to a simple overlap-derivative term. The third term is treated as follows.

3.1 Rearrangement of DP substitution term 3

When appropriate response density factors have been defined, the third term of Eq. (23) becomes

$$\sum_{p,q}^{\mathrm{DP}} P_{pq}^{(2)} \sum_{r\in R}^{\neq P} \left(U_{rp}^{\gamma} \varepsilon_{rq} + U_{rq}^{\gamma} \varepsilon_{rp} \right) \ , \tag{60}$$

which can be separated into the individual shell contributions as follows,

$$\begin{aligned} &= \sum_{i,j}^{\mathrm{c.d.}} P_{ij}^{(2)} \left[\sum_{x} \left(U_{xi}^{\gamma} \varepsilon_{xj} + U_{xj}^{\gamma} \varepsilon_{xi} \right) + \sum_{a} \left(U_{ai}^{\gamma} \varepsilon_{aj} + U_{aj}^{\gamma} \varepsilon_{ai} \right) \right] \\ &\quad + \sum_{x,y} P_{xy}^{(2)} \left[\sum_{i}^{\mathrm{c.d.}} \left(U_{ix}^{\gamma} \varepsilon_{iy} + U_{iy}^{\gamma} \varepsilon_{ix} \right) + \sum_{a} \left(U_{ax}^{\gamma} \varepsilon_{ay} + U_{ay}^{\gamma} \varepsilon_{ax} \right) \right] \\ &\quad + \sum_{a,b} P_{ab}^{(2)} \left[\sum_{i}^{\mathrm{c.d.}} \left(U_{ia}^{\gamma} \varepsilon_{ib} + U_{ib}^{\gamma} \varepsilon_{ia} \right) + \sum_{x} \left(U_{xa}^{\gamma} \varepsilon_{xb} + U_{xb}^{\gamma} \varepsilon_{xa} \right) \right] . \end{aligned} \tag{61}$$

In eq. (61) a summation over CORE and DOCC is indicated by “c.d.”. By recognizing symmetries amongst the summation indices and reordering summations, Eq. (61) may be rearranged as follows,

$$\begin{aligned} &= 2 \sum_{x} \sum_{i}^{\mathrm{c.d.}} U_{xi}^{\gamma} \sum_{j}^{\mathrm{c.d.}} P_{ij}^{(2)} \varepsilon_{xj} + 2 \sum_{x} \sum_{i}^{\mathrm{c.d.}} U_{ix}^{\gamma} \sum_{y} P_{xy}^{(2)} \varepsilon_{iy} \\ &\quad + 2 \sum_{a} \sum_{i}^{\mathrm{c.d.}} U_{ai}^{\gamma} \sum_{j}^{\mathrm{c.d.}} P_{ij}^{(2)} \varepsilon_{aj} + 2 \sum_{a} \sum_{i}^{\mathrm{c.d.}} U_{ia}^{\gamma} \sum_{b} P_{ab}^{(2)} \varepsilon_{ib} \\ &\quad + 2 \sum_{a,x} U_{ax}^{\gamma} \sum_{y} P_{xy}^{(2)} \varepsilon_{ay} + 2 \sum_{a,x} U_{xa}^{\gamma} \sum_{b} P_{ab}^{(2)} \varepsilon_{xb} \ . \end{aligned} \tag{62}$$

Equation (62) contains (IP) responses from both above and below the diagonal of the rotation matrix. Equation (19) can be used to remove either the upper or lower set in Eq. (62) as follows,

$$\begin{aligned} &= \sum_{x} \sum_{i}^{\mathrm{c.d.}} U_{xi}^{\gamma} \left[2 \sum_{j}^{\mathrm{c.d.}} P_{ij}^{(2)} \varepsilon_{xj} - 2 \sum_{y} P_{xy}^{(2)} \varepsilon_{iy} \right] \\ &\quad + \sum_{x} \sum_{i}^{\mathrm{c.d.}} S_{xi}^{\gamma} \left[-2 \sum_{y} P_{xy}^{(2)} \varepsilon_{iy} \right] \\ &\quad + \sum_{a} \sum_{i}^{\mathrm{c.d.}} U_{ai}^{\gamma} \left[2 \sum_{j}^{\mathrm{c.d.}} P_{ij}^{(2)} \varepsilon_{aj} - 2 \sum_{b} P_{ab}^{(2)} \varepsilon_{ib} \right] \\ &\quad + \sum_{a} \sum_{i}^{\mathrm{c.d.}} S_{ai}^{\gamma} \left[-2 \sum_{b} P_{ab}^{(2)} \varepsilon_{ib} \right] \\ &\quad + \sum_{a,x} U_{ax}^{\gamma} \left[2 \sum_{y} P_{xy}^{(2)} \varepsilon_{ay} - 2 \sum_{b} P_{ab}^{(2)} \varepsilon_{xb} \right] \\ &\quad + \sum_{a,x} S_{ax}^{\gamma} \left[-2 \sum_{b} P_{ab}^{(2)} \varepsilon_{xb} \right] \ . \end{aligned} \tag{63}$$

In so doing the size of the subsequent *Z*-vector problem (Eq. 54) is minimized. Again, factors inside brackets multiplying orbital responses contribute to the Lagrangian, while the factors multiplying overlap-derivative integrals become terms of the “energy-weighted” response density, $\mathbf{W}^{(2)}$.

3.2 Rearrangement of DP substitution term 4

The sum over IP indices in term 4 of Eq. (23) can be split into individual shell–shell summations as follows,

$$\sum_{p,q}^{\mathrm{DP}} P_{pq}^{(2)} \sum_{r>s}^{\mathrm{IP}} U_{rs}^{\gamma}(f_s - f_r) G_{pqrs}$$

$$= \sum_{p,q}^{\mathrm{DP}} P_{pq}^{(2)} \begin{bmatrix} \sum\limits_{x} \sum\limits_{i}^{\mathrm{c.d.}} U_{xi}^{\gamma}(f_i - f_x) G_{pqxi} \\ + \sum\limits_{a} \sum\limits_{i}^{\mathrm{c.d.}} U_{ai}^{\gamma}(f_i - f_a) G_{pqai} \\ + \sum\limits_{a,x} U_{ax}^{\gamma}(f_x - f_a) G_{pqax} \end{bmatrix} . \tag{64}$$

When the values of the shell occupation numbers are accounted for the resulting expression,

$$= \sum_{x} \sum_{i}^{\mathrm{c.d.}} U_{xi}^{\gamma} \left[\frac{1}{2} \sum_{p,q}^{\mathrm{DP}} P_{pq}^{(2)} G_{pqxi} \right] + \sum_{a} \sum_{i}^{\mathrm{c.d.}} U_{ai}^{\gamma} \left[\sum_{p,q}^{\mathrm{DP}} P_{pq}^{(2)} G_{pqai} \right]$$

$$+ \sum_{a,x} U_{ax}^{\gamma} \left[\frac{1}{2} \sum_{p,q}^{\mathrm{DP}} P_{pq}^{(2)} G_{pqax} \right] , \tag{65}$$

yields terms of the ZAPT2 Lagrangian.

3.3 Rearrangement of DP substitution terms 5 and 6

Terms 5 and 6 of Eq. (23) yield terms of $\mathbf{W}^{(2)}$ which can be rearranged as follows. Starting from an appropriate definition of the DP response density,

$$\sum_{p,q}^{\mathrm{DP}} P_{pq}^{(2)} \left[- \sum_{r>s}^{\mathrm{occ}} S_{rs}^{\gamma} f_r G_{pqrs} - \frac{1}{2} \sum_{r}^{\mathrm{occ}} S_{rr}^{\gamma} f_r G_{pqrr} \right] , \tag{66}$$

the sum over occupied MOs can be separated into the individual shell summations weighted by their occupation numbers,

$$= \sum_{p,q}^{\mathrm{DP}} P_{pq}^{(2)}$$

$$\times \begin{bmatrix} - \sum\limits_{i>j}^{\mathrm{c.d.}} S_{ij}^{\gamma} G_{pqij} - \frac{1}{2} \sum\limits_{x} \sum\limits_{i}^{\mathrm{c.d.}} S_{xi}^{\gamma} G_{pqxi} - \frac{1}{2} \sum\limits_{x>y} S_{xy}^{\gamma} G_{pqxy} \\ - \frac{1}{2} \sum\limits_{i}^{\mathrm{c.d.}} S_{ii}^{\gamma} G_{pqii} - \frac{1}{4} \sum\limits_{x} S_{xx}^{\gamma} G_{pqxx} \end{bmatrix} . \tag{67}$$

Although the c.d. and SOCC summations (first and third terms of Eq. 67) are asymmetric, the factors summed in Eq. (67) are symmetric,

$$= \sum_{p,q}^{\mathrm{DP}} P_{pq}^{(2)}$$

$$\times \begin{bmatrix} - \frac{1}{2} \sum\limits_{i \neq j}^{\mathrm{c.d.}} S_{ij}^{\gamma} G_{pqij} - \frac{1}{2} \sum\limits_{x} \sum\limits_{i}^{\mathrm{c.d.}} S_{xi}^{\gamma} G_{pqxi} - \frac{1}{4} \sum\limits_{x \neq y} S_{xy}^{\gamma} G_{pqxy} \\ - \frac{1}{2} \sum\limits_{i}^{\mathrm{c.d.}} S_{ii}^{\gamma} G_{pqii} - \frac{1}{4} \sum\limits_{x} S_{xx}^{\gamma} G_{pqxx} \end{bmatrix} , \tag{68}$$

allowing four of the terms to be combined into two,

$$= \sum_{p,q}^{\mathrm{DP}} P_{pq}^{(2)}$$

$$\times \left[- \frac{1}{2} \sum_{i,j}^{\mathrm{c.d.}} S_{ij}^{\gamma} G_{pqij} - \frac{1}{2} \sum_{x} \sum_{i}^{\mathrm{c.d.}} S_{xi}^{\gamma} G_{pqxi} - \frac{1}{4} \sum_{x,y} S_{xy}^{\gamma} G_{pqxy} \right] . \tag{69}$$

Finally, the order of summation may be changed to show the contributions to $\mathbf{W}^{(2)}$,

$$= \sum_{i,j}^{\mathrm{c.d.}} S_{ij}^{\gamma} \left[- \frac{1}{2} \sum_{p,q}^{\mathrm{DP}} P_{pq}^{(2)} G_{pqij} \right] + \sum_{x} \sum_{i}^{\mathrm{c.d.}} S_{xi}^{\gamma} \left[- \frac{1}{2} \sum_{p,q}^{\mathrm{DP}} P_{pq}^{(2)} G_{pqxi} \right]$$

$$+ \sum_{x,y} S_{xy}^{\gamma} \left[- \frac{1}{4} \sum_{p,q}^{\mathrm{DP}} P_{pq}^{(2)} G_{pqxy} \right] . \tag{70}$$

This completes the rearrangements of terms in the DP substitution expression Eq. (23). The first two terms of Eq. (51) will be described later. Terms 3 and 4 are straightforward to rearrange as terms of $\mathbf{W}^{(2)}$.

3.4 Rearrangement of IP substitution term 5

Term 5 of Eq. (51) requires a straightforward evaluation of summation ranges and δs to rearrange the right-hand side of Eq. (53),

$$\sum_{r>s}^{\mathrm{IP}} B_{rs}^{\gamma} Z_{rs} = - \sum_{r>s}^{\mathrm{IP}} Z_{rs} \sum_{p>}^{\mathrm{all}} \sum_{q}^{\mathrm{occ}} S_{pq}^{\gamma} \times \left[\delta_{pr} \left(\xi_{qs}^{r} - \zeta_{sq} \right) \right.$$

$$\left. - \delta_{ps} \left(\xi_{qr}^{s} - \zeta_{rq} \right) \right] + \cdots , \tag{71}$$

where the p, q summation may be expanded as follows,

$$= \sum_{i>j}^{\mathrm{c.d.}} S_{ij}^{\gamma} \left[- \sum_{r>s}^{\mathrm{IP}} Z_{rs} \left\{ \delta_{ir} \left(\xi_{js}^{r} - \zeta_{sj} \right) - \delta_{is} \left(\xi_{jr}^{s} - \zeta_{rj} \right) \right\} \right]$$

$$+ \sum_{x} \sum_{i}^{\mathrm{c.d.}} S_{xi}^{\gamma} \left[- \sum_{r>s}^{\mathrm{IP}} Z_{rs} \left\{ \delta_{xr} \left(\xi_{is}^{r} - \zeta_{si} \right) - \delta_{xs} \left(\xi_{ir}^{s} - \zeta_{ri} \right) \right\} \right]$$

$$+ \sum_{a} \sum_{i}^{\mathrm{c.d.}} S_{ai}^{\gamma} \left[- \sum_{r>s}^{\mathrm{IP}} Z_{rs} \left\{ \delta_{ar} \left(\xi_{is}^{r} - \zeta_{si} \right) - \delta_{as} \left(\xi_{ir}^{s} - \zeta_{ri} \right) \right\} \right]$$

$$+ \sum_{x>y} S_{xy}^{\gamma} \left[- \sum_{r>s}^{\mathrm{IP}} Z_{rs} \left\{ \delta_{xr} \left(\xi_{ys}^{r} - \zeta_{sy} \right) - \delta_{xs} \left(\xi_{yr}^{s} - \zeta_{ry} \right) \right\} \right]$$

$$+ \sum_{a,x} S_{ax}^{\gamma} \left[- \sum_{r>s}^{\mathrm{IP}} Z_{rs} \left\{ \delta_{ar} \left(\xi_{xs}^{r} - \zeta_{sx} \right) - \delta_{as} \left(\xi_{xr}^{s} - \zeta_{rx} \right) \right\} \right] , \tag{72}$$

and the IP summation as follows,

$$
\begin{aligned}
&=\sum_{i>j}^{\text{c.d.}} S_{ij}^{\gamma}\left[\sum_{x,k} Z_{xk}\delta_{ik}\left(\xi_{jx}^{k}-\zeta_{xj}\right)+\sum_{a,k} Z_{ak}\delta_{ik}\left(\xi_{ja}^{k}-\zeta_{aj}\right)\right]\\
&\quad+\sum_{x}\sum_{i}^{\text{c.d.}} S_{xi}^{\gamma}\left[-\sum_{y,j} Z_{yj}\delta_{xy}\left(\xi_{ij}^{y}-\zeta_{ji}\right)+\sum_{a,y} Z_{ay}\delta_{xy}(\xi_{ia}^{y}-\zeta_{ai})\right]\\
&\quad+\sum_{a}\sum_{i}^{\text{c.d.}} S_{ai}^{\gamma}\left[-\sum_{b,j} Z_{bj}\delta_{ab}\left(\xi_{ij}^{b}-\zeta_{ji}\right)-\sum_{b,x} Z_{bx}\delta_{ab}(\xi_{ix}^{b}-\zeta_{xi})\right]\\
&\quad+\sum_{x>y} S_{xy}^{\gamma}\left[-\sum_{z,i} Z_{zi}\delta_{xz}\left(\xi_{yi}^{z}-\zeta_{iy}\right)+\sum_{a,z} Z_{az}\delta_{xz}\left(\xi_{ya}^{z}-\zeta_{ay}\right)\right]\\
&\quad+\sum_{a,x} S_{ax}^{\gamma}\left[-\sum_{b,i} Z_{bi}\delta_{ab}(\xi_{xi}^{b}-\zeta_{ix})-\sum_{b,y} Z_{by}\delta_{ab}\left(\xi_{xy}^{b}-\zeta_{yx}\right)\right],
\end{aligned}
\tag{73}
$$

and the δs can be evaluated to give

$$
\begin{aligned}
&=\sum_{i>j}^{\text{c.d.}} S_{ij}^{\gamma}\left[\sum_{x} Z_{xi}\left(\xi_{jx}^{i}-\zeta_{xj}\right)+\sum_{a} Z_{ai}\left(\xi_{ja}^{i}-\zeta_{aj}\right)\right]\\
&\quad+\sum_{x}\sum_{i}^{\text{c.d.}} S_{xi}^{\gamma}\left[-\sum_{j} Z_{xj}\left(\xi_{ij}^{x}-\zeta_{ji}\right)+\sum_{a} Z_{ax}(\xi_{ia}^{x}-\zeta_{ai})\right]\\
&\quad+\sum_{a}\sum_{i}^{\text{c.d.}} S_{ai}^{\gamma}\left[-\sum_{j} Z_{aj}\left(\xi_{ij}^{a}-\zeta_{ji}\right)-\sum_{x} Z_{ax}(\xi_{ix}^{a}-\zeta_{xi})\right]\\
&\quad+\sum_{x>y} S_{xy}^{\gamma}\left[-\sum_{i} Z_{xi}\left(\xi_{yi}^{x}-\zeta_{iy}\right)+\sum_{a} Z_{ax}\left(\xi_{ya}^{x}-\zeta_{ay}\right)\right]\\
&\quad+\sum_{a,x} S_{ax}^{\gamma}\left[-\sum_{i} Z_{ai}(\xi_{xi}^{a}-\zeta_{ix})-\sum_{y} Z_{ay}\left(\xi_{xy}^{a}-\zeta_{yx}\right)\right].
\end{aligned}
\tag{74}
$$

The most convenient means of handling the inequalities in the summations of terms 1 and 4 of Eq. (74) is to define a modified Kronecker delta,

$$
\begin{aligned}
\delta'_{pq}&=1, \quad p>q,\\
\delta'_{pq}&=0, \quad p\le q\ ,
\end{aligned}
\tag{75}
$$

for use when the contribution to $\mathbf{W}^{(2)}$ is defined (see Sect. 4).

3.5 Derivative of SOCC energy integral component

The remaining rearrangements are concerned mainly with the derivation of Γ^{S} terms. It is convenient to gather all terms involving the SOCC eigenvalue integral component (Eq. 9) together and symmetrize the overall term with respect to the x, y indices as follows,

$$
\frac{1}{2}\sum_{x,y}(xy|xy)^{(\gamma)}\chi_x=\frac{1}{4}\sum_{x,y}(xy|xy)^{(\gamma)}\left[\chi_x+\chi_y\right]\ ,
\tag{76}
$$

where

$$
\begin{aligned}
\chi_x=&\sum_{i,j}\sum_{p}^{\text{s.v.}}(ix|jp)[C_{xp}(ix|jp)-(ip|jx)]/\left(D_{ij}^{xp}\right)^2\\
&+\sum_{a,b}\sum_{p}^{\text{d.s.}}(xa|pb)[C_{xp}(xa|pb)-(xb|pa)]/\left(D_{xp}^{ab}\right)^2\\
&+\sum_{i,z}\sum_{a}\left[(ix|za)^2/\left(D_{iz}^{xa}\right)^2+(iz|xa)^2/\left(D_{ix}^{za}\right)^2\right].
\end{aligned}
\tag{77}
$$

Note that in the absence of the exchange integral terms of Eq. (9), Eq. (77) would have the same form (apart from two sign changes) as $P_{xx}^{(2)}$ (see Sect.4). Substituting Eq. (16) for the integral derivative in Eq. (77) and recognizing the symmetry amongst the four SOCC labels leads to

$$
=\frac{1}{4}\sum_{x,y}\left[(xy|xy)^{\gamma}+4\sum_{p}U_{px}^{\gamma}(py|xy)\right]\left(\chi_x+\chi_y\right)\ .
\tag{78}
$$

The first term of Eq. (78) yields a contribution to Γ^{S} as follows,

$$
\begin{aligned}
&\frac{1}{4}\sum_{x,y}(xy|xy)^{\gamma}\left[\chi_x+\chi_y\right]\\
&\quad=\frac{1}{4}\sum_{\mu,\nu,\lambda,\sigma}(\mu\nu|\lambda\sigma)^{\gamma}\left[\sum_{x,y}C_{\mu x}C_{\nu y}C_{\lambda x}C_{\sigma y}\left(\chi_x+\chi_y\right)\right]\\
&\quad=\frac{1}{4}\sum_{\mu,\nu,\lambda,\sigma}(\mu\nu|\lambda\sigma)^{\gamma}\left[\left(\sum_{x}C_{\mu x}C_{\lambda x}\chi_x\right)\left(\sum_{y}C_{\nu y}C_{\sigma y}\right)\right.\\
&\qquad\left.+\left(\sum_{x}C_{\mu x}C_{\lambda x}\right)\left(\sum_{y}C_{\nu y}C_{\sigma y}\chi_y\right)\right]\\
&\quad=\sum_{\mu,\nu,\lambda,\sigma}(\mu\nu|\lambda\sigma)^{\gamma}\left[\frac{1}{4}\chi_{\mu\lambda}P_{\nu\sigma}^{\mathrm{S}}+\frac{1}{4}\chi_{\nu\sigma}P_{\mu\lambda}^{\mathrm{S}}\right],
\end{aligned}
\tag{79}
$$

in which the following back-transformed densities were used,

$$
P_{\mu\nu}^{\mathrm{HF}}=\sum_{p}^{\text{occ}}f_pC_{\mu p}C_{\nu p}=P_{\mu\nu}^{\mathrm{D}}+P_{\mu\nu}^{\mathrm{S}}\ ,
\tag{80}
$$

$$
\chi_{\mu\nu}=\sum_{x}C_{\mu x}C_{\nu x}\chi_x\ .
\tag{81}
$$

In Eq. (80), the ROHF density is separated into its doubly occupied (D) and SOCC (S) components. The second term of Eq. (78) yields various contributions to $\mathbf{L}$ and $\mathbf{W}^{(2)}$, and the following terms for SOCC DP responses,

$$
\begin{aligned}
&\sum_{p,y}U_{py}^{\gamma}\sum_{z}(pz|yz)\left[\chi_y+\chi_z\right]\\
&\quad=\sum_{x,y}U_{xy}^{\gamma}\sum_{z}(xz|yz)\left[\chi_y+\chi_z\right]+\cdots\\
&\quad=\sum_{x,y}\frac{Q_{xy}^{\gamma}}{\left(\varepsilon_y-\varepsilon_x\right)}\sum_{z}(xz|yz)\left[\chi_y+\chi_z\right]+\cdots\ ,
\end{aligned}
\tag{82}
$$

where Eq. (26) is employed for the case $x = y$. For Eq. (82) to become singular in the case $x \neq y$, the MOs would need to be degenerate. However, if x, y belong to the different irreducible representations the numerator will vanish faster than the denominator [25]. We now return to the DP and IP substitutions to deduce further terms of Γ^{S}.

3.6 Separable two-particle term from the DP substitution

The first term of Eq. (23) is the integral derivative of a Fock matrix element; the right-hand side of Eq. (40) gives rise to a term of the form

$$\sum_{p,q}^{\mathrm{DP}} \varepsilon_{pq}^{\gamma} P_{pq}^{(2)}$$

$$= \sum_{p,q}^{\mathrm{DP}} h_{pq}^{\gamma} P_{pq}^{(2)} + \sum_{p,q}^{\mathrm{DP}} P_{pq}^{(2)} \sum_{r}^{\mathrm{occ}} f_r [2(pq|rr)^{\gamma} - (pr|qr)^{\gamma}] \ . \tag{83}$$

The two-particle term of Eq. (83) can be rearranged as follows,

$$\sum_{\mu,\nu,\lambda,\sigma} (\mu\nu|\lambda\sigma)^{\gamma} \left[2\left(\sum_{p,q}^{\mathrm{DP}} C_{\mu p} C_{\nu q} P_{pq}^{(2)} \right) \left(\sum_{r}^{\mathrm{occ}} f_r C_{\lambda r} C_{\sigma r} \right) \right.$$
$$\left. - \left(\sum_{p,q}^{\mathrm{DP}} C_{\mu p} C_{\lambda q} P_{pq}^{(2)} \right) \left(\sum_{r}^{\mathrm{occ}} f_r C_{\nu r} C_{\sigma r} \right) \right] \ . \tag{84}$$

Identifying back-transformed two-index quantities with density matrix elements leads to

$$= \sum_{\mu,\nu,\lambda,\sigma} (\mu\nu|\lambda\sigma)^{\gamma} \left[2P_{\mu\nu}^{(2)} P_{\lambda\sigma}^{\mathrm{HF}} - P_{\mu\lambda}^{(2)} P_{\nu\sigma}^{\mathrm{HF}} \right] \ , \tag{85}$$

where

$$P_{\mu\nu}^{(2)} = \sum_{p,q}^{\mathrm{DP}} C_{\mu p} C_{\nu q} P_{pq}^{(2)} \ . \tag{86}$$

In practice, Eq. (85) should reflect any four-label symmetries that are exploited in the implementation chosen.

3.7 Separable two-particle term from the IP substitution

The first two terms of Eq. (51) involve the general open-shell derivative Fock matrix elements (Eq. 52), so Eq. (53) gives rise to a term of the form

$$\sum_{p,q}^{\mathrm{IP}} Z_{pq} \left(\zeta_{pq}^{\gamma} - \zeta_{qp}^{\gamma} \right)$$

$$= \sum_{p,q}^{\mathrm{IP}} Z_{pq} \begin{pmatrix} f_p h_{pq}^{\gamma} + \sum\limits_{r}^{\mathrm{occ}} \left[\alpha_{pr} (pq|rr)^{\gamma} + \beta_{pr} (pr|qr)^{\gamma} \right] \\ -f_q h_{pq}^{\gamma} - \sum\limits_{r}^{\mathrm{occ}} \left[\alpha_{qr} (pq|rr)^{\gamma} + \beta_{qr} (pr|qr)^{\gamma} \right] \end{pmatrix} , \tag{87}$$

which yields one- and two-electron terms,

$$= \sum_{p,q}^{\mathrm{IP}} Z_{pq} \left(f_p - f_q \right) h_{pq}^{\gamma} + \sum_{p,q}^{\mathrm{IP}} Z_{pq}$$
$$\times \left(\sum_{r}^{\mathrm{occ}} \left[\left(\alpha_{pr} - \alpha_{qr} \right) (pq|rr)^{\gamma} + \left(\beta_{pr} - \beta_{qr} \right) (pr|qr)^{\gamma} \right] \right) \ . \tag{88}$$

The one-electron term of Eq. (88) defines the IP block of the response density,

$$P_{pq}^{(2)} = \left(f_p - f_q \right) Z_{pq}, \qquad \text{for } p, q = \mathrm{IP} \ . \tag{89}$$

Note that care must be taken to form Eq. (89) immediately prior to back-transformation (Eq. 58) and contraction with core-Hamiltonian derivative integrals in Eq. (59). The two-electron term of Eq. (88) may be rearranged as follows,

$$\sum_{\mu,\nu,\lambda,\sigma} (\mu\nu|\lambda\sigma)^{\gamma} \left[\begin{array}{l} \sum\limits_{p,q}^{\mathrm{IP}} C_{\mu p} C_{\nu q} Z_{pq} \sum\limits_{r}^{\mathrm{occ}} C_{\lambda r} C_{\sigma r} \left(\alpha_{pr} - \alpha_{qr} \right) \\ + \sum\limits_{p,q}^{\mathrm{IP}} C_{\mu p} C_{\lambda q} Z_{pq} \sum\limits_{r}^{\mathrm{occ}} C_{\nu r} C_{\sigma r} \left(\beta_{pr} - \beta_{qr} \right) \end{array} \right] \ . \tag{90}$$

Considering, for brevity, just the Coulomb density term in Eq. (90),

$$\sum_{p,q}^{\mathrm{IP}} C_{\mu p} C_{\nu q} Z_{pq} \sum_{r}^{\mathrm{occ}} C_{\lambda r} C_{\sigma r} \left(\alpha_{pr} - \alpha_{qr} \right) \ , \tag{91}$$

Eq. (91) appears nonseparable unless it is subdivided into summations over unique shells,

$$\begin{aligned} = & \sum_{x,i} C_{\mu x} C_{\nu i} Z_{xi} \sum_{j}^{\mathrm{c.d.}} C_{\lambda j} C_{\sigma j} \left(\alpha_{xj} - \alpha_{ij} \right) \\ & + \sum_{x,i} C_{\mu x} C_{\nu i} Z_{xi} \sum_{y} C_{\lambda y} C_{\sigma y} \left(\alpha_{xy} - \alpha_{iy} \right) \\ & + \sum_{a,i} C_{\mu a} C_{\nu i} Z_{ai} \sum_{j}^{\mathrm{c.d.}} C_{\lambda j} C_{\sigma j} \left(\alpha_{aj} - \alpha_{ij} \right) \\ & + \sum_{a,i} C_{\mu a} C_{\nu i} Z_{ai} \sum_{x} C_{\lambda x} C_{\sigma x} \left(\alpha_{ax} - \alpha_{ix} \right) \\ & + \sum_{a,x} C_{\mu a} C_{\nu x} Z_{ax} \sum_{i}^{\mathrm{c.d.}} C_{\lambda i} C_{\sigma i} \left(\alpha_{ai} - \alpha_{xi} \right) \\ & + \sum_{a,x} C_{\mu a} C_{\nu x} Z_{ax} \sum_{y} C_{\lambda y} C_{\sigma y} \left(\alpha_{ay} - \alpha_{xy} \right) \ , \end{aligned} \tag{92}$$

which allows the coupling factors in brackets to be evaluated from Eq. (50),

$$
\begin{aligned}
&= -\left(\sum_{x,i} C_{\mu x} C_{\nu i} Z_{xi}\right)\left(\sum_{j}^{\text{c.d.}} C_{\lambda j} C_{\sigma j}\right) \\
&\quad -\frac{1}{2}\left(\sum_{x,i} C_{\mu x} C_{\nu i} Z_{xi}\right)\left(\sum_{y} C_{\lambda y} C_{\sigma y}\right) \\
&\quad - 2\left(\sum_{a,i} C_{\mu a} C_{\nu i} Z_{ai}\right)\left(\sum_{j}^{\text{c.d.}} C_{\lambda j} C_{\sigma j}\right) \\
&\quad - \left(\sum_{a,i} C_{\mu a} C_{\nu i} Z_{ai}\right)\left(\sum_{x} C_{\lambda x} C_{\sigma x}\right) \\
&\quad - \left(\sum_{a,x} C_{\mu a} C_{\nu x} Z_{ax}\right)\left(\sum_{i}^{\text{c.d.}} C_{\lambda i} C_{\sigma i}\right) \\
&\quad -\frac{1}{2}\left(\sum_{a,x} C_{\mu a} C_{\nu x} Z_{ax}\right)\left(\sum_{y} C_{\lambda y} C_{\sigma y}\right) \ . \qquad (93)
\end{aligned}
$$

By defining the following back-transformed densities over IP shells,

$$
\begin{aligned}
Z_{\mu\nu}^{\mathrm{SD}} &= \sum_{x,i} C_{\mu x} C_{\nu i} Z_{xi}. \\
Z_{\mu\nu}^{\mathrm{VD}} &= \sum_{a,i} C_{\mu a} C_{\nu i} Z_{ai}, \qquad (94) \\
Z_{\mu\nu}^{\mathrm{VS}} &= \sum_{a,x} C_{\mu a} C_{\nu x} Z_{ax} \ ,
\end{aligned}
$$

substituting into Eq. (93), and repeating the process for the exchange-coupling terms, the two-electron term of Eq. (88) may be written in the following separable form in the AO basis,

$$
\begin{aligned}
&-Z_{\mu\nu}^{\mathrm{SD}} P_{\lambda\sigma}^{\mathrm{D}} - \frac{1}{2} Z_{\mu\nu}^{\mathrm{SD}} P_{\lambda\sigma}^{\mathrm{S}} - 2 Z_{\mu\nu}^{\mathrm{VD}} P_{\lambda\sigma}^{\mathrm{D}} - Z_{\mu\nu}^{\mathrm{VD}} P_{\lambda\sigma}^{\mathrm{S}} - Z_{\mu\nu}^{\mathrm{VS}} P_{\lambda\sigma}^{\mathrm{D}} \\
&\quad - \frac{1}{2} Z_{\mu\nu}^{\mathrm{VS}} P_{\lambda\sigma}^{\mathrm{S}} + \frac{1}{2} Z_{\mu\lambda}^{\mathrm{SD}} P_{\nu\sigma}^{\mathrm{D}} + Z_{\mu\lambda}^{\mathrm{VD}} P_{\nu\sigma}^{\mathrm{D}} \\
&\quad + \frac{1}{2} Z_{\mu\lambda}^{\mathrm{VD}} P_{\nu\sigma}^{\mathrm{S}} + \frac{1}{2} Z_{\mu\lambda}^{\mathrm{VS}} P_{\nu\sigma}^{\mathrm{D}} + \frac{1}{2} Z_{\mu\lambda}^{\mathrm{VS}} P_{\nu\sigma}^{\mathrm{S}} \ , \qquad (95)
\end{aligned}
$$

which can be rearranged to give

$$
\begin{aligned}
&= -\left(Z_{\mu\nu}^{\mathrm{SD}} + 2 Z_{\mu\nu}^{\mathrm{VD}} + Z_{\mu\nu}^{\mathrm{VS}}\right) P_{\lambda\sigma}^{\mathrm{HF}} \\
&\quad + \left(\frac{1}{2} Z_{\mu\lambda}^{\mathrm{SD}} + Z_{\mu\lambda}^{\mathrm{VD}} + \frac{1}{2} Z_{\mu\lambda}^{\mathrm{VS}}\right) P_{\nu\sigma}^{\mathrm{HF}} + \frac{1}{2}\left(Z_{\mu\lambda}^{\mathrm{VS}} - Z_{\mu\lambda}^{\mathrm{SD}}\right) P_{\nu\sigma}^{\mathrm{S}} \ . \qquad (96)
\end{aligned}
$$

This contribution to the overall separable two-particle density requires three new matrices of order n^2, where n is the number of basis functions, which is principally a storage issue since

$$
Z_{\mu\nu} = \sum_{p,q}^{\mathrm{IP}} C_{\mu p} C_{\nu q} Z_{pq} = Z_{\mu\nu}^{\mathrm{SD}} + Z_{\mu\nu}^{\mathrm{VD}} + Z_{\mu\nu}^{\mathrm{VS}} \ . \qquad (97)
$$

This completes the rearrangements made to simplify the evaluation of the gradient expression (Eq. 56).

4 Gradient expression

In this section, the density-like quantities $\mathbf{P}^{(2)}$, $\mathbf{W}^{(2)}$, Γ^{S}, and Γ^{NS}, and the Lagrangian, $\mathbf{L}$, are summarized in terms of the matrix elements of their various shell–shell blocks. The CORE–CORE response density is null ($P_{mn}^{(2)} = 0$).

DOCC-CORE response density:

$$
P_{im}^{(2)} = \frac{1}{(\varepsilon_i - \varepsilon_m)} \times \left[
\begin{array}{c}
2\sum_{j}\sum_{p,q}^{\text{s.v.}} (mp|jq)[C_{pq}(ip|jq) - (iq|jp)]/D_{ij}^{pq} \\
+2\sum_{a,b}\sum_{p}^{\text{d.s.}} (ma|pb)[2(ia|pb) - (ib|pa)]/D_{ip}^{ab} \\
+2\sum_{x,y}\sum_{a} (mx|ya)(ix|ya)/D_{iy}^{xa} + \sum_{x,y,a} (mx|xa)(iy|ya)/D_{i}^{a}
\end{array}
\right] .
$$

DOCC–DOCC response density:

$$
\begin{aligned}
P_{ij}^{(2)} &= -\sum_{k}\sum_{p,q}^{\text{s.v.}} (ip|kq)[C_{pq}(jp|kq) - (jq|kp)]/D_{ik}^{pq} D_{jk}^{pq} \\
&\quad - \sum_{a,b}\sum_{p}^{\text{d.s.}} (ia|pb)[2(ja|pb) - (jb|pa)]/D_{ip}^{ab} D_{jp}^{ab} \\
&\quad - \sum_{x,y}\sum_{a} (ix|ya)(jx|ya)/D_{iy}^{xa} D_{jy}^{xa} \\
&\quad - \frac{1}{2}\sum_{x,y,a} (jx|xa)(jy|ya)/D_{i}^{a} D_{j}^{a} \ .
\end{aligned}
$$

SOCC–SOCC response density (see Eq. 77):

$$
\begin{aligned}
P_{xy}^{(2)} &= \sum_{i,j}\sum_{p}^{\text{s.v.}} (ix|jp)\left[C_{yp}(iy|jp) - (ip|jy)\right]/D_{ij}^{xp} D_{ij}^{yp} \\
&\quad - \sum_{a,b}\sum_{p}^{\text{d.s.}} (xa|pb)\left[C_{yp}(ya|pb) - (yb|pa)\right]/D_{xp}^{ab} D_{yp}^{ab} \\
&\quad + \sum_{i,z}\sum_{a}\left[(ix|za)(iy|za)/D_{iz}^{xa} D_{iz}^{ya}\right. \\
&\qquad\qquad \left. - (iz|xa)(iz|ya)/D_{ix}^{za} D_{iy}^{za}\right] \\
&\quad + \frac{(1-\delta_{xy})}{(\varepsilon_y - \varepsilon_x)}\sum_{z}(xz|yz)\left[\chi_y + \chi_z\right] \ .
\end{aligned}
$$

VIRT–VIRT response density:

$$\begin{aligned}P_{ab}^{(2)} = {} & \sum_{i,j}\sum_{p}^{\text{s.v.}}(ia|jp)[2(ib|jp)-(ip|jb)]/D_{ij}^{ap}D_{ij}^{bp}\\ & +\sum_{c}\sum_{p,q}^{\text{d.s.}}(pa|qc)\left[C_{pq}(pb|qc)-(pc|qb)\right]/D_{pq}^{ac}D_{pq}^{bc}\\ & +\sum_{x,y}\sum_{i}(ix|ya)(ix|yb)/D_{iy}^{xa}D_{iy}^{xb}\\ & +\frac{1}{2}\sum_{i,x,y}(ix|xa)(iy|yb)/D_i^a D_i^b \ .\end{aligned}$$

The IP, or off-diagonal response density, is given by Eq. (89).

CORE–CORE energy-weighted response density:

$$\begin{aligned}W_{mn}^{(2)} = {} & -\frac{1}{2}\sum_{p,q}^{\text{DP}}P_{pq}^{(2)}G_{pqmn}-\frac{\delta_{mn}}{2}\sum_{p>q}^{\text{IP}}Z_{pq}\tau_{pq}^{mm}\\ & +\delta'_{mn}\left[\sum_{x}Z_{xm}\left(\xi_{nx}^{m}-\zeta_{xn}\right)\right.\\ & \left.+\sum_{a}Z_{am}\left(\xi_{na}^{m}-\zeta_{an}\right)-\sum_{p,q}^{\text{IP}}Z_{pq}\tau_{pq}^{mn}\right] \ .\end{aligned}$$

DOCC–CORE energy-weighted response density:

$$\begin{aligned}W_{im}^{(2)} = {} & -\sum_{p,q}^{\text{DP}}P_{pq}^{(2)}G_{pqim}-P_{im}^{(2)}\varepsilon_m-\sum_{p>q}^{\text{DP}}Z_{pq}\tau_{pq}^{im}\\ & +\sum_{x}Z_{xi}\left(\xi_{mx}^{i}-\zeta_{xm}\right)+\sum_{a}Z_{ai}\left(\xi_{ma}^{i}-\zeta_{am}\right) \ .\end{aligned}$$

DOCC–DOCC energy-weighted response density:

$$\begin{aligned}W_{ij}^{(2)} = {} & -\sum_{k}\sum_{p,q}^{\text{s.v.}}(ip|kq)\left[C_{pq}(jp|kq)-(jq|kp)\right]/D_{jk}^{pq}\\ & -\sum_{a,b}\sum_{p}^{\text{d.s.}}(ia|pb)[2(ja|pb)-(jb|pa)]/D_{jp}^{ab}\\ & -\sum_{x,y}\sum_{a}(ix|ya)(jx|ya)/D_{jy}^{xa}-\frac{1}{2}\sum_{x,y,a}(ix|xa)(jy|ya)/D_j^a\\ & -\frac{1}{2}\sum_{p,q}^{\text{DP}}P_{pq}^{(2)}G_{pqij}-P_{ij}^{(2)}\varepsilon_j-\frac{\delta_{ij}}{2}\sum_{p>q}^{\text{DP}}Z_{pq}\tau_{pq}^{ii}\\ & +\delta'_{ij}\left[\sum_{x}Z_{xi}\left(\xi_{jx}^{i}-\zeta_{xj}\right)+\sum_{a}Z_{ai}\left(\xi_{ja}^{i}-\zeta_{aj}\right)\right.\\ & \left.-\sum_{p>q}^{\text{IP}}Z_{pq}\tau_{pq}^{ij}\right] \ .\end{aligned}$$

SOCC–SOCC energy-weighted response density:

$$\begin{aligned}W_{xy}^{(2)} = {} & -\sum_{i,j}\sum_{p}^{\text{s.v.}}(ix|jp)[2(iy|jp)-(ip|jy)]/D_{ij}^{yp}\\ & -\sum_{a,b}\sum_{p}^{\text{d.s.}}(xa|pb)\left[C_{yp}(ya|pb)-(yb|pa)\right]/D_{yp}^{ab}\\ & -\sum_{z,a}\sum_{i}\left[(ix|za)(iy|za)/D_{iz}^{ya}+(iz|xa)(iz|ya)/D_{iy}^{za}\right]\\ & -\frac{1}{2}\sum_{i,z,a}(ix|ya)(iz|za)/D_i^a-\frac{1}{4}\sum_{p,q}^{\text{DP}}P_{pq}^{(2)}G_{pqxy}-P_{xy}^{(2)}\varepsilon_y\\ & -\delta'_{xy}\left[\sum_{i}^{\text{c.d.}}Z_{xi}\left(\xi_{yi}^{x}-\zeta_{iy}\right)-\sum_{a}Z_{ax}\left(\xi_{ya}^{x}-\zeta_{ay}\right)\right.\\ & \left.+\sum_{p>q}^{\text{IP}}Z_{pq}\tau_{pq}^{xy}\right]-\frac{\delta_{xy}}{2}\sum_{p>q}^{\text{IP}}Z_{pq}\tau_{pq}^{xx}-\frac{\delta_{xy}}{2}\sum_{z}(xz|xz)[\chi_x+\chi_z] \ .\end{aligned}$$

VIRT–VIRT energy-weighted response density:

$$\begin{aligned}W_{ab}^{(2)} = {} & -\sum_{i,j}\sum_{p}^{\text{s.v.}}(ia|jp)[2(ib|jp)-(ip|jb)]/D_{ij}^{pb}\\ & -\sum_{c}\sum_{p,q}^{\text{d.s.}}(pa|qc)\left[C_{pq}(pb|qc)-(pc|qb)\right]/D_{pq}^{bc}\\ & -\sum_{x,y}\sum_{i}(ix|ya)(ix|yb)/D_{iy}^{xb}\\ & -\frac{1}{2}\sum_{i,x,y}(ix|xa)(iy|yb)/D_i^b-P_{ab}^{(2)}\varepsilon_b \ .\end{aligned}$$

SOCC–CORE and SOCC–DOCC energy-weighted response density:

$$\begin{aligned}W_{xr}^{(2)} = {} & -2\sum_{i,j}\sum_{p}^{\text{s.v.}}(ir|jp)[C_{xp}(ix|jp)-(ip|jx)]/D_{ij}^{xp}\\ & -2\sum_{a,b}\sum_{p}^{\text{d.s.}}(ra|pb)[C_{xp}(xa|pb)-(xb|pa)]/D_{xp}^{ab}\\ & -2\sum_{y,a}\sum_{i}\left[(ir|ya)(ix|ya)/D_{iy}^{xa}+(iy|ra)(iy|xa)/D_{ix}^{ya}\right]\\ & -\sum_{i,y,a}[(ix|ra)+(ir|xa)](iy|ya)/D_i^a\\ & -\frac{1}{2}\sum_{p,q}^{\text{DP}}P_{pq}^{(2)}G_{pqxr}-2\sum_{y}P_{xy}^{(2)}\varepsilon_{yr}-\sum_{p>q}^{\text{IP}}Z_{pq}\tau_{pq}^{xr}\\ & -\sum_{i}^{\text{c.d.}}Z_{xi}\left(\xi_{ri}^{x}-\zeta_{ir}\right)+\sum_{a}Z_{ax}\left(\xi_{ra}^{x}-\zeta_{ar}\right)\\ & -\sum_{z}(rz|xz)[\chi_x+\chi_z] \ ,\end{aligned}$$

where r indexes a CORE or a DOCC MO.

VIRT–CORE, VIRT–DOCC, and VIRT–SOCC energy-weighted response density:

$$
\begin{aligned}
W_{ar}^{(2)} = &- 2\sum_{i,j}\sum_{p}^{\text{s.v.}}(ir|jp)[2(ia|jp) - (ip|ja)]/D_{ij}^{ap} \\
&- 2\sum_{b}\sum_{p,q}^{\text{d.s.}}(pr|qb)\left[C_{pq}(pa|qb) - (pb|qa)\right]/D_{pq}^{ab} \\
&- 2\sum_{x,y}\sum_{i}(ix|yr)(ix|ya)/D_{iy}^{xa} \\
&- \sum_{i,x,y}(ix|xr)(iy|ya)/D_{i}^{a} - 2\sum_{b}P_{ab}^{(2)}\varepsilon_{br} - \sum_{p>q}^{\text{IP}}Z_{pq}\tau_{pq}^{ar} \\
&- \sum_{i}^{\text{c.d.}}Z_{ai}\left(\xi_{ri}^{a} - \zeta_{ir}\right) - \sum_{x}Z_{ax}\left(\xi_{rx}^{a} - \zeta_{xr}\right) \quad ,
\end{aligned}
$$

where r indexes a CORE, DOCC, or SOCC MO.

SOCC–CORE Lagrangian elements:

$$
\begin{aligned}
L_{xm} = &- 2\sum_{i,j}\sum_{p}^{\text{s.v.}}(im|jp)\left[C_{xp}(ix|jp) - (ip|jx)\right]/D_{ij}^{xp} \\
&- 2\sum_{a,b}\sum_{p}^{\text{d.s.}}(ma|pb)\left[C_{xp}(xa|pb) - (xb|pa)\right]/D_{xp}^{ab} \\
&- 2\sum_{y,a}\sum_{i}\left[(im|ya)(ix|ya)/D_{iy}^{xa} + (iy|ma)(iy|xa)/D_{ix}^{ya}\right] \\
&- \sum_{i,y,a}[(ix|ma) + (im|xa)](iy|ya)/D_{i}^{a} \\
&+ \frac{1}{2}\sum_{pq}^{\text{DP}}P_{pq}^{(2)}G_{pqxm} + 2\sum_{i}^{\text{c.d.}}P_{im}^{(2)}\varepsilon_{xi} - 2\sum_{y}P_{xy}^{(2)}\varepsilon_{ym} \; .
\end{aligned}
$$

VIRT–CORE Lagrangian elements:

$$
\begin{aligned}
L_{am} = &- 2\sum_{i,j}\sum_{p}^{\text{s.v.}}(im|jp)[2(ia|jp) - (ip|ja)]/D_{ij}^{ap} \\
&- 2\sum_{b}\sum_{p,q}^{\text{d.s.}}(pm|qb)\left[C_{pq}(pa|qb) - (pb|qa)\right]/D_{pq}^{ab} \\
&- 2\sum_{x,y}\sum_{i}(ix|ym)(ix|ya)/D_{iy}^{xa} \\
&- \sum_{i,x,y}(ix|xm)(iy|ya)/D_{i}^{a} \\
&+ \sum_{pq}^{\text{DP}}P_{pq}^{(2)}G_{pqam} + 2\sum_{i}^{\text{c.d.}}P_{im}^{(2)}\varepsilon_{ai} - 2\sum_{b}P_{ab}^{(2)}\varepsilon_{bm} \quad .
\end{aligned}
$$

SOCC–DOCC Lagrangian elements:

$$
\begin{aligned}
L_{xi} = &\; 2\sum_{j}\sum_{p,q}^{\text{s.v.}}(xp|jq)\left[C_{pq}(ip|jq) - (iq|jp)\right]/D_{ij}^{pq} \\
&- 2\sum_{j,k}\sum_{p}^{\text{s.v.}}(ik|jp)\left[C_{xp}(kx|jp) - (kp|jx)\right]/D_{jk}^{xp} \\
&+ 2\sum_{a,b}\sum_{p}^{\text{d.s.}}(xa|pb)[2(ia|pb) - (ib|pa)]/D_{ip}^{ab} \\
&- 2\sum_{a,b}\sum_{p}^{\text{d.s.}}(ia|pb)\left[C_{xp}(xa|pb) - (xb|pa)\right]/D_{xp}^{ab} \\
&+ 2\sum_{y,z}\sum_{a}(xy|za)(iy|za)/D_{iz}^{ya} \\
&- 2\sum_{y,a}\sum_{j}\left[(ij|ya)(jx|ya)/D_{jy}^{xa} + (jy|ia)(jy|xa)/D_{jx}^{ya}\right] \\
&- \sum_{j,y,a}[(jx|ia) + (ij|xa)](jy|ya)/D_{j}^{a} \\
&+ \sum_{y,z,a}(xy|ya)(iz|za)/D_{i}^{a} \\
&- \sum_{z}(iz|xz)[\chi_x + \chi_z] + \frac{1}{2}\sum_{pq}^{\text{DP}}P_{pq}^{(2)}G_{pqxi} \\
&+ 2\sum_{j}^{\text{c.d.}}P_{ij}^{(2)}\varepsilon_{xj} - 2\sum_{y}P_{xy}^{(2)}\varepsilon_{yi} \quad .
\end{aligned}
$$

VIRT–DOCC Lagrangian elements:

$$
\begin{aligned}
L_{ai} = &\; 2\sum_{j}\sum_{p,q}^{\text{s.v.}}(pa|jq)\left[C_{pq}(ip|jq) - (iq|jp)\right]/D_{ij}^{pq} \\
&- 2\sum_{j,k}\sum_{p}^{\text{s.v.}}(ik|jp)[2(ka|jp) - (kp|ja)]/D_{jk}^{ap} \\
&+ 2\sum_{b,c}\sum_{p}^{\text{d.s.}}(ab|pc)[2(ib|pc) - (ic|pb)]/D_{ip}^{bc} \\
&- 2\sum_{b}\sum_{p,q}^{\text{d.s.}}(ip|qb)\left[C_{pq}(pa|qb) - (pb|qa)\right]/D_{pq}^{ab} \\
&+ 2\sum_{x,y}\sum_{b}(xa|yb)(ix|yb)/D_{iy}^{xb} \\
&- 2\sum_{x,y}\sum_{j}(iy|jx)(jx|ya)/D_{jy}^{xa} \\
&+ \sum_{x,y,b}(xa|xb)(iy|yb)/D_{i}^{b} - \sum_{j,x,y}(ix|jx)(jy|ya)/D_{j}^{a} \\
&+ \sum_{pq}^{\text{DP}}P_{pq}^{(2)}G_{pqai} + 2\sum_{j}^{\text{c.d.}}P_{ij}^{(2)}\varepsilon_{aj} - 2\sum_{b}P_{ab}^{(2)}\varepsilon_{bi} \; .
\end{aligned}
$$

VIRT–SOCC Lagrangian elements:

$$
\begin{aligned}
L_{ax} = &\; 2\sum_{i,j}\sum_{p}^{\text{s.v.}}(ia|jp)\left[C_{xp}(ix|jp) - (ip|jx)\right]/D_{ij}^{xp} \\
&- 2\sum_{i,j}\sum_{p}^{\text{s.v.}}(ix|jp)[2(ia|jp) - (ip|ja)]/D_{ij}^{ap} \\
&+ 2\sum_{b,c}\sum_{p}^{\text{d.s.}}(ab|pc)\left[C_{xp}(xb|pc) - (xc|pb)\right]/D_{xp}^{bc} \\
&- 2\sum_{b}\sum_{p,q}^{\text{d.s.}}(xp|qb)\left[C_{pq}(pa|qb) - (pb|qa)\right]/D_{pq}^{ab}
\end{aligned}
$$

$$\begin{aligned}
&+2\sum_{i,y}\sum_{b}\left[(ia|yb)(ix|yb)/D_{iy}^{xb}+(iy|ab)(iy|xb)/D_{ix}^{yb}\right]\\
&-2\sum_{y,z}\sum_{i}(iz|xy)(iz|ya)/D_{iy}^{za}\\
&+\sum_{i,y,b}[(ix|ab)+(ia|xb)](iy|yb)/D_{i}^{b}\\
&-\sum_{i,y,z}(iy|xy)(iz|za)/D_{i}^{a}\\
&+\frac{1}{2}\sum_{pq}^{\mathrm{DP}}P_{pq}^{(2)}G_{pqax}+2\sum_{y}P_{xy}^{(2)}\varepsilon_{ay}\\
&-2\sum_{b}P_{ab}^{(2)}\varepsilon_{bx}-\sum_{y}(xy|ya)\left[\chi_{x}+\chi_{y}\right]\ .
\end{aligned}$$

Separable two-particle density:

$$\begin{aligned}
\Gamma_{\mu\nu\lambda\sigma}^{\mathrm{S}}=\;&2P_{\mu\nu}^{(2)}P_{\lambda\sigma}^{\mathrm{HF}}-P_{\mu\lambda}^{(2)}P_{\nu\sigma}^{\mathrm{HF}}+\tfrac{1}{4}\chi_{\mu\lambda}P_{\nu\sigma}^{\mathrm{S}}\\
&+\tfrac{1}{4}\chi_{\nu\sigma}P_{\mu\lambda}^{\mathrm{S}}+\tfrac{1}{2}\left(Z_{\mu\lambda}^{\mathrm{VS}}-Z_{\mu\lambda}^{\mathrm{SD}}\right)P_{\nu\sigma}^{\mathrm{S}}\\
&-\left(Z_{\mu\nu}^{\mathrm{SD}}+2Z_{\mu\nu}^{\mathrm{VD}}+Z_{\mu\nu}^{\mathrm{VS}}\right)P_{\lambda\sigma}^{\mathrm{HF}}\\
&+\left(\tfrac{1}{2}Z_{\mu\lambda}^{\mathrm{SD}}+Z_{\mu\lambda}^{\mathrm{VD}}+\tfrac{1}{2}Z_{\mu\lambda}^{\mathrm{VS}}\right)P_{\nu\sigma}^{\mathrm{HF}}\ .
\end{aligned}$$

Nonseparable two-particle density:

$$\Gamma_{\mu\nu\lambda\sigma}^{\mathrm{NS}}=\sum_{p,q}^{\mathrm{d.s.}}\sum_{r,s}^{\mathrm{s.v.}}C_{\mu p}C_{\nu q}C_{\lambda r}C_{\sigma s}T_{pq}^{rs}\ ,$$

where

$$\begin{aligned}
T_{ij}^{ab}&=2[2(ia|jb)-(ib|ja)]/D_{ij}^{ab},\\
T_{ij}^{ax}&=[2(ia|jx)-(ix|ja)]/D_{ij}^{ax},\\
T_{ij}^{xa}&=[2(ix|ja)-(ia|jx)]/D_{ij}^{xa},\\
T_{ij}^{xy}&=[(ix|jy)-(iy|jx)]/D_{ij}^{xy},\\
T_{iy}^{xa}&=2(ix|ya)/D_{iy}^{xa}+(ix|xa)(iy|ya)/D_{i}^{a},\\
T_{ix}^{ab}&=[2(ia|xb)-(ib|xa)]/D_{ix}^{ab},\\
T_{xi}^{ab}&=[2(xa|ib)-(xb|ia)]/D_{xi}^{ab},\\
T_{xy}^{ab}&=[(xa|yb)-(xb|ya)]/D_{xy}^{ab},\\
T_{ix}^{yz}&=T_{xi}^{yz}=T_{xy}^{za}=T_{xy}^{az}=T_{wx}^{yz}=0\ .
\end{aligned}$$

5 Conclusion

While second-order UMP theory admits a relatively simple explicit derivative expression [26, 27], the situation for RMP [28–30], ROMP, OPT1, OPT2, and ZAPT is evidently more complex. These gradients give rise to a number of issues not found in the closed-shell MP2 case. Firstly, the energy expressions contain several terms. One may attempt to take the derivative of each term separately then combine the results; however, this would be a tedious exercise and is likely to produce many more terms than necessary. Secondly, the DP and IP responses have quite different forms for their substitutions (comparing Eqs. 23 and 51, their counterparts in the closed-shell case differ by only one term [31]). Of course, there are also four classes of MO to consider if frozen cores are included.

However, it has been shown that when these factors are taken into account the results are quite tractable. Indeed, though the gradient expression given in this work involves many more terms than its closed-shell counterpart, the new terms are all associated with summations over SOCC indices, which are likely to be short. It is not expected, therefore, that the evaluation of the ZAPT2 gradient will be significantly more expensive than comparable closed-shell MP2 calculations.

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