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A derivation of the frozen-orbital unrestricted open-shell and restricted closed-shell second-order perturbation theory analytic gradient expressions

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Abstract. A detailed derivation of the frozen-orbital second-order perturbation theory (MP2) analytic gradient in the spin-orbital basis is presented. The summation ranges and modification of the MP2 gradient terms that result from the frozen-orbital approximation are clearly identified. The frozen-orbital analytic gradients for unrestricted MP2 and closed-shell MP2 are determined from the spin-orbital derivation. A discussion of useful implementation procedures is included. Timings from full and frozen-orbital MP2 gradient calculations on the molecule silicocene (the silicon analog of the sandwich compound ferrocene) are also presented.

Keywords: Analytic derivative – Møller-Plesset perturbation theory – Frozen core

1 Introduction

The analytic expression for the derivative of the full second-order perturbation theory (MP2) energy (all electrons correlated) with respect to nuclear coordinate displacement for closed-shell systems has long been known [1]. In addition, perturbation theory with unrestricted wavefunctions has been used to describe open-shell systems for many years. With the development and implementation of more efficient methodology and algorithms [2] has come the widespread use of MP2 gradients to include the effects of dynamic electron correlation in the determination of molecular structure. The recent development of parallel algorithms [3, 4] has greatly extended the size of the systems to which the method can be applied.

Usually, the effects of including dynamic correlation in the inner shell or core electrons of a molecule are minimal in terms of relative energies and geometry parameters, and therefore core electrons are often not included in the perturbation treatment; this is known as the frozen-core approximation. In addition to an associated reduction in computational effort [2], the frozen-core approximation can be preferable to full MP2, as the description of core electrons is of lower quality than the description of valence electrons in many basis sets. Virtual orbitals may also be frozen or "deleted"; this corresponds to neglecting the excitations into these orbitals.

The modification of the MP2 energy expression to exclude electrons in frozen core or virtual orbitals is a trivial matter which requires simply that the summation over the orbitals excludes those chosen to be frozen. Using the notation defined in the next section, the frozen-orbital MP2 energy expression is

$$E^{(2)} = \frac{1}{4}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}(ia||jb)T_{ij}^{ab} \ , \tag{1}$$

where an amplitude in the spin-orbital basis is defined as

$$T_{ij}^{ab} = (ia||jb)/D_{ij}^{ab} \ , \tag{2}$$

where

$$(ia||jb) \equiv (ia|jb) - (ib|ja) \tag{3}$$

and

$$D_{ij}^{ab} = \varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b \ . \tag{4}$$

The reduction in the number of transformed two-electron integrals required in Eq. (1) results in a reduction of the computation time needed for the calculation. Although the modification required for the MP2 energy

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expression is minor, that for the MP2 analytic gradient expression is far from trivial and involves so-called dependent-pair contributions.

Groundwork for the treatment of frozen-orbital dependent-pair contributions, as well as other types of dependent-pair contributions, to analytic energy gradients was carried out in the mid 1980s [5, 6]. Since then, these techniques have been further developed and applied to numerous correlated methods [7, 8, 9, 10, 11, 12, 13, 14, 15]. For example, Rice et al. [5] and Lee at al. [8] have discussed dependent-pair contributions in configuration interaction methods, while Scheiner et al. [7], Rice et al. [9], Rendell and Lee [10], and Lee and Rendell [11] have discussed such contributions in coupled-cluster methods. More recently, some of the complications involved in frozen-core analytic energy gradient methods for various coupled-cluster and perturbation theory methods have been briefly discussed by Baeck et al. [13] and the derivation of the frozen-orbital closed-shell MP2 gradient expression has been presented by Lee et al. [14] and Webb et al. [15]. However, no explicit derivation of the analytic frozen-orbital spin-orbital or unrestricted MP2 (UMP2) gradient expression is currently available in the literature, even though UMP2 gradients have previously been implemented in various electronic structure programs.

The aim of this overview is twofold. The first is to present a detailed, step-by-step, derivation of the analytic frozen-orbital spin-orbital gradient expression and subsequent spin-integration to UMP2 and MP2 expressions, in order to provide a pedagogical application of dependent-pair techniques that is useful to new researches in this field. The second goal is to present the UMP2 frozen-orbital gradient expression in sufficient detail to facilitate serial and parallel implementation in electronic structure codes such as GAMESS [16].

2 Notation, definitions, and techniques

The notation, definitions, and techniques that will be used extensively during the course of the derivation of the MP2 frozen-orbital gradient are introduced. Considerable use is made of the excellent book by Yamaguchi et al. [17].

2.1 Notation

The indices, summation ranges, and symbols used throughout the derivation are summarized here.

Indices

- J, K: frozen-core molecular orbital (MO).
- i, j, k, l: any occupied MO.
- a, b, c: any virtual MO.
- B, C: frozen virtual MO.
- p, q, r, s, t: any MO.
- μ,ν,λ,σ: atomic orbital (AO).
- Superscript x: derivative with respect to nuclear displacement x.
- Superscript (x): derivatives of AO integrals only (not expansion coefficients).
- Superscript α: α MO, orbital energy, etc. (for unrestricted Hartree–Fock, UHF).
- Superscript β: β MO, orbital energy, etc. (for UHF).
- Superscript CS: closed-shell matrix.
- Superscript (2): MP2 energy or density correction.

Summation ranges

- act: active occupied MOs (usually valence orbitals).
- core: frozen-core MOs (usually inner shells).
- occ: all occupied MOs (core + act).
- vact: active virtual MOs.
- vf: frozen virtual MOs.
- vall: all virtual MOs (vact + vf).
- all: all MOs.

Symbols

- $(pq|rs)$: electron repulsion integral (ERI) in the MO basis, where p and q refer to electron 1 and r and s refer to electron 2.
- H_{pq}: one-electron Hamiltonian integral.
- S_{pq}: overlap integral.
- ε_p: self-consistent-field (SCF) orbital energy.
- U^x_{pq}: orbital response to nuclear displacement x.
- $|p\rangle$: MO in bra-ket notation.
- L: so-called MP2 Lagrangian.

2.2 Definitions

Definitions used in the derivation are summarized here.

Derivatives with respect to a perturbation x

The derivative of a MO is given by [17]

$$\frac{\partial|p\rangle}{\partial x} \equiv |p\rangle^x = \left(\sum_\mu^{\mathrm{AO}} C_{\mu p}|\mu\rangle\right)^x = \sum_\mu^{\mathrm{AO}} C_{\mu p}|\mu\rangle^x + \sum_\mu^{\mathrm{AO}} C^x_{\mu p}|\mu\rangle$$
$$= |p\rangle^{(x)} + \sum_\mu^{\mathrm{AO}}\sum_q^{\mathrm{all}} U^x_{qp} C_{\mu q}|\mu\rangle = |p\rangle^{(x)} + \sum_q^{\mathrm{all}} U^x_{qp}|q\rangle \quad . \tag{5}$$

Since an ERI in the MO basis is a linear combination of ERIs in the AO basis

$$(pq|rs) = \sum_{\mu\nu\lambda\sigma} C_{\mu p}C_{\nu q}C_{\lambda r}C_{\sigma s}(\mu\nu|\lambda\sigma) \quad , \tag{6}$$

it follows that

$$(pq|rs)^x = (pq|rs)^{(x)} + \sum_t^{\text{all}} U^x_{tp}(tq|rs) + \sum_t^{\text{all}} U^x_{tq}(pt|rs) + \sum_t^{\text{all}} U^x_{tr}(pq|ts) + \sum_t^{\text{all}} U^x_{ts}(pq|rt) \ . \quad (7)$$

The derivative of the orthonormality constraint $S_{pq} = \delta_{pq}$ yields

$$U^x_{pq} + U^x_{qp} + S^{(x)}_{pq} = 0 \ , \quad (8)$$

and thus

$$U^x_{pp} = -\frac{1}{2} S^{(x)}_{pp} \ . \quad (9)$$

Coupled perturbed Hartree–Fock equations in the spin-orbital basis

These equations are derived by taking the derivative of the Fock matrix equation in the spin-orbital basis. (See related closed-shell derivation in Ref. [17]). The orbital responses may be expressed in terms of orbital energies, overlap integrals, and other quantities by writing

$$U^x_{pq} = \frac{1}{(\varepsilon_q - \varepsilon_p)} Q^x_{pq} \ , \quad (10)$$

where

$$Q^x_{pq} \equiv B^x_{pq} + \sum_c^{\text{vall}} \sum_k^{\text{occ}} U^x_{ck} A_{pqck} \ , \quad (11)$$

$$A_{pqrs} = 2(pq|rs) - (pr|qs) - (ps|qr) \ , \quad (12)$$

$$B^x_{pq} = F^{(x)}_{pq} - S^{(x)}_{pq}\varepsilon_q - \frac{1}{2}\sum_{kl}^{\text{occ}} S^{(x)}_{kl} A_{pqlk} \ , \quad (13)$$

$$F^{(x)}_{pq} = H^{(x)}_{pq} + \sum_k^{\text{occ}} \left[(pq|kk)^{(x)} - (pk|qk)^{(x)} \right] \ . \quad (14)$$

If $p = q$, it may be shown that Eq. (11) can be written in the simpler form

$$\varepsilon^x_p = Q^x_{pp} \ . \quad (15)$$

The coupled perturbed Hartree–Fock (CPHF) equations are then written as

$$\sum_i^{\text{occ}} \sum_a^{\text{vall}} \left[\delta_{ab}\delta_{ij}(\varepsilon_i - \varepsilon_a) - A_{aibj} \right] U^x_{ai} = B^x_{bj} \ , \quad (16)$$

or, in matrix form, as

$$\mathbf{A}'\mathbf{U}^x = \mathbf{B}^x, \quad (17)$$

where

$$A'_{aibj} = \delta_{ab}\delta_{ij}(\varepsilon_i - \varepsilon_a) - A_{aibj}. \quad (18)$$

2.3 Techniques

There are several important tools used throughout the paper, some familiar and some less well known, that are summarized here.

Interchange of indices owing to equivalence on summation

For example,

$$\sum_{ab} (ia|jb)^x (ib|ja) = \sum_{ab} (ia|jb)(ib|ja)^x \ . \quad (19)$$

$$\sum_{ij} [(i^x a|jb) + (ia|j^x b)] = 2\sum_{ij} (i^x a|jb) \ . \quad (20)$$

Splitting summations

For example,

$$\sum_k U^x_{ki} = \sum_{k \neq i} U^x_{ki} + U^x_{ii} = \sum_{k>i} U^x_{ki} + \sum_{k<i} U^x_{ki} + U^x_{ii} \ . \quad (21)$$

The chain rule

For example,

$$\frac{\partial}{\partial x}\left(\frac{1}{D^{ab}_{ij}}\right) = \frac{\partial}{\partial D^{ab}_{ij}}\left(\frac{1}{D^{ab}_{ij}}\right)\frac{\partial D^{ab}_{ij}}{\partial x} = -\left(\frac{1}{D^{ab}_{ij}}\right)^2 \left(D^{ab}_{ij}\right)^x \ . \quad (22)$$

Cross-multiplication

For example,

$$\frac{1}{D^{ab}_{ij}} - \frac{1}{D^{ab}_{kj}} = \frac{D^{ab}_{kj} - D^{ab}_{ij}}{D^{ab}_{ij} D^{ab}_{kj}} = \frac{\varepsilon_k - \varepsilon_i}{D^{ab}_{ij} D^{ab}_{kj}} \ . \quad (23)$$

3 Derivation of the MP2 gradient equation in the spin-orbital basis

In this section, the frozen-orbital MP2 gradient expression is derived in the spin-orbital basis. First, the general form of the MP2 gradient is examined. Then, the derivative of the MP2 gradient expression is considered, orbital responses are introduced, density matrices are introduced, and the CPHF equations are solved. Subsequently, the resulting one-particle density matrices are summarized.

3.1 General form of the MP2 gradient

When written in the AO basis, the MP2 energy gradient takes the following general form that applies to all analytic first derivatives with respect to a nuclear displacement x:

$$E^{x}=\sum_{\mu\nu}^{\mathrm{AO}}P_{\mu\nu}^{\mathrm{MP2}}H_{\mu\nu}^{x}+\sum_{\mu\nu}^{\mathrm{AO}}W_{\mu\nu}^{\mathrm{MP2}}S_{\mu\nu}^{x}+\sum_{\mu\nu\lambda\sigma}^{\mathrm{AO}}\Gamma_{\mu\nu\lambda\sigma}^{\mathrm{MP2}}(\mu\nu|\lambda\sigma)^{x}\ . \tag{24}$$

In Eq. (24), $P_{\mu\gamma}^{\mathrm{MP2}}$ is the one-particle density matrix, $W_{\mu\gamma}^{\mathrm{MP2}}$ is the energy-weighted density matrix, and $\Gamma_{\mu\gamma\lambda\sigma}^{\mathrm{MP2}}$ is the two-particle density matrix (in the AO basis). In practice, Eq. (24) is evaluated by forming the density matrices in the MO basis and back-transforming these matrices to the AO basis for contraction with AO integral derivatives. The task ahead, then, is to apply the appropriate restrictions to introduce the frozen-orbital approximation and derive the MO counterparts of the density matrices in Eq. (24). The MP2 density matrices are expressed as a sum of the SCF density matrices plus the MP2 density correction matrices; therefore, more specifically, the MP2 density correction matrices must be derived.

3.2 Derivative of the MP2 energy correction

Taking the derivative of the frozen-orbital MP2 energy contribution (Eq. 1) with respect to nuclear displacement x gives

$$E^{(2)^{x}}=\frac{1}{4}\sum_{ij}^{\mathrm{act}}\sum_{ab}^{\mathrm{virt}}\left[(ia||jb)^{x}T_{ij}^{ab}+(ia||jb)\left(T_{ij}^{ab}\right)^{x}\right]\ . \tag{25}$$

The amplitude derivative is

$$\left(T_{ij}^{ab}\right)^{x}=(ia||jb)^{x}/D_{ij}^{ab}+(ia||jb)\left(1/D_{ij}^{ab}\right)^{x}\ . \tag{26}$$

Substituting Eq. (26) into Eq. (25), and recognizing that the first term of Eq. (26) yields a term equivalent to the first term (in the brackets) of Eq. (25), gives

$$\begin{aligned}E^{(2)^{x}}=&\frac{1}{2}\sum_{ij}^{\mathrm{act}}\sum_{ab}^{\mathrm{vact}}(ia||jb)^{x}T_{ij}^{ab}\\&+\frac{1}{4}\sum_{ij}^{\mathrm{act}}\sum_{ab}^{\mathrm{vact}}(ia||jb)(ia||jb)\left(1/D_{ij}^{ab}\right)^{x}\ .\end{aligned} \tag{27}$$

Applying the chain rule (Eq. 22) to the second term of Eq. (27) yields

$$\begin{aligned}E^{(2)^{x}}=&\frac{1}{2}\sum_{ij}^{\mathrm{act}}\sum_{ab}^{\mathrm{vact}}(ia||jb)^{x}T_{ij}^{ab}\\&-\frac{1}{4}\sum_{ij}^{\mathrm{act}}\sum_{ab}^{\mathrm{vact}}(ia||jb)(ia||jb)\left(D_{ij}^{ab}\right)^{x}\Big/\left(D_{ij}^{ab}\right)^{2}\ .\end{aligned} \tag{28}$$

3.3 Expansion using orbital responses

The next step is to expand the derivative ERIs $(ia||jb)^{x}$ in terms of orbital responses. The expression for ERI derivatives (Eq. 7) is substituted into Eq. (28), which introduces the unknown expansion coefficients or orbital responses U_{pq}^{x}. $\left(D_{ij}^{ab}\right)^{x}$ is replaced with specific orbital energy derivatives (derivative of Eq. 4), leading to

$$\begin{aligned}E^{(2)^{x}}=&\frac{1}{2}\sum_{ij}^{\mathrm{act}}\sum_{ab}^{\mathrm{vact}}T_{ij}^{ab}\left[(ia||jb)^{(x)}+\sum_{p}^{\mathrm{all}}U_{pi}^{x}(pa||jb)\right.\\&\left.+\sum_{p}^{\mathrm{all}}U_{pa}^{x}(ip||jb)+\sum_{p}^{\mathrm{all}}U_{pj}^{x}(ia||pb)+\sum_{p}^{\mathrm{all}}U_{pb}^{x}(ia||jp)\right]\\&-\frac{1}{4}\sum_{ij}^{\mathrm{act}}\sum_{ab}^{\mathrm{vact}}\frac{(ia||jb)}{D_{ij}^{ab}}T_{ij}^{ab}\left(\varepsilon_{i}^{x}+\varepsilon_{j}^{x}-\varepsilon_{a}^{x}-\varepsilon_{b}^{x}\right)\ .\end{aligned} \tag{29}$$

Since the summation ranges of i and j are identical, as are those for a and b, Eq. (29) simplifies to

$$\begin{aligned}E^{(2)^{x}}=&\frac{1}{2}\sum_{ij}^{\mathrm{act}}\sum_{ab}^{\mathrm{vact}}T_{ij}^{ab}\left[(ia||jb)^{(x)}+2\sum_{p}^{\mathrm{all}}U_{pi}^{x}(pa||jb)\right.\\&\left.+2\sum_{p}^{\mathrm{all}}U_{pa}^{x}(ip||jb)\right]-\frac{1}{2}\sum_{ij}^{\mathrm{act}}\sum_{ab}^{\mathrm{vact}}\frac{(ia||jb)}{D_{ij}^{ab}}T_{ij}^{ab}\left(\varepsilon_{i}^{x}-\varepsilon_{a}^{x}\right)\ .\end{aligned} \tag{30}$$

The two different types of orbital responses in Eq. (30) can be visualized in Fig. 1. Both have a summation over the full range of orbitals, $\sum_{p}^{\mathrm{all}}$, which will be divided in two different ways into occupied and virtual ranges according to $\sum_{p}^{\mathrm{all}}=\sum_{K}^{\mathrm{core}}+\sum_{k}^{\mathrm{act}}+\sum_{c}^{\mathrm{vall}}$ and $\sum_{p}^{\mathrm{all}}=\sum_{k}^{\mathrm{occ}}+\sum_{c}^{\mathrm{vact}}+\sum_{C}^{\mathrm{vf}}$. This creates six different types of responses:

$$\begin{aligned}E^{(2)^{x}}=&\frac{1}{2}\sum_{ij}^{\mathrm{act}}\sum_{ab}^{\mathrm{vact}}T_{ij}^{ab}\left[(ia||jb)^{(x)}+2\sum_{K}^{\mathrm{core}}U_{Ki}^{x}(Ka||jb)\right.\\&+2\sum_{k}^{\mathrm{act}}U_{ki}^{x}(ka||jb)+2\sum_{c}^{\mathrm{vall}}U_{ci}^{x}(ca||jb)\\&+2\sum_{k}^{\mathrm{occ}}U_{ka}^{x}(ik||jb)+2\sum_{c}^{\mathrm{vact}}U_{ca}^{x}(ic||jb)\\&\left.+2\sum_{C}^{\mathrm{vf}}U_{Ca}^{x}(iC||jb)\right]-\frac{1}{2}\sum_{ij}^{\mathrm{act}}\sum_{ab}^{\mathrm{vact}}T_{ij}^{ab}T_{ij}^{ab}\left(\varepsilon_{i}^{x}-\varepsilon_{a}^{x}\right)\ .\end{aligned} \tag{31}$$

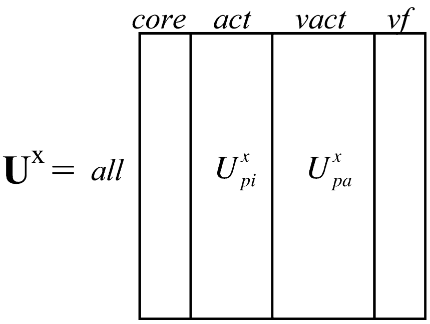

Fig. 1. Pictorial representation of the orbital response matrix, where *all*, *core*, *act*, *vact*, and *vf* are the relevant summation ranges

In this way, the orbital responses are divided into diagonal blocks of responses (occupied–occupied and virtual–virtual responses such as U_{Ki}^{x}, U_{ki}^{x}, U_{ca}^{x}, and U_{Ca}^{x}) and off-diagonal blocks of responses (virtual–occupied and occupied–virtual responses such as U_{ci}^{x} and U_{ka}^{x}). These responses may be visualized in Fig. 2. They are divided this way because some of the techniques used in the next section require that indices run over the same summation ranges; for example, k and i both run over active MOs in the third term of Eq. (31).

3.4 Replacement of unknown responses and removal of singularities

Both the diagonal and off-diagonal responses must be replaced with known quantities before the expression resembles the general form of the MP2 gradient (Eq. 24). The unknown occupied–occupied and virtual–virtual orbital responses in Eq. (31) will be substituted with Q_{pq}^{x} terms using Eq. (10). The issue of potential singularities introduced by this substitution must also be addressed.

Starting with the active–active term in Eq. (31), the response term is split into two equal parts. In the second of these parts, U_{ki}^{x} is substituted using Eq. (8):

$$\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{k}^{\text{act}} T_{ij}^{ab}U_{ki}^{x}(ka||jb) = \frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\left[\sum_{k}^{\text{act}} U_{ki}^{x}T_{ij}^{ab}(ka||jb) - \sum_{k}^{\text{act}} U_{ik}^{x}T_{ij}^{ab}(ka||jb)\right] - \frac{1}{2}\sum_{ijk}^{\text{act}}\sum_{ab}^{\text{vact}} S_{ki}^{(x)}T_{ij}^{ab}(ka||jb) \qquad (32)$$

Next, the summations are split according to Eq. (21) (note that this can only be done because the summation ranges of k and i are equal in Eq. 32), as

$$\sum_{k}^{\text{act}} U_{ki}^{x}T_{ij}^{ab}(ka||jb) = \sum_{k>i}^{\text{act}} U_{ki}^{x}T_{ij}^{ab}(ka||jb) + \sum_{k<i}^{\text{act}} U_{ki}^{x}T_{ij}^{ab}(ka||jb) + U_{ii}^{x}T_{ij}^{ab}(ia||jb). \qquad (33)$$

Substituting Eq. (33) into Eq. (32) for both the U_{ki}^{x} and U_{ik}^{x} terms yields the following active–active expression:

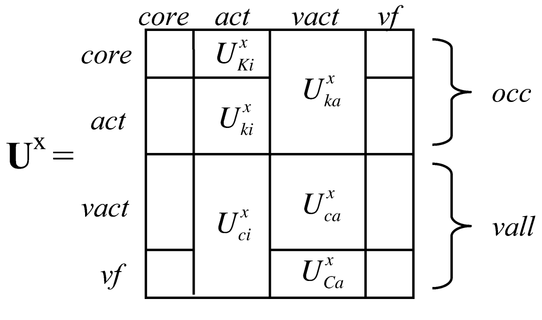

Fig. 2. Pictorial representation of the orbital response matrix, where *core*, *act*, *occ*, *vact*,*vf*, and *vall* are the relevant summation ranges

$$\begin{aligned}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{k}^{\text{act}} T_{ij}^{ab}U_{ki}^{x}(ka||jb) &= \frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\left[\sum_{k>i}^{\text{act}} U_{ki}^{x}T_{ij}^{ab}(ka||jb) + \sum_{k<i}^{\text{act}} U_{ki}^{x}T_{ij}^{ab}(ka||jb)\right] + \frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}} U_{ii}^{x}T_{ij}^{ab}(ka||jb)\\ &\quad - \frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\left[\sum_{k>i}^{\text{act}} U_{ik}^{x}T_{ij}^{ab}(ka||jb) + \sum_{k<i}^{\text{act}} U_{ik}^{x}T_{ij}^{ab}(ka||jb)\right]\\ &\quad - \frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}} U_{ii}^{x}T_{ij}^{ab}(ka||jb) - \frac{1}{2}\sum_{ijk}^{\text{act}}\sum_{ab}^{\text{vact}} S_{ki}^{(x)}T_{ij}^{ab}(ka||jb)\end{aligned} \qquad (34)$$

The two U_{ii}^{x} terms cancel. Interchanging $i \leftrightarrow k$ in each sum over $k<i$ (second term in each set of brackets) in Eq. (34) yields

$$\begin{aligned}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{k}^{\text{act}} T_{ij}^{ab}U_{ki}^{x}(ka||jb) &= \frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{k>i}^{\text{act}}\left[U_{ki}^{x}T_{ij}^{ab}(ka||jb) + U_{ik}^{x}T_{kj}^{ab}(ia||jb)\right]\\ &\quad - \frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{k>i}^{\text{act}}\left[U_{ik}^{x}T_{ij}^{ab}(ka||jb) + U_{ki}^{x}T_{kj}^{ab}(ia||jb)\right]\\ &\quad - \frac{1}{2}\sum_{ijk}^{\text{act}}\sum_{ab}^{\text{vact}} S_{ki}^{(x)}T_{ij}^{ab}(ka||jb)\ .\end{aligned} \qquad (35)$$

The U_{ki}^{x} and U_{ik}^{x} terms are collected, forming

$$\begin{aligned}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{k}^{\text{act}} T_{ij}^{ab}U_{ki}^{x}(ka||jb) &= \frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{k>i}^{\text{act}}\left[U_{ki}^{x}T_{ij}^{ab}(ka||jb) - U_{ki}^{x}T_{kj}^{ab}(ia||jb)\right]\\ &\quad - \frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{k>i}^{\text{act}}\left[U_{ik}^{x}T_{ij}^{ab}(ka||jb) - U_{ik}^{x}T_{kj}^{ab}(ia||jb)\right]\\ &\quad - \frac{1}{2}\sum_{ijk}^{\text{act}}\sum_{ab}^{\text{vact}} S_{ki}^{(x)}T_{ij}^{ab}(ka||jb)\ .\end{aligned} \qquad (36)$$

The numerators of the terms multiplying the U_{ki}^{x} and U_{ik}^{x} responses in Eq. (36) are equivalent and may be combined:

$$\begin{aligned}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{k}^{\text{act}} T_{ij}^{ab}U_{ki}^{x}(ka||jb) &= \frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{k>i}^{\text{act}} U_{ki}^{x}(ia||jb)(ka||jb)\left(\frac{1}{D_{ij}^{ab}} - \frac{1}{D_{kj}^{ab}}\right)\\ &\quad - \frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{k>i}^{\text{act}} U_{ik}^{x}(ia||jb)(ka||jb)\left(\frac{1}{D_{ij}^{ab}} - \frac{1}{D_{kj}^{ab}}\right)\\ &\quad - \frac{1}{2}\sum_{ijk}^{\text{act}}\sum_{ab}^{\text{vact}} S_{ki}^{(x)}T_{ij}^{ab}(ka||jb)\ .\end{aligned} \qquad (37)$$

Now, substitution for U^x_{ki} and U^x_{ik} occurs according to Eq. (10) and the denominators are cross-multiplied (Eq. 23), which enables cancellation of the orbital energy terms that otherwise would result in singularities when MOs k and i are degenerate. The first term in Eq. (37) is then

$$\frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{k>i}^{\text{act}}\frac{-Q^x_{ki}}{(\varepsilon_k-\varepsilon_i)}(ia||jb)(ka||jb)\frac{(\varepsilon_k-\varepsilon_i)}{D^{ab}_{ij}D^{ab}_{kj}}$$

$$=-\frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{k>i}^{\text{act}}Q^x_{ki}T^{ab}_{ij}T^{ab}_{kj}\ . \tag{38}$$

The second term in Eq. (37) is

$$-\frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{k>i}^{\text{act}}\frac{Q^x_{ik}}{(\varepsilon_k-\varepsilon_i)}(ia||jb)(ka||jb)\frac{(\varepsilon_k-\varepsilon_i)}{D^{ab}_{ij}D^{ab}_{kj}}$$

$$=-\frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{k>i}^{\text{act}}Q^x_{ik}T^{ab}_{ij}T^{ab}_{kj}\ . \tag{39}$$

Collecting like terms gives

$$\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{k}^{\text{act}}T^{ab}_{ij}U^x_{ki}(ka||jb)$$

$$=-\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{k>i}^{\text{act}}\left(\frac{Q^x_{ki}+Q^x_{ik}}{2}\right)T^{ab}_{ij}T^{ab}_{kj}$$

$$-\frac{1}{2}\sum_{ijk}^{\text{act}}\sum_{ab}^{\text{vact}}S^{(x)}_{ki}T^{ab}_{ij}(ka||jb)\ . \tag{40}$$

Now, the substitution of Q^x_{ii} for ε^x_i (Eq. 15) in Eq. (31) and the combination of this term with the first term in Eq. (40) produces

$$-\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{k>i}^{\text{act}}\left(\frac{Q^x_{ki}+Q^x_{ik}}{2}\right)T^{ab}_{ij}T^{ab}_{kj}-\frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}Q^x_{ii}T^{ab}_{ij}T^{ab}_{ij}$$

$$=-\frac{1}{2}\sum_{ijk}^{\text{act}}\sum_{ab}^{\text{vact}}\left(\frac{Q^x_{ki}+Q^x_{ik}}{2}\right)T^{ab}_{ij}T^{ab}_{kj}\ , \tag{41}$$

where the sum over k has been expanded to include all active orbitals and divided by 2. This procedure is the reverse of that in Eq. (33). All terms in the expression for Q^x_{pq} (Eqs. 11, 13) except for the orbital energy term (second term in Eq. 13) are symmetric with respect to interchange of p and q, so the symmetrized expression in Eq. (41) may be simplified later.

The vact–vact rotations are dealt with in an exactly analogous manner. Owing to the opposite signs of the virtual orbital energies, the cross-multiplication step (Eqs. 37, 38) results in the opposite sign to the active–active case:

$$\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{c>a}^{\text{vact}}\left(\frac{Q^x_{ca}+Q^x_{ac}}{2}\right)T^{ab}_{ij}T^{cb}_{ij}+\frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}Q^x_{aa}T^{ab}_{ij}T^{ab}_{ij}$$

$$=\frac{1}{2}\sum_{ij}^{\text{act}}\sum_{abc}^{\text{vact}}\left(\frac{Q^x_{ca}+Q^x_{ac}}{2}\right)T^{ab}_{ij}T^{cb}_{ij}\ . \tag{42}$$

Now consider the frozen-core–active term that was separated from the active–active term in Eq. (31). Splitting the term into two equal parts, substituting for U^x_{Ki} using Eq. (8) in the second of these parts, and then making the appropriate substitutions according to Eq. (10) gives

$$\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{K}^{\text{core}}U^x_{Ki}T^{ab}_{ij}(Ka||jb)$$

$$=\frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{K}^{\text{core}}\left[U^x_{Ki}T^{ab}_{ij}(Ka||jb)+U^x_{Ki}T^{ab}_{ij}(Ka||jb)\right] \tag{43}$$

$$=\frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{K}^{\text{core}}U^x_{Ki}T^{ab}_{ij}(Ka||jb)$$

$$-\frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{K}^{\text{core}}U^x_{iK}T^{ab}_{ij}(Ka||jb)$$

$$-\frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{K}^{\text{core}}S^{(x)}_{iK}T^{ab}_{ij}(Ka||jb) \tag{44}$$

$$=\frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{K}^{\text{core}}\frac{Q^x_{Ki}}{(\varepsilon_i-\varepsilon_K)}T^{ab}_{ij}(Ka||jb)$$

$$+\frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{K}^{\text{core}}\frac{Q^x_{iK}}{(\varepsilon_i-\varepsilon_K)}T^{ab}_{ij}(Ka||jb)$$

$$-\frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{K}^{\text{core}}S^{(x)}_{iK}T^{ab}_{ij}(Ka||jb)\ . \tag{45}$$

It is not necessary to remove the orbital energy difference (ε_i–ε_K) that could potentially produce singularities because, as Rice et al. [5] point out for the configuration interaction case, if the core and active MOs are chosen sensibly (usually chemical cores and valence orbitals) K and i should never be degenerate and singularities are always avoided. A similar procedure may be followed for the frozen virtual–active virtual responses, yielding

$$\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{C}^{\text{vf}}U^x_{Ca}T^{ab}_{ij}(iC||jb)$$

$$=\frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{C}^{\text{vf}}\frac{Q^x_{Ca}}{(\varepsilon_a-\varepsilon_C)}T^{ab}_{ij}(iC||jb)$$

$$+\frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{C}^{\text{vf}}\frac{Q^x_{aC}}{(\varepsilon_a-\varepsilon_C)}T^{ab}_{ij}(iC||jb)$$

$$-\frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{C}^{\text{vf}}S^{(x)}_{aC}T^{ab}_{ij}(iC||jb)\ . \tag{46}$$

3.5 Identification of density matrices

At this point, the diagonal responses (terms 2, 3, and 6 in Eq. 31) and the orbital energy derivatives (term 7 in Eq. 31) have been replaced with terms involving Q^x_{pq} and $S^{(x)}_{pq}$. The general form of the energy derivative (Eq. 24) enables identification of density matrices. Any term that multiples a one-electron Hamiltonian derivative integral $H^{(x)}_{pq}$ is defined as an MP2 density correction term $P^{(2)}_{pq}$. Likewise, any term that multiplies an overlap integral derivative $S^{(x)}_{pq}$ is an energy-weighted density correction term $W^{(2)}_{pq}$ [18].

By inspection of Eq. (41) and by recalling that the expanded definition of Q^x_{pq} (Eq. 11) contains $H^{(x)}_{pq}$ (Eqs. 13, 14), the active–active MP2 density correction $P^{(2)}_{ki}$ is defined as

$$-\frac{1}{2}\sum_{ijk}^{\text{act}}\sum_{ab}^{\text{vall}}\left(\frac{Q^x_{ki}+Q^x_{ik}}{2}\right)T^{ab}_{ij}T^{ab}_{kj} \equiv \sum_{ki}^{\text{act}}\left(\frac{Q^x_{ki}+Q^x_{ik}}{2}\right)P^{(2)}_{ki}; \tag{47}$$

the core–active MP2 density correction $P^{(2)}_{Ki}$, by inspection of Eq. (45), is defined by

$$\frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vall}}\sum_{K}^{\text{core}}\frac{Q^x_{Ki}}{(\varepsilon_i-\varepsilon_K)}T^{ab}_{ij}(Ka\|jb) \equiv \sum_{i}^{\text{act}}\sum_{K}^{\text{core}}Q^x_{Ki}P^{(2)}_{Ki}. \tag{48}$$

Note that Eq. (47) shows that $P^{(2)}_{ki}=P^{(2)}_{ik}$, i.e., $-\frac{1}{2}\sum_j^{\text{act}}\sum_{ab}^{\text{vall}}T^{ab}_{ij}T^{ab}_{kj} = -\frac{1}{2}\sum_j^{\text{act}}\sum_{ab}^{\text{vall}}T^{ab}_{kj}T^{ab}_{ij}$. In addition, terms 1 and 2 of Eq. (45) clearly show that $P^{(2)}_{Ki}=P^{(2)}_{iK}$.

An active–active energy-weighted density correction $W^{(2)}_{ki}[I]$ (labeled $[I]$ because additional energy-weighted density correction terms labeled $[II]$ and $[III]$ follow) is defined by inspection of the second term in Eq. (40),

$$-\frac{1}{2}\sum_{ijk}^{\text{act}}\sum_{ab}^{\text{vall}}S^{(x)}_{ki}T^{ab}_{ij}(ka\|jb) \equiv \sum_{ki}^{\text{act}}S^{(x)}_{ki}W^{(2)}_{ki}[I]\ . \tag{49}$$

The third term in Eq. (45) defines $W^{(2)}_{iK}$,

$$-\frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vall}}\sum_{K}^{\text{core}}S^{(x)}_{iK}T^{ab}_{ij}(Ka\|jb) \equiv \sum_{i}^{\text{act}}\sum_{K}^{\text{core}}S^{(x)}_{iK}W^{(2)}_{iK}[I]\ . \tag{50}$$

Virtual–virtual densities $P^{(2)}_{ca}$, $P^{(2)}_{Ca}$, $W^{(2)}_{ca}$, and $W^{(2)}_{Ca}$ may be defined in an exactly analogous manner.

3.6 MP2 Lagrangian, CPHF equations, and **Z**-vector method

If the relevant substitutions into Eq. (31) are made, the derivative of the frozen-orbital MP2 energy at this point is given by

$$\begin{aligned}E^{(2)^x} ={}& \sum_{ij}^{\text{act}}\left(\frac{Q^x_{ij}+Q^x_{ji}}{2}\right)P^{(2)}_{ij}+\sum_{ij}^{\text{act}}S^{(x)}_{ij}W^{(2)}_{ij}[I]\\ &+\sum_{ab}^{\text{vact}}\left(\frac{Q^x_{ab}+Q^x_{ba}}{2}\right)P^{(2)}_{ab}+\sum_{ab}^{\text{vact}}S^{(x)}_{ab}W^{(2)}_{ab}[I]\\ &+\sum_{i}^{\text{act}}\sum_{K}^{\text{core}}(Q^x_{Ki}+Q^x_{iK})P^{(2)}_{Ki}+\sum_{i}^{\text{act}}\sum_{K}^{\text{core}}S^{(x)}_{iK}W^{(2)}_{iK}[I]\\ &+\sum_{a}^{\text{vact}}\sum_{C}^{\text{vf}}(Q^x_{Ca}+Q^x_{aC})P^{(2)}_{aC}+\sum_{a}^{\text{vact}}\sum_{C}^{\text{vf}}S^{(x)}_{aC}W^{(2)}_{aC}[I]\\ &+\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{c}^{\text{vall}}U^x_{ci}(ca\|jb)T^{ab}_{ij}\\ &+\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{k}^{\text{occ}}U^x_{ka}(ik\|jb)T^{ab}_{ij}+\frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}T^{ab}_{ij}(ia\|jb)^{(x)}.\end{aligned} \tag{51}$$

The remaining unknowns are now virtual–occupied and occupied–virtual orbital responses such as those in the ninth and tenth terms in Eq. (51) (U^x_{ci} and U^x_{ka}). In addition, the substitution of the diagonal responses by Q^x_{pq} terms (first, third, fifth, and seventh terms of Eq. 51) introduces virtual–occupied responses through Eq. (11). Substitution of Eq. (11) for Q^x_{pq} in Eq. (51) leads to

$$\begin{aligned}E^{(2)^x} ={}& \sum_{ij}^{\text{act}}\left(\frac{B^x_{ij}+B^x_{ji}}{2}\right)P^{(2)}_{ij}+\sum_{ij}^{\text{act}}S^{(x)}_{ij}W^{(2)}_{ij}[I]\\ &+\sum_{ab}^{\text{vact}}\left(\frac{B^x_{ab}+B^x_{ba}}{2}\right)P^{(2)}_{ab}+\sum_{ab}^{\text{vact}}S^{(x)}_{ab}W^{(2)}_{ab}[I]\\ &+\sum_{i}^{\text{act}}\sum_{K}^{\text{core}}(B^x_{Ki}+B^x_{iK})P^{(2)}_{Ki}+\sum_{i}^{\text{act}}\sum_{K}^{\text{core}}S^{(x)}_{iK}W^{(2)}_{iK}[I]\\ &+\sum_{a}^{\text{vact}}\sum_{C}^{\text{vf}}(B^x_{Ca}+B^x_{aC})P^{(2)}_{aC}+\sum_{a}^{\text{vact}}\sum_{C}^{\text{vf}}S^{(x)}_{aC}W^{(2)}_{aC}[I]\\ &+\sum_{ij}^{\text{act}}\sum_{c}^{\text{vall}}\sum_{k}^{\text{occ}}U^x_{ck}A_{ijck}P^{(2)}_{ij}+\sum_{ab}^{\text{vact}}\sum_{c}^{\text{vall}}\sum_{k}^{\text{occ}}U^x_{ck}A_{abck}P^{(2)}_{ab}\\ &+2\sum_{i}^{\text{act}}\sum_{J}^{\text{core}}\sum_{c}^{\text{vall}}\sum_{k}^{\text{occ}}U^x_{ck}A_{iJck}P^{(2)}_{iJ}\\ &+2\sum_{a}^{\text{vact}}\sum_{B}^{\text{vf}}\sum_{c}^{\text{vall}}\sum_{k}^{\text{occ}}U^x_{ck}A_{aBck}P^{(2)}_{aB}\\ &+\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{c}^{\text{vall}}U^x_{ci}(ca\|jb)T^{ab}_{ij}\\ &+\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{k}^{\text{occ}}U^x_{ka}(ik\|jb)T^{ab}_{ij}\\ &+\frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}T^{ab}_{ij}(ia\|jb)^{(x)}\ ,\end{aligned} \tag{52}$$

where the symmetry property

$$\sum_{pq}\sum_{c}^{\text{vall}}\sum_{k}^{\text{occ}} U^x_{ck}A_{pqck} = \sum_{pq}\sum_{c}^{\text{vall}}\sum_{k}^{\text{occ}} U^x_{ck}A_{qpck} \tag{53}$$

has been used to simplify the form of the response terms that came from Q^x_{pq}.

Before carrying out the CPHF procedure on Eq. (52), Eq. (8) must be applied to the 14th term in order to switch the response indices. This introduces an occupied–virtual energy-weighted density term:

$$\begin{aligned}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{k}^{\text{occ}} U^x_{ka}(ik||jb)T^{ab}_{ij} = &-\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{k}^{\text{occ}} U^x_{ak}(ik||jb)T^{ab}_{ij} \\ &-\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}\sum_{k}^{\text{occ}} S^{(x)}_{ak}(ik||jb)T^{ab}_{ij} \ .\end{aligned} \tag{54}$$

The core and active summations in terms 9 and 11 of Eq. (52) may be combined into an occupied summation, and a similar procedure may be used on terms 10 and 12. Next, Eq. (54) is substituted into Eq. (52) and virtual–occupied response terms are grouped as

$$\begin{aligned}E^{(2)^x} = &\sum_{ij}^{\text{act}}\left(\frac{B^x_{ij}+B^x_{ji}}{2}\right)P^{(2)}_{ij} + \sum_{ij}^{\text{act}} S^{(x)}_{ij}W^{(2)}_{ij}[I] \\ &+\sum_{ab}^{\text{vact}}\left(\frac{B^x_{ab}+B^x_{ba}}{2}\right)P^{(2)}_{ab} + \sum_{ab}^{\text{vact}} S^{(x)}_{ab}W^{(2)}_{ab}[I] \\ &+\sum_{i}^{\text{act}}\sum_{K}^{\text{core}}\left(B^x_{Ki}+B^x_{iK}\right)P^{(2)}_{Ki} + \sum_{i}^{\text{act}}\sum_{K}^{\text{core}} S^{(x)}_{iK}W^{(2)}_{iK}[I] \\ &+\sum_{a}^{\text{vact}}\sum_{k}^{\text{occ}} S^{(x)}_{ak}W^{(2)}_{ak}[I] + \sum_{a}^{\text{vact}}\sum_{C}^{\text{vf}}\left(B^x_{Ca}+B^x_{aC}\right)P^{(2)}_{aC} \\ &+\sum_{a}^{\text{vact}}\sum_{C}^{\text{vf}} S^{(x)}_{aC}W^{(2)}_{aC}[I] + \sum_{c}^{\text{vall}}\sum_{k}^{\text{occ}} U^x_{ck} \\ &\times\left[\sum_{ij}^{\text{occ}} P^{(2)}_{ij}A_{ijck} + \sum_{ab}^{\text{vall}} P^{(2)}_{ab}A_{abck}\right. \\ &\left.-N_c\sum_{ij}^{\text{act}}\sum_{b}^{\text{vact}} T^{cb}_{ij}(ik||jb) + N_k\sum_{j}^{\text{act}}\sum_{ab}^{\text{vact}} T^{ab}_{kj}(ca||jb)\right] \\ &+\frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}(ia||jb)^{(x)}T^{ab}_{ij} \ ,\end{aligned} \tag{55}$$

where

$$N_k \equiv \begin{cases} 1, & \text{for } k = \text{active} \\ 0, & \text{for } k = \text{core} \end{cases}$$

and

$$N_c \equiv \begin{cases} 1, & \text{for } c = \text{vact} \\ 0, & \text{for } c = \text{vf} \end{cases} \ .$$

The terms in the brackets in Eq. (55) may be defined as the MP2 Lagrangian. After changing indices, the off-diagonal term has the form

$$\sum_{ai} U^x_{ai}L_{ai} \ , \tag{56}$$

where

$$\begin{aligned}L_{ai} = &+\sum_{jk}^{\text{occ}} P^{(2)}_{jk}A_{aijk} + \sum_{bc}^{\text{vall}} P^{(2)}_{bc}A_{aibc} \\ &-N_a\sum_{jk}^{\text{act}}\sum_{b}^{\text{vact}} T^{ab}_{jk}(ij||bk) + N_i\sum_{j}^{\text{act}}\sum_{bc}^{\text{vact}} T^{bc}_{ij}(ab||jc) \ .\end{aligned} \tag{57}$$

The virtual–occupied responses U^x_{ai} must be determined using the CPHF equations (Eq. 16). So far, only the derivative with respect to x has been shown, but there are derivatives with respect to x, y, and z for each atom. The number of unknown response vectors may be reduced from $3N$, where N is the number of atoms, to 1 by using the **Z**-vector method of Handy and Schaefer [19] as follows:

$$\sum_{ai} U^x_{ai}L_{ai} \equiv \mathbf{L}^{\mathrm{T}}\mathbf{U}^x \tag{58}$$

$$\mathbf{A}'\mathbf{U}^x = \mathbf{B}^x \tag{59}$$

$$\mathbf{U}^x = (\mathbf{A}')^{-1}\mathbf{B}^x \tag{60}$$

$$\mathbf{L}^{\mathrm{T}}\mathbf{U}^x = \mathbf{L}^{\mathrm{T}}(\mathbf{A}')^{-1}\mathbf{B}^x \tag{61}$$

$$= \mathbf{Z}^{\mathrm{T}}\mathbf{B}^x \ , \tag{62}$$

where

$$\mathbf{Z}^{\mathrm{T}} = \mathbf{L}^{\mathrm{T}}(\mathbf{A}')^{-1} \ . \tag{63}$$

Thus, the following set of simultaneous equations must be solved for **Z**:

$$(\mathbf{A}')^{\mathrm{T}}\mathbf{Z} = \mathbf{L}. \tag{64}$$

The elements of **Z** are obtained from solution of linear Eq. (64) and the contribution from Eq. (58) is evaluated according to Eq. (62) as

$$\sum_{ai} U^x_{ai}L_{ai} = \sum_{ai} B^x_{ai}Z_{ai} \ . \tag{65}$$

Since **B** contains core Hamiltonian derivatives (Eqs. 13, 14), the elements of **Z** may be used to define the virtual–occupied block of the density matrix:

$$\sum_{ai} B^x_{ai}Z_{ai} \equiv \sum_{ai} B^x_{ai}P^{(2)}_{ai} \ . \tag{66}$$

From Eqs. (16), (64), and (66), the following CPHF equations are solved to find the virtual–occupied blocks of the density matrix:

$$\sum_{b}^{\text{vall}}\sum_{j}^{\text{occ}}\left[A_{aibj}+\delta_{ab}\delta_{ij}\left(\varepsilon_b-\varepsilon_j\right)\right]P_{bj}^{(2)}=-L_{ai}\ . \tag{67}$$

At this point, the gradient expression (Eq. 55) may be written more simply as

$$\begin{aligned}
E^{(2)^x}=&\sum_{ij}^{\text{occ}}\left(\frac{B_{ij}^x+B_{ji}^x}{2}\right)P_{ij}^{(2)}+\sum_{ij}^{\text{occ}}S_{ij}^{(x)}W_{ij}^{(2)}[I]\\
&+\sum_{ab}^{\text{vall}}\left(\frac{B_{ab}^x+B_{ba}^x}{2}\right)P_{ab}^{(2)}+\sum_{ab}^{\text{vall}}S_{ab}^{(x)}W_{ab}^{(2)}[I]\\
&+\sum_{a}^{\text{vall}}\sum_{i}^{\text{occ}}B_{ai}^xP_{ai}^{(2)}+\sum_{a}^{\text{vact}}\sum_{i}^{\text{occ}}S_{ai}^{(x)}W_{ai}^{(2)}[I]\\
&+\frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}(ia||jb)^{(x)}T_{ij}^{ab}\ ,
\end{aligned} \tag{68}$$

where the active–active and active–core contributions have been combined into an occupied–occupied contribution and the vact–vact and vact–vf contributions have been combined into a virtual–virtual contribution.

3.7 Additional energy-weighted density terms

In Eq. (68), the MP2 density correction terms $P_{pq}^{(2)}$ are multiplied by B_{pq}^x, which gives rise to additional energy-weighted density terms which are labeled [*II*] and [*III*] (listed in Sect. 3.8)). Making the appropriate substitutions for B_{pq}^x according to Eq. (13) (and recognizing that the first and third terms in Eq. 13 are symmetric to p and q interchange), the MP2 frozen-orbital gradient expression may now be written as

$$\begin{aligned}
E^{(2)^x}=&\sum_{ij}^{\text{occ}}P_{ij}^{(2)}\left[F_{ij}^{(x)}-S_{ij}^{(x)}\left(\frac{\varepsilon_i+\varepsilon_j}{2}\right)-\frac{1}{2}\sum_{kl}^{\text{occ}}S_{kl}^{(x)}A_{ijlk}\right]\\
&+\sum_{i}^{\text{occ}}\sum_{a}^{\text{vall}}P_{ai}^{(2)}\left[F_{ai}^{(x)}-S_{ai}^{(x)}\varepsilon_i-\frac{1}{2}\sum_{kl}^{\text{occ}}S_{kl}^{(x)}A_{ailk}\right]\\
&+\sum_{ab}^{\text{vall}}P_{ab}^{(2)}\left[F_{ab}^{(x)}-S_{ab}^{(x)}\left(\frac{\varepsilon_a+\varepsilon_b}{2}\right)-\frac{1}{2}\sum_{kl}^{\text{occ}}S_{kl}^{(x)}A_{ablk}\right]\\
&+\sum_{ij}^{\text{occ}}S_{ij}^{(x)}W_{ij}^{(2)}[I]+\sum_{ab}^{\text{vall}}S_{ab}^{(x)}W_{ab}^{(2)}[I]\\
&+\sum_{a}^{\text{vact}}\sum_{i}^{\text{occ}}S_{ai}^{(x)}W_{ai}^{(2)}[I]+\frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}(ia||jb)^{(x)}T_{ij}^{ab}\ .
\end{aligned} \tag{69}$$

Factors multiplying $S_{pq}^{(x)}$terms are defined as $W_{pq}^{(2)}[II]$ and $W_{pq}^{(2)}[III]$ matrices (see Sect. 3.8). The $F_{pq}^{(x)}$ terms may now be substituted according to Eq. (14). At this point, the MP2 frozen-orbital gradient expression is

$$\begin{aligned}
E^{(2)^x}=&\sum_{ij}^{\text{occ}}P_{ij}^{(2)}\left\{H_{ij}^{(x)}+\sum_{k}^{\text{occ}}\left[(ij|kk)^{(x)}-(ik|jk)^{(x)}\right]\right\}\\
&+\sum_{i}^{\text{occ}}\sum_{a}^{\text{vall}}P_{ai}^{(2)}\left\{H_{ai}^{(x)}+\sum_{k}^{\text{occ}}\left[(ai|kk)^{(x)}-(ak|ik)^{(x)}\right]\right\}\\
&+\sum_{ab}^{\text{vall}}P_{ab}^{(2)}\left\{H_{ab}^{(x)}+\sum_{k}^{\text{occ}}\left[(ab|kk)^{(x)}-(ak|bk)^{(x)}\right]\right\}\\
&+\sum_{ij}^{\text{occ}}S_{ij}^{(x)}W_{ij}^{(2)}[I]+\sum_{ab}^{\text{vall}}S_{ab}^{(x)}W_{ab}^{(2)}[I]+\sum_{a}^{\text{vact}}\sum_{i}^{\text{occ}}S_{ai}^{(x)}W_{ai}^{(2)}[I]\\
&+\sum_{ij}^{\text{occ}}S_{ij}^{(x)}W_{ij}^{(2)}[II]+\sum_{ab}^{\text{vall}}S_{ab}^{(x)}W_{ab}^{(2)}[II]\\
&+\sum_{a}^{\text{vall}}\sum_{i}^{\text{occ}}S_{ai}^{(x)}W_{ai}^{(2)}[II]\\
&+\sum_{ij}^{\text{occ}}S_{ij}^{(x)}W_{ij}^{(2)}[III]+\frac{1}{2}\sum_{ij}^{\text{act}}\sum_{ab}^{\text{vact}}(ia||jb)^{(x)}T_{ij}^{ab}\ .
\end{aligned} \tag{70}$$

The ERI derivatives in terms 1, 2, 3, and 11 in Eq. (70) will contribute to the two-electron density matrix. Since a wavefunction type should be defined before dealing further with these terms, the one-particle gradient terms in the spin-orbital basis will be briefly summarized before moving to specifics for UHF and restricted Hartree–Fock wavefunctions.

3.8 Summary of the one-particle gradient

The one-particle density matrix terms for the MP2 gradient in the spin-orbital basis are summarized here.

MP2 density correction terms

$KJ=\text{core}-\text{core}$

$$P_{KJ}^{(2)}=0 \tag{71}$$

$Ki=\text{core}-\text{act}$

$$P_{Ki}^{(2)}=P_{iK}^{(2)}=\frac{1}{2(\varepsilon_i-\varepsilon_K)}\sum_{j}^{\text{act}}\sum_{ab}^{\text{vact}}T_{ij}^{ab}(Ka||jb) \tag{72}$$

$ij=\text{act}-\text{act}$

$$P_{ij}^{(2)}=-\frac{1}{2}\sum_{k}^{\text{act}}\sum_{ab}^{\text{vact}}T_{ik}^{ab}T_{jk}^{ab} \tag{73}$$

$ab=\text{vact}-\text{vact}$

$$P_{ab}^{(2)}=\frac{1}{2}\sum_{ij}^{\text{act}}\sum_{c}^{\text{vact}}T_{ij}^{ac}T_{ij}^{bc} \tag{74}$$

$Ca = \mathrm{vf} - \mathrm{vact}$

$$P_{Ca}^{(2)} = P_{aC}^{(2)} = \frac{1}{2(\varepsilon_a - \varepsilon_C)} \sum_{ij}^{\mathrm{act}} \sum_{b}^{\mathrm{vact}} T_{ij}^{ab} (iC||jb) \tag{75}$$

$ai = \mathrm{vall} - \mathrm{occ}$

$$P_{ai}^{(2)} = Z_{ai} \tag{76}$$

MP2 energy-weighted density correction terms

[*I*] terms:

$ij = \mathrm{act} - \mathrm{occ}$

$$W_{ij}^{(2)}[I] = -\frac{1}{2} \sum_{k}^{\mathrm{act}} \sum_{ab}^{\mathrm{vact}} T_{ik}^{ab} (ja||kb) \tag{77}$$

$ab = \mathrm{vact} - \mathrm{vall}$

$$W_{ab}^{(2)}[I] = -\frac{1}{2} \sum_{ij}^{\mathrm{act}} \sum_{c}^{\mathrm{vact}} T_{ij}^{ac} (ib||jc) \tag{78}$$

$ai = \mathrm{vact} - \mathrm{occ}$

$$W_{ai}^{(2)}[I] = -\sum_{jk}^{\mathrm{act}} \sum_{b}^{\mathrm{vact}} T_{jk}^{ab} (ij||bk) \tag{79}$$

[*II*] terms:

$ij = \mathrm{act} - \mathrm{occ}$

$$W_{ij}^{(2)}[II] = -\frac{1}{2} P_{ij}^{(2)} \left(\varepsilon_i + \varepsilon_j\right) \tag{80}$$

$ab = \mathrm{vact} - \mathrm{vall}$

$$W_{ab}^{(2)}[II] = -\frac{1}{2} P_{ab}^{(2)} (\varepsilon_a + \varepsilon_b) \tag{81}$$

$ai = \mathrm{vall} - \mathrm{occ}$

$$W_{ai}^{(2)}[II] = -P_{ai}^{(2)} \varepsilon_i \tag{82}$$

[*III*] terms:

$ij = \mathrm{occ} - \mathrm{occ}$

$$W_{ij}^{(2)}[III] = -\frac{1}{2} \sum_{pq}^{\mathrm{all}} P_{pq}^{(2)} A_{pqji} \tag{83}$$

4 Derivation of the MP2 gradient equation in the unrestricted basis

In this section, the results from the spin-orbital basis derivation in Sect. 3 are specialized to the unrestricted basis. The one-particle density matrices, Lagrangian, CPHF equations, and two-particle density matrices in the unrestricted basis are considered. Finally, the one- and two- particle gradients are summarized.

4.1 One-particle density matrices

The UMP2 gradient equations are derived straightforwardly from the spin-orbital results. The subspace of spin orbitals must be divided into two subspaces: one with α spatial orbitals and α spin and one with β spatial orbitals and β spin:

$$\sum_{p}^{\mathrm{subspace}} = \sum_{p^\alpha}^{\mathrm{subspace}^\alpha} + \sum_{p^\beta}^{\mathrm{subspace}^\beta} \quad . \tag{84}$$

The active–active density matrix $P_{ij}^{(2)}$ may be divided into four parts:

$$P_{ij}^{(2)} = P_{i^\alpha j^\alpha}^{(2)} + P_{i^\alpha j^\beta}^{(2)} + P_{i^\beta j^\alpha}^{(2)} + P_{i^\beta j^\beta}^{(2)} \quad . \tag{85}$$

The “mixed” densities $P_{i^\alpha j^\beta}^{(2)}$ and $P_{i^\beta j^\alpha}^{(2)}$ are zero, so this leaves an ($\alpha\alpha$) density and a ($\beta\beta$) density. These will be the same if α and β are exchanged, so the ($\alpha\alpha$) density will be considered in more detail. Dividing the subspaces yields

$$\begin{aligned}
P_{i^\alpha j^\alpha}^{(2)} &= -\frac{1}{2} \sum_{k}^{\mathrm{act}} \sum_{ab}^{\mathrm{vact}} T_{i^\alpha k}^{ab} T_{j^\alpha k}^{ab} = -\frac{1}{2} \left(\sum_{k^\alpha}^{\mathrm{act}^\alpha} + \sum_{k^\beta}^{\mathrm{act}^\beta} \right) \\
&\quad \times \left(\sum_{a^\alpha}^{\mathrm{vact}^\alpha} + \sum_{a^\beta}^{\mathrm{vact}^\beta} \right) \left(\sum_{b^\alpha}^{\mathrm{vact}^\alpha} + \sum_{b^\beta}^{\mathrm{vact}^\beta} \right) T_{i^\alpha k}^{ab} T_{j^\alpha k}^{ab} \\
&= -\frac{1}{2} \left[\sum_{k^\alpha}^{\mathrm{act}^\alpha} \sum_{a^\alpha}^{\mathrm{vact}^\alpha} \sum_{b^\alpha}^{\mathrm{vact}^\alpha} T_{i^\alpha k^\alpha}^{a^\alpha b^\alpha} T_{j^\alpha k^\alpha}^{a^\alpha b^\alpha} + \sum_{k^\beta}^{\mathrm{act}^\beta} \sum_{a^\alpha}^{\mathrm{vact}^\alpha} \sum_{b^\alpha}^{\mathrm{vact}^\alpha} T_{i^\alpha k^\beta}^{a^\alpha b^\alpha} T_{j^\alpha k^\beta}^{a^\alpha b^\alpha} \right. \\
&\quad + \sum_{k^\alpha}^{\mathrm{act}^\alpha} \sum_{a^\beta}^{\mathrm{vact}^\beta} \sum_{b^\alpha}^{\mathrm{vact}^\alpha} T_{i^\alpha k^\alpha}^{a^\beta b^\alpha} T_{j^\alpha k^\alpha}^{a^\beta b^\alpha} + \sum_{k^\alpha}^{\mathrm{act}^\alpha} \sum_{a^\alpha}^{\mathrm{vact}^\alpha} \sum_{b^\beta}^{\mathrm{vact}^\beta} T_{i^\alpha k^\alpha}^{a^\alpha b^\beta} T_{j^\alpha k^\alpha}^{a^\alpha b^\beta} \\
&\quad + \sum_{k^\beta}^{\mathrm{act}^\beta} \sum_{a^\beta}^{\mathrm{vact}^\beta} \sum_{b^\alpha}^{\mathrm{vact}^\alpha} T_{i^\alpha k^\beta}^{a^\beta b^\alpha} T_{j^\alpha k^\beta}^{a^\beta b^\alpha} + \sum_{k^\beta}^{\mathrm{act}^\beta} \sum_{a^\alpha}^{\mathrm{vact}^\alpha} \sum_{b^\beta}^{\mathrm{vact}^\beta} T_{i^\alpha k^\beta}^{a^\alpha b^\beta} T_{j^\alpha k^\beta}^{a^\alpha b^\beta} \\
&\quad \left. + \sum_{k^\alpha}^{\mathrm{act}^\alpha} \sum_{a^\beta}^{\mathrm{vact}^\beta} \sum_{b^\beta}^{\mathrm{vact}^\beta} T_{i^\alpha k^\alpha}^{a^\beta b^\beta} T_{j^\alpha k^\alpha}^{a^\beta b^\beta} + \sum_{k^\beta}^{\mathrm{act}^\beta} \sum_{a^\beta}^{\mathrm{vact}^\beta} \sum_{b^\beta}^{\mathrm{vact}^\beta} T_{i^\alpha k^\beta}^{a^\beta b^\beta} T_{j^\alpha k^\beta}^{a^\beta b^\beta} \right]
\end{aligned} \tag{86}$$

Terms 2, 3, 4, and 8 in Eq. (86) contain an odd number of β spins, so the spin functions will integrate to zero. The spin functions in term 7 in Eq. (86) also integrate to zero. This leaves three terms. Substitution of the form of the amplitude (Eq. 2) gives

$$\begin{aligned}
P_{i^\alpha j^\alpha}^{(2)} = &-\frac{1}{2} \left\{ \sum_{k^\alpha}^{\mathrm{act}^\alpha} \sum_{a^\alpha}^{\mathrm{vact}^\alpha} \sum_{b^\alpha}^{\mathrm{vact}^\alpha} \frac{[(i^\alpha a^\alpha | k^\alpha b^\alpha) - (i^\alpha b^\alpha | k^\alpha a^\alpha)]}{D_{i^\alpha k^\alpha}^{a^\alpha b^\alpha}} \right. \\
&\times \frac{[(j^\alpha a^\alpha | k^\alpha b^\alpha) - (j^\alpha b^\alpha | k^\alpha a^\alpha)]}{D_{j^\alpha k^\alpha}^{a^\alpha b^\alpha}} \\
&+ \sum_{k^\beta}^{\mathrm{act}^\beta} \sum_{a^\beta}^{\mathrm{vact}^\beta} \sum_{b^\alpha}^{\mathrm{vact}^\alpha} \frac{\left[-\left(i^\alpha b^\alpha \middle| k^\beta a^\beta\right)\right]}{D_{i^\alpha k^\beta}^{a^\beta b^\alpha}} \frac{\left[-\left(j^\alpha b^\alpha \middle| k^\beta a^\beta\right)\right]}{D_{j^\alpha k^\beta}^{a^\beta b^\alpha}} \\
&\left. + \sum_{k^\beta}^{\mathrm{act}^\beta} \sum_{a^\alpha}^{\mathrm{vact}^\alpha} \sum_{b^\beta}^{\mathrm{vact}^\beta} \frac{\left[\left(i^\alpha a^\alpha \middle| k^\beta b^\beta\right)\right]}{D_{i^\alpha k^\beta}^{a^\alpha b^\beta}} \frac{\left[\left(j^\alpha a^\alpha \middle| k^\beta b^\beta\right)\right]}{D_{j^\alpha k^\beta}^{a^\alpha b^\beta}} \right\} \quad .
\end{aligned} \tag{87}$$

The last two terms are the same if indices a and b are interchanged. The first term may also be simplified by expanding the equation and interchanging indices a and b in appropriate terms, yielding

$$P^{(2)}_{i^\alpha j^\alpha} = -\sum_{k^\alpha}^{\mathrm{act}^\alpha}\sum_{a^\alpha}^{\mathrm{vact}^\alpha}\sum_{b^\alpha}^{\mathrm{vact}^\alpha}\frac{\left[(i^\alpha a^\alpha|k^\alpha b^\alpha)-(i^\alpha b^\alpha|k^\alpha a^\alpha)\right]}{D^{a^\alpha b^\alpha}_{i^\alpha k^\alpha}}\frac{(j^\alpha a^\alpha|k^\alpha b^\alpha)}{D^{a^\alpha b^\alpha}_{j^\alpha k^\alpha}} - \sum_{k^\beta}^{\mathrm{act}^\beta}\sum_{a^\alpha}^{\mathrm{vact}^\alpha}\sum_{b^\beta}^{\mathrm{vact}^\beta}\frac{\left[(i^\alpha a^\alpha|k^\beta b^\beta)\right]}{D^{a^\alpha b^\beta}_{i^\alpha k^\beta}}\frac{\left[(j^\alpha a^\alpha|k^\beta b^\beta)\right]}{D^{a^\alpha b^\beta}_{j^\alpha k^\beta}} \ . \tag{88}$$

The $(\beta\beta)$ density matrices will not be considered in detail since they may be determined simply by interchanging α and β in the appropriate $(\alpha\alpha)$ density matrix. For example, the corresponding active–active $(\beta\beta)$ density matrix becomes

$$P^{(2)}_{i^\beta j^\beta} = -\sum_{k^\beta}^{\mathrm{act}^\beta}\sum_{a^\beta}^{\mathrm{vact}^\beta}\sum_{b^\beta}^{\mathrm{vact}^\beta}\frac{\left[(i^\beta a^\beta|k^\beta b^\beta)-(i^\beta b^\beta|k^\beta a^\beta)\right]}{D^{a^\beta b^\beta}_{i^\beta k^\beta}}\frac{(j^\beta a^\beta|k^\beta b^\beta)}{D^{a^\beta b^\beta}_{j^\beta k^\beta}} - \sum_{k^\alpha}^{\mathrm{act}^\alpha}\sum_{a^\beta}^{\mathrm{vact}^\beta}\sum_{b^\alpha}^{\mathrm{vact}^\alpha}\frac{\left[(i^\beta a^\beta|k^\alpha b^\alpha)\right]}{D^{a^\beta b^\alpha}_{i^\beta k^\alpha}}\frac{\left[(j^\beta a^\beta|k^\alpha b^\alpha)\right]}{D^{a^\beta b^\alpha}_{j^\beta k^\alpha}} . \tag{89}$$

The last of the one-particle density matrices that deserves mention is the third term in the energy-weighted density matrix. The $(\alpha\alpha)$ term is transformed as

$$W^{(2)}_{i^\alpha j^\alpha}[III] = -\frac{1}{2}\sum_{pq}^{\mathrm{all}}P^{(2)}_{pq}A_{pqj^\alpha i^\alpha} = -\frac{1}{2}\sum_{p^\alpha q^\alpha}^{\mathrm{all}^\alpha}P^{(2)}_{p^\alpha q^\alpha}A_{p^\alpha q^\alpha j^\alpha i^\alpha} - \frac{1}{2}\sum_{p^\beta q^\beta}^{\mathrm{all}^\beta}P^{(2)}_{p^\beta q^\beta}A_{p^\beta q^\beta j^\alpha i^\alpha} \ , \tag{90}$$

where it is again recognized that the mixed densities $P^{(2)}_{p^\alpha q^\beta}$ and $P^{(2)}_{p^\beta q^\alpha}$ are zero. Four types of the A_{pqrs} must be considered:

$$A_{p^\alpha q^\alpha r^\alpha s^\alpha} = 2(p^\alpha q^\alpha|r^\alpha s^\alpha) - (p^\alpha r^\alpha|q^\alpha s^\alpha) - (p^\alpha s^\alpha|q^\alpha r^\alpha) \ , \tag{91}$$

$$A_{p^\alpha q^\alpha r^\beta s^\beta} = 2(p^\alpha q^\alpha|r^\beta s^\beta) \ , \tag{92}$$

$$A_{p^\beta q^\beta r^\alpha s^\alpha} = 2(p^\beta q^\beta|r^\alpha s^\alpha) \ , \tag{93}$$

$$A_{p^\beta q^\beta r^\beta s^\beta} = 2(p^\beta q^\beta|r^\beta s^\beta) - (p^\beta r^\beta|q^\beta s^\beta) - (p^\beta s^\beta|q^\beta r^\beta) \ . \tag{94}$$

Substitution of Eqs. (91) and (93) into Eq. (90) yields

$$W^{(2)}_{i^\alpha j^\alpha}[III] = -\frac{1}{2}\sum_{p^\alpha q^\alpha}^{\mathrm{all}^\alpha}P^{(2)}_{p^\alpha q^\alpha}\Big[2(p^\alpha q^\alpha|j^\alpha i^\alpha) - (p^\alpha j^\alpha|q^\alpha i^\alpha) - (p^\alpha i^\alpha|q^\alpha j^\alpha)\Big] - \frac{1}{2}\sum_{p^\beta q^\beta}^{\mathrm{all}^\beta}P^{(2)}_{p^\beta q^\beta}\left[2(p^\beta q^\beta|j^\alpha i^\alpha)\right] \ . \tag{95}$$

Owing to equivalent summations over p and q, the matrix contribution may be written as

$$W^{(2)}_{i^\alpha j^\alpha}[III] = -\sum_{p^\alpha q^\alpha}^{\mathrm{all}^\alpha}P^{(2)}_{p^\alpha q^\alpha}\left[(p^\alpha q^\alpha|i^\alpha j^\alpha) - (p^\alpha i^\alpha|q^\alpha j^\alpha)\right] - \sum_{p^\beta q^\beta}^{\mathrm{all}^\beta}P^{(2)}_{p^\beta q^\beta}(p^\beta q^\beta|i^\alpha j^\alpha) \ . \tag{96}$$

4.2 Lagrangian

The virtual–occupied response term must be considered next. This term (Eq. 56) has both $(\alpha\alpha)$ and $(\beta\beta)$ contributions:

$$\sum_{i}^{\mathrm{occ}}\sum_{a}^{\mathrm{vall}}U^x_{ai}L_{ai} = \sum_{i^\alpha}^{\mathrm{occ}^\alpha}\sum_{a^\alpha}^{\mathrm{vall}^\alpha}U^x_{a^\alpha i^\alpha}L_{a^\alpha i^\alpha} + \sum_{i^\beta}^{\mathrm{occ}^\beta}\sum_{a^\beta}^{\mathrm{vall}^\beta}U^x_{a^\beta i^\beta}L_{a^\beta i^\beta} \ . \tag{97}$$

The next task is to find the form of the $(\alpha\alpha)$ Lagrangian. The first and second terms in the Lagrangian in the spin-orbital basis (Eq. 57) transform as in Eq. (90). The third and fourth terms may be transformed with the techniques used for the other density matrices. This yields the following form for the $(\alpha\alpha)$ Lagrangian:

$$\begin{aligned}L_{a^\alpha i^\alpha} = {} & \sum_{j^\alpha k^\alpha}^{\mathrm{occ}^\alpha}P^{(2)}_{j^\alpha k^\alpha}A_{a^\alpha i^\alpha j^\alpha k^\alpha} + \sum_{j^\beta k^\beta}^{\mathrm{occ}^\beta}P^{(2)}_{j^\beta k^\beta}A_{a^\alpha i^\alpha j^\beta k^\beta} \\ & + \sum_{b^\alpha c^\alpha}^{\mathrm{vall}^\alpha}P^{(2)}_{b^\alpha c^\alpha}A_{a^\alpha i^\alpha b^\alpha c^\alpha} + \sum_{b^\beta c^\beta}^{\mathrm{vall}^\beta}P^{(2)}_{b^\beta c^\beta}A_{a^\alpha i^\alpha b^\beta c^\beta} \\ & - 2N_{a^\alpha}\sum_{j^\alpha k^\alpha}^{\mathrm{act}^\alpha}\sum_{b^\alpha}^{\mathrm{vact}^\alpha}\frac{(j^\alpha a^\alpha|k^\alpha b^\alpha) - (j^\alpha b^\alpha|k^\alpha a^\alpha)}{D^{a^\alpha b^\alpha}_{j^\alpha k^\alpha}}(i^\alpha j^\alpha|b^\alpha k^\alpha) \\ & - 2N_{a^\alpha}\sum_{j^\alpha}^{\mathrm{act}^\alpha}\sum_{k^\beta}^{\mathrm{act}^\beta}\sum_{b^\beta}^{\mathrm{vact}^\beta}\frac{(j^\alpha a^\alpha|k^\beta b^\beta)}{D^{a^\alpha b^\beta}_{j^\alpha k^\beta}}(i^\alpha j^\alpha|b^\beta k^\beta) \\ & + 2N_{i^\alpha}\sum_{j^\alpha}^{\mathrm{act}^\alpha}\sum_{b^\alpha c^\alpha}^{\mathrm{vact}^\alpha}\frac{(i^\alpha b^\alpha|j^\alpha c^\alpha) - (i^\alpha c^\alpha|j^\alpha b^\alpha)}{D^{b^\alpha c^\alpha}_{i^\alpha j^\alpha}}(a^\alpha b^\alpha|j^\alpha c^\alpha) \\ & + 2N_{i^\alpha}\sum_{j^\beta}^{\mathrm{act}^\beta}\sum_{b^\alpha}^{\mathrm{vact}^\alpha}\sum_{c^\beta}^{\mathrm{vact}^\beta}\frac{(i^\alpha b^\alpha|j^\beta c^\beta)}{D^{b^\alpha c^\beta}_{i^\alpha j^\beta}}(a^\alpha b^\alpha|j^\beta c^\beta) \ .\end{aligned} \tag{98}$$

Again, the $(\beta\beta)$ Lagrangian will be related to the $(\alpha\alpha)$ Lagrangian by an interchange of all α and β spin terms.

4.3 CPHF equations

Equation (67) may be expressed in the unrestricted basis as

$$\sum_{b^\alpha}^{\mathrm{vall}^\alpha}\sum_{j^\alpha}^{\mathrm{occ}^\alpha}\left\{A_{a^\alpha i^\alpha b^\alpha j^\alpha} + \delta_{a^\alpha b^\alpha}\delta_{i^\alpha j^\alpha}\left(\varepsilon^\alpha_b - \varepsilon^\alpha_j\right)\right\}P^{(2)}_{b^\alpha j^\alpha} + \sum_{b^\beta}^{\mathrm{vall}^\beta}\sum_{j^\beta}^{\mathrm{occ}^\beta}\left\{A_{a^\alpha i^\alpha b^\beta j^\beta} + \delta_{a^\alpha b^\beta}\delta_{i^\alpha j^\beta}\left(\varepsilon^\beta_b - \varepsilon^\beta_j\right)\right\}P^{(2)}_{b^\beta j^\beta} = -L_{a^\alpha i^\alpha}, \tag{99}$$

$$\sum_{b^\alpha}^{\mathrm{vall}^\alpha}\sum_{j^\alpha}^{\mathrm{occ}^\alpha}\left\{A_{a^\beta i^\beta b^\alpha j^\alpha}+\delta_{a^\beta b^\alpha}\delta_{i^\beta j^\alpha}\left(\varepsilon_b^\alpha-\varepsilon_j^\alpha\right)\right\}P^{(2)}_{b^\alpha j^\alpha}$$
$$+\sum_{b^\beta}^{\mathrm{vall}^\beta}\sum_{j^\beta}^{\mathrm{occ}^\beta}\left\{A_{a^\beta i^\beta b^\beta j^\beta}+\delta_{a^\beta b^\beta}\delta_{i^\beta j^\beta}\left(\varepsilon_b^\beta-\varepsilon_j^\beta\right)\right\}P^{(2)}_{b^\beta j^\beta}=-L_{a^\beta i^\beta}\ . \tag{100}$$

The Kronecker δs of mixed spins are zero, leading to

$$\sum_{b^\alpha}^{\mathrm{vall}^\alpha}\sum_{j^\alpha}^{\mathrm{occ}^\alpha}\left\{A_{a^\alpha i^\alpha b^\alpha j^\alpha}+\delta_{ab}\delta_{ij}\left(\varepsilon_b^\alpha-\varepsilon_j^\alpha\right)\right\}P^{(2)}_{b^\alpha j^\alpha}$$
$$+\sum_{b^\beta}^{\mathrm{vall}^\beta}\sum_{j^\beta}^{\mathrm{occ}^\beta}\left\{A_{a^\alpha i^\alpha b^\beta j^\beta}\right\}P^{(2)}_{b^\beta j^\beta}=-L_{a^\alpha i^\alpha}\ , \tag{101}$$

$$\sum_{b^\beta}^{\mathrm{vall}^\beta}\sum_{j^\beta}^{\mathrm{occ}^\beta}\left\{A_{a^\beta i^\beta b^\beta j^\beta}+\delta_{ab}\delta_{ij}\left(\varepsilon_b^\beta-\varepsilon_j^\beta\right)\right\}P^{(2)}_{b^\beta j^\beta}$$
$$+\sum_{b^\alpha}^{\mathrm{vall}^\alpha}\sum_{j^\alpha}^{\mathrm{occ}^\alpha}\left\{A_{a^\beta i^\beta b^\alpha j^\alpha}\right\}P^{(2)}_{b^\alpha j^\alpha}=-L_{a^\beta i^\beta}\ . \tag{102}$$

Equations (101) and (102) may be solved for $P^{(2)}_{b^\alpha j^\alpha}$ and $P^{(2)}_{b^\beta j^\beta}$. The contribution to the gradient expression comes from the following equations:

$$\sum_{a^\alpha i^\alpha}U^x_{a^\alpha i^\alpha}L_{a^\alpha i^\alpha}=\sum_{a^\alpha i^\alpha}B^x_{a^\alpha i^\alpha}P^{(2)}_{a^\alpha i^\alpha}, \tag{103}$$

$$\sum_{a^\beta i^\beta}U^x_{a^\beta i^\beta}L_{a^\beta i^\beta}=\sum_{a^\beta i^\beta}B^x_{a^\beta i^\beta}P^{(2)}_{a^\beta i^\beta}. \tag{104}$$

The form of the $B^x_{b^\alpha j^\alpha}$ term may be determined in the following manner:

$$B^x_{p^\alpha q^\alpha}=F^{(x)}_{p^\alpha q^\alpha}-S^{(x)}_{p^\alpha q^\alpha}\varepsilon_q^\alpha-\frac{1}{2}\sum_{k^\alpha l^\alpha}^{\mathrm{occ}^\alpha}S^{(x)}_{k^\alpha l^\alpha}A_{p^\alpha q^\alpha l^\alpha k^\alpha}$$
$$-\frac{1}{2}\sum_{k^\beta l^\beta}^{\mathrm{occ}^\beta}S^{(x)}_{k^\beta l^\beta}A_{p^\alpha q^\alpha l^\beta k^\beta} \tag{105}$$

$$=F^{(x)}_{p^\alpha q^\alpha}-S^{(x)}_{p^\alpha q^\alpha}\varepsilon_q^\alpha-\frac{1}{2}\sum_{k^\alpha l^\alpha}^{\mathrm{occ}^\alpha}S^{(x)}_{k^\alpha l^\alpha}[2(p^\alpha q^\alpha|k^\alpha l^\alpha)-(p^\alpha k^\alpha|q^\alpha l^\alpha)$$
$$-(p^\alpha l^\alpha|q^\alpha k^\alpha)]-\frac{1}{2}\sum_{k^\beta l^\beta}^{\mathrm{occ}^\beta}S^{(x)}_{k^\beta l^\beta}\left[2\left(p^\alpha q^\alpha|k^\beta l^\beta\right)\right]\ . \tag{106}$$

Owing to equivalent summation over k and l, Eq. (106) may be simplified to

$$B^x_{p^\alpha q^\alpha}=F^{(x)}_{p^\alpha q^\alpha}-S^{(x)}_{p^\alpha q^\alpha}\varepsilon_q^\alpha-\sum_{k^\alpha l^\alpha}^{\mathrm{occ}}S^{(x)}_{k^\alpha l^\alpha}[(p^\alpha q^\alpha|k^\alpha l^\alpha)-(p^\alpha k^\alpha|q^\alpha l^\alpha)]$$
$$-\sum_{k^\beta l^\beta}^{\mathrm{occ}^\beta}S^{(x)}_{k^\beta l^\beta}\left(p^\alpha q^\alpha|k^\beta l^\beta\right)\ , \tag{107}$$

where

$$F^{(x)}_{p^\alpha q^\alpha}=H^{(x)}_{p^\alpha q^\alpha}+\sum_{k^\alpha}^{\mathrm{occ}^\alpha}\left[(p^\alpha q^\alpha|k^\alpha k^\alpha)^{(x)}-(p^\alpha k^\alpha|q^\alpha k^\alpha)^{(x)}\right]$$
$$+\sum_{k^\beta}^{\mathrm{occ}^\beta}\left[\left(p^\alpha q^\alpha|k^\beta k^\beta\right)^{(x)}\right]\ . \tag{108}$$

4.4 Two-particle density matrices

The nonseparable density term in the spin-orbital basis (term 11 in Eq. 70) is

$$\frac{1}{2}\sum_{ij}^{\mathrm{act}}\sum_{ab}^{\mathrm{vact}}(ia\|jb)^{(x)}T_{ij}^{ab}. \tag{109}$$

Summing over spin gives

$$\frac{1}{2}\left\{\sum_{i^\alpha j^\alpha}^{\mathrm{act}^\alpha}\sum_{a^\alpha b^\alpha}^{\mathrm{vact}^\alpha}\frac{[(i^\alpha a^\alpha|j^\alpha b^\alpha)-(i^\alpha b^\alpha|j^\alpha a^\alpha)]}{\varepsilon_i^\alpha+\varepsilon_j^\alpha-\varepsilon_a^\alpha-\varepsilon_b^\alpha}\right.$$
$$\times\left[\left(i^\alpha a^\alpha|j^\alpha b^\alpha\right)^{(x)}-\left(i^\alpha b^\alpha|j^\alpha a^\alpha\right)^{(x)}\right]$$
$$+\sum_{i^\alpha}^{\mathrm{act}^\alpha}\sum_{j^\beta}^{\mathrm{act}^\beta}\sum_{a^\alpha}^{\mathrm{vact}^\alpha}\sum_{b^\beta}^{\mathrm{vact}^\beta}\frac{\left(i^\alpha a^\alpha|j^\beta b^\beta\right)\left(i^\alpha a^\alpha|j^\beta b^\beta\right)^{(x)}}{\varepsilon_i^\alpha+\varepsilon_j^\beta-\varepsilon_a^\alpha-\varepsilon_b^\beta}$$
$$+\sum_{i^\alpha}^{\mathrm{act}^\alpha}\sum_{j^\beta}^{\mathrm{act}^\beta}\sum_{a^\beta}^{\mathrm{vact}^\beta}\sum_{b^\alpha}^{\mathrm{vact}^\alpha}\frac{\left(i^\alpha b^\alpha|j^\beta a^\beta\right)\left(i^\alpha b^\alpha|j^\beta a^\beta\right)^{(x)}}{\varepsilon_i^\alpha+\varepsilon_j^\beta-\varepsilon_a^\beta-\varepsilon_b^\alpha}$$
$$+\sum_{i^\beta}^{\mathrm{act}^\beta}\sum_{j^\alpha}^{\mathrm{act}^\alpha}\sum_{a^\alpha}^{\mathrm{vact}^\alpha}\sum_{b^\beta}^{\mathrm{vact}^\beta}\frac{\left(j^\alpha a^\alpha|i^\beta b^\beta\right)\left(j^\alpha a^\alpha|i^\beta b^\beta\right)^{(x)}}{\varepsilon_i^\beta+\varepsilon_j^\alpha-\varepsilon_a^\alpha-\varepsilon_b^\beta}$$
$$+\sum_{i^\beta}^{\mathrm{act}^\beta}\sum_{j^\alpha}^{\mathrm{act}^\alpha}\sum_{a^\beta}^{\mathrm{vact}^\beta}\sum_{b^\alpha}^{\mathrm{vact}^\alpha}\frac{\left(j^\alpha b^\alpha|i^\beta a^\beta\right)\left(j^\alpha b^\alpha|i^\beta a^\beta\right)^{(x)}}{\varepsilon_i^\beta+\varepsilon_j^\alpha-\varepsilon_a^\beta-\varepsilon_b^\alpha}$$
$$+\sum_{i^\beta j^\beta}^{\mathrm{act}^\beta}\sum_{a^\beta b^\beta}^{\mathrm{vact}^\beta}\frac{\left[\left(i^\beta a^\beta|j^\beta b^\beta\right)-\left(i^\beta b^\beta|j^\beta a^\beta\right)\right]}{\varepsilon_i^\beta+\varepsilon_j^\beta-\varepsilon_a^\beta-\varepsilon_b^\beta}$$
$$\left.\times\left[\left(i^\beta a^\beta|j^\beta b^\beta\right)^{(x)}-\left(i^\beta b^\beta|j^\beta a^\beta\right)^{(x)}\right]\right\}\ . \tag{110}$$

Terms 2, 3, 4, and 5 in Eq. (110) are the same if indices (*i,j*) or (*a,b*) are interchanged. Terms 1 and 6 may also be simplified by expanding the terms and interchanging appropriate indices. This yields

$$\sum_{i^\alpha j^\alpha}^{\mathrm{act}^\alpha}\sum_{a^\alpha b^\alpha}^{\mathrm{vact}^\alpha}\frac{[(i^\alpha a^\alpha|j^\alpha b^\alpha)-(i^\alpha b^\alpha|j^\alpha a^\alpha)]}{\varepsilon_i^\alpha+\varepsilon_j^\alpha-\varepsilon_a^\alpha-\varepsilon_b^\alpha}(i^\alpha a^\alpha|j^\alpha b^\alpha)^{(x)}$$
$$+2\sum_{i^\alpha}^{\mathrm{act}^\alpha}\sum_{j^\beta}^{\mathrm{act}^\beta}\sum_{a^\alpha}^{\mathrm{vact}^\alpha}\sum_{b^\beta}^{\mathrm{vact}^\beta}\frac{\left(i^\alpha a^\alpha|j^\beta b^\beta\right)\left(i^\alpha a^\alpha|j^\beta b^\beta\right)^{(x)}}{\varepsilon_i^\alpha+\varepsilon_j^\beta-\varepsilon_a^\alpha-\varepsilon_b^\beta}$$
$$+\sum_{i^\beta j^\beta}^{\mathrm{act}^\beta}\sum_{a^\beta b^\beta}^{\mathrm{vact}^\beta}\frac{\left[\left(i^\beta a^\beta|j^\beta b^\beta\right)-\left(i^\beta b^\beta|j^\beta a^\beta\right)\right]}{\varepsilon_i^\beta+\varepsilon_j^\beta-\varepsilon_a^\beta-\varepsilon_b^\beta}\left(i^\beta a^\beta|j^\beta b^\beta\right)^{(x)}\ . \tag{111}$$

At this point, AO ERI derivatives may be substituted for the MO ERI derivatives using Eq. (6), which gives

$$
\begin{aligned}
&\sum_{\mu\nu\lambda\sigma}\left(\sum_{i^\alpha j^\alpha}^{\mathrm{act}^\alpha}\sum_{a^\alpha b^\alpha}^{\mathrm{vact}^\alpha}\frac{\left[(i^\alpha a^\alpha|j^\alpha b^\alpha)-(i^\alpha b^\alpha|j^\alpha a^\alpha)\right]}{\varepsilon_i^\alpha+\varepsilon_j^\alpha-\varepsilon_a^\alpha-\varepsilon_b^\alpha}C_{\mu i}^\alpha C_{\nu a}^\alpha C_{\lambda j}^\alpha C_{\sigma b}^\alpha\right.\\
&\quad+2\sum_{i^\alpha}^{\mathrm{act}^\alpha}\sum_{j^\beta}^{\mathrm{act}^\beta}\sum_{a^\alpha}^{\mathrm{vact}^\alpha}\sum_{b^\beta}^{\mathrm{vact}^\beta}\frac{\left(i^\alpha a^\alpha\middle|j^\beta b^\beta\right)}{\varepsilon_i^\alpha+\varepsilon_j^\beta-\varepsilon_a^\alpha-\varepsilon_b^\beta}C_{\mu i}^\alpha C_{\nu a}^\alpha C_{\lambda j}^\beta C_{\sigma b}^\beta\\
&\quad\left.+\sum_{i^\beta j^\beta}^{\mathrm{act}^\beta}\sum_{a^\beta b^\beta}^{\mathrm{vact}^\beta}\frac{\left[\left(i^\beta a^\beta\middle|j^\beta b^\beta\right)-\left(i^\beta b^\beta\middle|j^\beta a^\beta\right)\right]}{\varepsilon_i^\beta+\varepsilon_j^\beta-\varepsilon_a^\beta-\varepsilon_b^\beta}C_{\mu i}^\beta C_{\nu a}^\beta C_{\lambda j}^\beta C_{\sigma b}^\beta\right)\\
&\quad\times(\mu\nu|\lambda\sigma)^x\ . \qquad (112)
\end{aligned}
$$

The quantity in large parentheses in Eq. (112) may be identified as the nonseparable two-particle density matrix $\Gamma^{\mathrm{NS}}_{\mu\nu\lambda\sigma}$, which gives a term of the form

$$\sum_{\mu\nu\lambda\sigma}\Gamma^{\mathrm{NS}}_{\mu\nu\lambda\sigma}(\mu\nu|\lambda\sigma)^x\ . \qquad (113)$$

Finally, the separable two-particle density comes from terms 1, 2, and 3 in Eq. (70), which have the form

$$\sum_{pq}^{\mathrm{all}}P_{pq}^{(2)}\sum_{k}^{\mathrm{occ}}\left[(ij|kk)^{(x)}-(ik|jk)^{(x)}\right]\ . \qquad (114)$$

Summation over spin yields

$$
\begin{aligned}
&\sum_{p^\alpha q^\alpha}^{\mathrm{all}^\alpha}P_{p^\alpha q^\alpha}^{(2)}\left\{\sum_{k^\alpha}^{\mathrm{occ}^\alpha}\left[(p^\alpha q^\alpha|k^\alpha k^\alpha)^{(x)}-(p^\alpha k^\alpha|q^\alpha k^\alpha)^{(x)}\right]\right.\\
&\qquad\left.+\sum_{k^\beta}^{\mathrm{occ}^\beta}\left(p^\alpha q^\alpha\middle|k^\beta k^\beta\right)^{(x)}\right\}\\
&\qquad+\sum_{p^\beta q^\beta}^{\mathrm{all}^\beta}P_{p^\beta q^\beta}^{(2)}\left\{\sum_{k^\beta}^{\mathrm{occ}^\beta}\left[\left(p^\beta q^\beta\middle|k^\beta k^\beta\right)^{(x)}\right.\right.\\
&\qquad\left.\left.-\left(p^\beta k^\beta\middle|q^\beta k^\beta\right)^{(x)}\right]+\sum_{k^\alpha}^{\mathrm{occ}^\alpha}\left(p^\beta q^\beta\middle|k^\alpha k^\alpha\right)^{(x)}\right\}. \qquad (115)
\end{aligned}
$$

Expressing Eq. (115) in terms of AO derivatives (Eq. 6) gives

$$
\begin{aligned}
&\sum_{p^\alpha q^\alpha}^{\mathrm{all}^\alpha}P_{p^\alpha q^\alpha}^{(2)}\sum_{\mu\nu\lambda\sigma}\sum_{k^\alpha}^{\mathrm{occ}^\alpha}\left(C_{\mu p}^\alpha C_{\nu q}^\alpha C_{\lambda k}^\alpha C_{\sigma k}^\alpha-C_{\mu p}^\alpha C_{\nu k}^\alpha C_{\lambda q}^\alpha C_{\sigma k}^\alpha\right)(\mu\nu|\lambda\sigma)^x\\
&+\sum_{p^\alpha q^\alpha}^{\mathrm{all}^\alpha}P_{p^\alpha q^\alpha}^{(2)}\sum_{\mu\nu\lambda\sigma}\sum_{k^\beta}^{\mathrm{occ}^\beta}C_{\mu p}^\alpha C_{\nu q}^\alpha C_{\lambda k}^\beta C_{\sigma k}^\beta(\mu\nu|\lambda\sigma)^x\\
&+\sum_{p^\beta q^\beta}^{\mathrm{all}^\beta}P_{p^\beta q^\beta}^{(2)}\sum_{\mu\nu\lambda\sigma}\sum_{k^\beta}^{\mathrm{occ}^\beta}\left(C_{\mu p}^\beta C_{\nu q}^\beta C_{\lambda k}^\beta C_{\sigma k}^\beta-C_{\mu p}^\beta C_{\nu k}^\beta C_{\lambda q}^\beta C_{\sigma k}^\beta\right)(\mu\nu|\lambda\sigma)^x\\
&+\sum_{p^\beta q^\beta}^{\mathrm{all}^\beta}P_{p^\beta q^\beta}^{(2)}\sum_{\mu\nu\lambda\sigma}\sum_{k^\alpha}^{\mathrm{occ}^\alpha}C_{\mu p}^\beta C_{\nu q}^\beta C_{\lambda k}^\alpha C_{\sigma k}^\alpha(\mu\nu|\lambda\sigma)^x\ . \qquad (116)
\end{aligned}
$$

Factoring Eq. (116) yields

$$
\begin{aligned}
&\sum_{\mu\nu\lambda\sigma}\left[\left(\sum_{k^\alpha}^{\mathrm{occ}^\alpha}C_{\lambda k}^\alpha C_{\sigma k}^\alpha\right)\left(\sum_{p^\alpha q^\alpha}^{\mathrm{all}^\alpha}P_{p^\alpha q^\alpha}^{(2)}C_{\mu p}^\alpha C_{\nu q}^\alpha\right)\right.\\
&\quad\left.-\left(\sum_{k^\alpha}^{\mathrm{occ}^\alpha}C_{\nu k}^\alpha C_{\sigma k}^\alpha\right)\left(\sum_{p^\alpha q^\alpha}^{\mathrm{all}^\alpha}P_{p^\alpha q^\alpha}^{(2)}C_{\mu p}^\alpha C_{\lambda q}^\alpha\right)\right](\mu\nu|\lambda\sigma)^x\\
&+\sum_{\mu\nu\lambda\sigma}\left[\left(\sum_{k^\beta}^{\mathrm{occ}^\beta}C_{\lambda k}^\beta C_{\sigma k}^\beta\right)\left(\sum_{p^\alpha q^\alpha}^{\mathrm{all}^\alpha}P_{p^\alpha q^\alpha}^{(2)}C_{\mu p}^\alpha C_{\nu q}^\alpha\right)\right](\mu\nu|\lambda\sigma)^x\\
&+\sum_{\mu\nu\lambda\sigma}\left[\left(\sum_{k^\beta}^{\mathrm{occ}^\beta}C_{\lambda k}^\beta C_{\sigma k}^\beta\right)\left(\sum_{p^\beta q^\beta}^{\mathrm{all}^\beta}P_{p^\beta q^\beta}^{(2)}C_{\mu p}^\beta C_{\nu q}^\beta\right)\right.\\
&\quad\left.-\left(\sum_{k^\beta}^{\mathrm{occ}^\beta}C_{\nu k}^\beta C_{\sigma k}^\beta\right)\left(\sum_{p^\beta q^\beta}^{\mathrm{all}^\beta}P_{p^\beta q^\beta}^{(2)}C_{\mu p}^\beta C_{\lambda q}^\beta\right)\right](\mu\nu|\lambda\sigma)^x\\
&+\sum_{\mu\nu\lambda\sigma}\left[\left(\sum_{k^\alpha}^{\mathrm{occ}^\alpha}C_{\lambda k}^\alpha C_{\sigma k}^\alpha\right)\left(\sum_{p^\beta q^\beta}^{\mathrm{all}^\beta}P_{p^\beta q^\beta}^{(2)}C_{\mu p}^\beta C_{\nu q}^\beta\right)\right](\mu\nu|\lambda\sigma)^x\ . \qquad (117)
\end{aligned}
$$

Identification of appropriate SCF density matrices such as

$$P_{\mu\nu}^{\alpha\mathrm{SCF}}=\sum_{k^\alpha}^{\mathrm{occ}^\alpha}C_{\mu k}^\alpha C_{\nu k}^\alpha \qquad (118)$$

and transformed MP2 correction density matrices such as

$$P_{\mu\nu}^{(2)}(\alpha\alpha)=\sum_{p^\alpha q^\alpha}^{\mathrm{all}^\alpha}C_{\mu p}^\alpha C_{\nu q}^\alpha P_{p^\alpha q^\alpha}^{(2)} \qquad (119)$$

allows Eq. (117) to be written as

$$
\begin{aligned}
&\sum_{\mu\nu\lambda\sigma}\left[P_{\mu\nu}^{(2)}(\alpha\alpha)P_{\lambda\sigma}^{\alpha\mathrm{SCF}}-P_{\mu\lambda}^{(2)}(\alpha\alpha)P_{\nu\sigma}^{\alpha\mathrm{SCF}}+P_{\mu\nu}^{(2)}(\alpha\alpha)P_{\lambda\sigma}^{\beta\mathrm{SCF}}\right.\\
&\quad\left.+P_{\mu\nu}^{(2)}(\beta\beta)P_{\lambda\sigma}^{\beta\mathrm{SCF}}-P_{\mu\lambda}^{(2)}(\beta\beta)P_{\nu\sigma}^{\beta\mathrm{SCF}}+P_{\mu\nu}^{(2)}(\beta\beta)P_{\lambda\sigma}^{\alpha\mathrm{SCF}}\right]\\
&\quad\times(\mu\nu|\lambda\sigma)^x. \qquad (120)
\end{aligned}
$$

The quantity in brackets in Eq. (120) can be identified as the separable two-particle density matrix $\Gamma^{\mathrm{S}}_{\mu\nu\lambda\sigma}$, yielding a term of the form

$$\sum_{\mu\nu\lambda\sigma}\Gamma^{\mathrm{S}}_{\mu\nu\lambda\sigma}\ (\mu\nu|\lambda\sigma)^x\ . \qquad (121)$$

4.5 One-particle gradient summary

The $(\alpha\alpha)$ terms of the one-particle density matrices are summarized here. All $(\beta\beta)$ one-particle gradient terms are direct analogs of the corresponding $(\alpha\alpha)$ terms.

MP2 density correction terms $(\alpha\alpha)$

$$
\begin{aligned}
&KJ=\mathrm{core}-\mathrm{core}\\
&P_{K^\alpha J^\alpha}^{(2)}=0
\end{aligned}
\qquad (122)
$$

$$
\begin{aligned}
&Ki{=}\mathrm{core}{-}\mathrm{act}\quad P_{K^\alpha i^\alpha}^{(2)}{=}P_{i^\alpha K^\alpha}^{(2)}\\
&\quad=\frac{1}{(\varepsilon_i^\alpha-\varepsilon_K^\alpha)}\sum_{j^\alpha}^{\mathrm{act}^\alpha}\sum_{a^\alpha b^\alpha}^{\mathrm{vact}^\alpha}\left\{\frac{\left[(i^\alpha a^\alpha|j^\alpha b^\alpha)-(i^\alpha b^\alpha|j^\alpha a^\alpha)\right]}{D_{i^\alpha j^\alpha}^{a^\alpha b^\alpha}}(K^\alpha a^\alpha|j^\alpha b^\alpha)\right.\\
&\quad\left.+\sum_{j^\beta}^{\mathrm{act}^\beta}\sum_{a^\alpha}^{\mathrm{vact}^\alpha}\sum_{b^\beta}^{\mathrm{vact}^\beta}\frac{(i^\alpha a^\alpha|j^\beta b^\beta)}{D_{i^\alpha j^\beta}^{a^\alpha b^\beta}}(K^\alpha a^\alpha|j^\beta b^\beta)\right\} \qquad (123)
\end{aligned}
$$

$ij = \text{act} - \text{act}$

$$P^{(2)}_{i^\alpha j^\alpha} = -\sum_{k^\alpha}^{\text{act}^\alpha}\sum_{a^\alpha}^{\text{vact}^\alpha}\sum_{b^\alpha}^{\text{vact}^\alpha}\frac{[(i^\alpha a^\alpha|k^\alpha b^\alpha) - (i^\alpha b^\alpha|k^\alpha a^\alpha)]}{D^{a^\alpha b^\alpha}_{i^\alpha k^\alpha}}\frac{(j^\alpha a^\alpha|k^\alpha b^\alpha)}{D^{a^\alpha b^\alpha}_{j^\alpha k^\alpha}} - \sum_{k^\beta}^{\text{act}^\beta}\sum_{a^\alpha}^{\text{vact}^\alpha}\sum_{b^\beta}^{\text{vact}^\beta}\frac{[(i^\alpha a^\alpha|k^\beta b^\beta)]}{D^{a^\alpha b^\beta}_{i^\alpha k^\beta}}\frac{[(j^\alpha a^\alpha|k^\beta b^\beta)]}{D^{a^\alpha b^\beta}_{j^\alpha k^\beta}} \tag{124}$$

$ab = \text{vact} - \text{vact}$

$$P^{(2)}_{a^\alpha b^\alpha} = \sum_{i^\alpha}^{\text{act}^\alpha}\sum_{j^\alpha}^{\text{act}^\alpha}\sum_{c^\alpha}^{\text{vact}^\alpha}\frac{[(i^\alpha a^\alpha|j^\alpha c^\alpha) - (i^\alpha c^\alpha|j^\alpha a^\alpha)]}{D^{a^\alpha c^\alpha}_{i^\alpha j^\alpha}}\frac{(i^\alpha b^\alpha|j^\alpha c^\alpha)}{D^{b^\alpha c^\alpha}_{i^\alpha j^\alpha}} + \sum_{i^\alpha}^{\text{act}^\alpha}\sum_{j^\beta}^{\text{act}^\beta}\sum_{c^\beta}^{\text{vact}^\beta}\frac{(i^\alpha a^\alpha|j^\beta c^\beta)}{D^{a^\alpha c^\beta}_{i^\alpha j^\beta}}\frac{(i^\alpha b^\alpha|j^\beta c^\beta)}{D^{b^\alpha c^\beta}_{i^\alpha j^\beta}} \tag{125}$$

$Ca = \text{vf} - \text{vact} \quad P^{(2)}_{C^\alpha a^\alpha} = P^{(2)}_{a^\alpha C^\alpha}$

$$= \frac{1}{(\varepsilon^\alpha_a - \varepsilon^\alpha_C)}\left\{\sum_{i^\alpha}^{\text{act}^\alpha}\sum_{j^\alpha}^{\text{act}^\alpha}\sum_{b^\alpha}^{\text{vact}^\alpha}\frac{[(i^\alpha a^\alpha|j^\alpha b^\alpha) - (i^\alpha b^\alpha|j^\alpha a^\alpha)]}{D^{a^\alpha b^\alpha}_{i^\alpha j^\alpha}}(i^\alpha C^\alpha|j^\alpha b^\alpha) + \sum_{i^\alpha}^{\text{act}^\alpha}\sum_{j^\beta}^{\text{act}^\beta}\sum_{b^\beta}^{\text{vact}^\beta}\frac{(i^\alpha a^\alpha|j^\beta b^\beta)}{D^{a^\alpha b^\beta}_{i^\alpha j^\beta}}(i^\alpha C^\alpha|j^\beta b^\beta)\right\} \tag{126}$$

$ai = \text{vall} - \text{occ}$

$$P^{(2)}_{a^\alpha i^\alpha} = Z_{a^\alpha i^\alpha} \tag{127}$$

MP2 energy-weighted density correction terms (αα)

[*I*] terms:

$ij = \text{act} - \text{occ} \quad W^{(2)}_{i^\alpha j^\alpha}[I]$

$$= -\sum_{k^\alpha}^{\text{act}^\alpha}\sum_{a^\alpha b^\alpha}^{\text{vall}^\alpha}\frac{(i^\alpha a^\alpha|k^\alpha b^\alpha) - (i^\alpha b^\alpha|k^\alpha a^\alpha)}{D^{a^\alpha b^\alpha}_{i^\alpha k^\alpha}}(j^\alpha a^\alpha|k^\alpha b^\alpha) - \sum_{k^\beta}^{\text{act}^\beta}\sum_{a^\alpha}^{\text{vall}^\alpha}\sum_{b^\alpha}^{\text{vall}^\beta}\frac{(i^\alpha a^\alpha|k^\beta b^\beta)}{D^{a^\alpha b^\beta}_{i^\alpha k^\beta}}(j^\alpha a^\alpha|k^\beta b^\beta) \tag{128}$$

$ab = \text{vact} - \text{vall}$

$$W^{(2)}_{a^\alpha b^\alpha}[I] = -\sum_{i^\alpha j^\alpha}^{\text{act}^\alpha}\sum_{c^\alpha}^{\text{vact}^\alpha}\frac{(i^\alpha a^\alpha|j^\alpha c^\alpha) - (i^\alpha c^\alpha|j^\alpha a^\alpha)}{D^{a^\alpha c^\alpha}_{i^\alpha j^\alpha}}(i^\alpha b^\alpha|j^\alpha c^\alpha) - \sum_{i^\alpha}^{\text{act}^\alpha}\sum_{j^\beta}^{\text{act}^\beta}\sum_{c^\beta}^{\text{vact}^\beta}\frac{(i^\alpha a^\alpha|j^\beta c^\beta)}{D^{a^\alpha c^\beta}_{i^\alpha j^\beta}}(i^\alpha b^\alpha|j^\beta c^\beta) \tag{129}$$

$ai = \text{vact} - \text{occ}$

$$W^{(2)}_{a^\alpha i^\alpha}[I] = -2\sum_{j^\alpha k^\alpha}^{\text{act}^\alpha}\sum_{b^\alpha}^{\text{vact}^\alpha}\frac{(j^\alpha a^\alpha|k^\alpha b^\alpha) - (j^\alpha b^\alpha|k^\alpha a^\alpha)}{D^{a^\alpha b^\alpha}_{j^\alpha k^\alpha}}(i^\alpha j^\alpha|b^\alpha k^\alpha) - 2\sum_{j^\alpha}^{\text{act}^\alpha}\sum_{k^\beta}^{\text{act}^\beta}\sum_{b^\beta}^{\text{vact}^\beta}\frac{(j^\alpha a^\alpha|k^\beta b^\beta)}{D^{a^\alpha b^\beta}_{j^\alpha k^\beta}}(i^\alpha j^\alpha|b^\beta k^\beta) \tag{130}$$

[*II*] terms:

$$ij = \text{act} - \text{occ} \quad W^{(2)}_{i^\alpha j^\alpha}[II] = -\frac{1}{2}P^{(2)}_{i^\alpha j^\alpha}\left(\varepsilon^\alpha_i + \varepsilon^\alpha_j\right) \tag{131}$$

$$ab = \text{vact} - \text{vall} \quad W^{(2)}_{a^\alpha b^\alpha}[II] = -\frac{1}{2}P^{(2)}_{a^\alpha b^\alpha}\left(\varepsilon^\alpha_a + \varepsilon^\alpha_b\right) \tag{132}$$

$$ai = \text{vall} - \text{occ} \quad W^{(2)}_{a^\alpha i^\alpha}[II] = -P^{(2)}_{a^\alpha i^\alpha}\varepsilon^\alpha_i \tag{133}$$

[*III*] terms:

$ij = \text{occ} - \text{occ}$

$$W^{(2)}_{i^\alpha j^\alpha}[III] = -\sum_{p^\alpha q^\alpha}^{\text{all}^\alpha}P^{(2)}_{p^\alpha q^\alpha}[(p^\alpha q^\alpha|i^\alpha j^\alpha) - (p^\alpha i^\alpha|q^\alpha j^\alpha)] - \sum_{p^\beta q^\beta}^{\text{all}^\beta}P^{(2)}_{p^\beta q^\beta}(p^\beta q^\beta|i^\alpha j^\alpha) \tag{134}$$

4.6 Two-particle gradient summary

The two-electron density can be expressed as a sum of the nonseparable two-particle density and the separable two-particle density:

$$\Gamma^{(2)}_{\mu\nu\lambda\sigma} = \Gamma^{\text{NS}}_{\mu\nu\lambda\sigma} + \Gamma^{\text{S}}_{\mu\nu\lambda\sigma}. \tag{135}$$

Nonseparable density:

$$\Gamma^{\text{NS}}_{\mu\nu\lambda\sigma} = \sum_{i^\alpha j^\alpha}^{\text{act}^\alpha}\sum_{a^\alpha b^\alpha}^{\text{vact}^\alpha}\frac{[(i^\alpha a^\alpha|j^\alpha b^\alpha) - (i^\alpha b^\alpha|j^\alpha a^\alpha)]}{\varepsilon^\alpha_i + \varepsilon^\alpha_j - \varepsilon^\alpha_a - \varepsilon^\alpha_b}C^\alpha_{\mu i}C^\alpha_{\nu a}C^\alpha_{\lambda j}C^\alpha_{\sigma b} + 2\sum_{i^\alpha}^{\text{act}^\alpha}\sum_{j^\beta}^{\text{act}^\beta}\sum_{a^\alpha}^{\text{vact}^\alpha}\sum_{b^\beta}^{\text{vact}^\beta}\frac{(i^\alpha a^\alpha|j^\beta b^\beta)}{\varepsilon^\alpha_i + \varepsilon^\beta_j - \varepsilon^\alpha_a - \varepsilon^\beta_b}C^\alpha_{\mu i}C^\alpha_{\nu a}C^\beta_{\lambda j}C^\beta_{\sigma b} + \sum_{i^\beta j^\beta}^{\text{act}^\beta}\sum_{a^\beta b^\beta}^{\text{vact}^\beta}\frac{[(i^\beta a^\beta|j^\beta b^\beta) - (i^\beta b^\beta|j^\beta a^\beta)]}{\varepsilon^\beta_i + \varepsilon^\beta_j - \varepsilon^\beta_a - \varepsilon^\beta_b}C^\beta_{\mu i}C^\beta_{\nu a}C^\beta_{\lambda j}C^\beta_{\sigma b} \tag{136}$$

Separable density

$$\Gamma^{\text{S}}_{\mu\nu\lambda\sigma} = P^{(2)}_{\mu\nu}(\alpha\alpha)P^{\alpha\text{SCF}}_{\lambda\sigma} - P^{(2)}_{\mu\lambda}(\alpha\alpha)P^{\alpha\text{SCF}}_{\nu\sigma} + P^{(2)}_{\mu\nu}(\alpha\alpha)P^{\beta\text{SCF}}_{\lambda\sigma} + P^{(2)}_{\mu\nu}(\beta\beta)P^{\beta\text{SCF}}_{\lambda\sigma} - P^{(2)}_{\mu\lambda}(\beta\beta)P^{\beta\text{SCF}}_{\nu\sigma} + P^{(2)}_{\mu\nu}(\beta\beta)P^{\alpha\text{SCF}}_{\lambda\sigma}\ . \tag{137}$$

5 Derivation of the closed-shell MP2 gradient equation

If only the closed-shell gradient equations are desired, the gradient expression may be derived directly from the closed-shell MP2 equation [14, 15, 20]. However, when the unrestricted gradient expression has already been derived, the simplest pedagogical derivation for the closed-shell expression comes from simplifying the unrestricted expression, as shown in this section. Several formulations have been presented to improve the computational efficiency of the closed-shell frozen-orbital MP2 gradient algorithm [14, 20], and we note that the derived expression presented here is not the most efficient to date; however, the approach presented is more than adequate for the purpose of demonstration of dependent-pair and gradient theory techniques.

For the closed-shell system, all α and β spatial orbitals are equal and all α and β orbital energies are equal. Thus,

$$|p^\alpha\rangle = |p^\beta\rangle \tag{138}$$

and

$$\varepsilon_p^\alpha = \varepsilon_p^\beta \ . \tag{139}$$

5.1 One-particle density matrices

The one-particle density matrices may be derived from their unrestricted counterparts. The closed-shell density correction matrix $P_{ij}^{\mathrm{CS}(2)}$ is the sum of the $\alpha\alpha$ and $\beta\beta$ unrestricted density matrices (from Eq. 85). So, the form of the density matrices in the closed-shell basis can be determined by setting $\alpha = \beta$ in the unrestricted matrix equations. Thus,

$$P_{pq}^{\mathrm{CS}(2)} = P_{p^\alpha q^\alpha}^{(2)} + P_{p^\beta q^\beta}^{(2)} = 2P_{p^\alpha q^\alpha}^{(2)} \tag{140}$$

and

$$W_{pq}^{\mathrm{CS}(2)} = W_{p^\alpha q^\alpha}^{(2)} + W_{p^\beta q^\beta}^{(2)} = 2W_{p^\alpha q^\alpha}^{(2)} \ . \tag{141}$$

The active–active density matrix can be evaluated using $\alpha = \beta$:

$$\begin{aligned} P_{ij}^{\mathrm{CS}(2)} &= 2P_{i^\alpha j^\alpha}^{(2)} = \\ &-2\sum_{k^\alpha}^{\mathrm{act}^\alpha}\sum_{a^\alpha}^{\mathrm{vact}^\alpha}\sum_{b^\alpha}^{\mathrm{vact}^\alpha} \frac{[(i^\alpha a^\alpha|k^\alpha b^\alpha) - (i^\alpha b^\alpha|k^\alpha a^\alpha)]}{D_{i^\alpha k^\alpha}^{a^\alpha b^\alpha}} \frac{(j^\alpha a^\alpha|k^\alpha b^\alpha)}{D_{j^\alpha k^\alpha}^{a^\alpha b^\alpha}} \\ &-2\sum_{k^\alpha}^{\mathrm{act}^\alpha}\sum_{a^\alpha}^{\mathrm{vact}^\alpha}\sum_{b^\alpha}^{\mathrm{vact}^\alpha} \frac{[(i^\alpha a^\alpha|k^\alpha b^\alpha)]}{D_{i^\alpha k^\alpha}^{a^\alpha b^\alpha}} \frac{[(j^\alpha a^\alpha|k^\alpha b^\alpha)]}{D_{j^\alpha k^\alpha}^{a^\alpha b^\alpha}} \end{aligned} \tag{142}$$

The second term on the right-hand side of Eq. (142) may be combined with the first part of the first term. Since a closed-shell system contains only one type of spatial orbital and orbital energy, the α designation on MOs and orbital energies will be dropped. This notation should not be confused with the spin-orbital notation (which looks the same). With these simplifications, the matrix may now be written as

$$P_{ij}^{\mathrm{CS}(2)} = -2\sum_{k}^{\mathrm{act}}\sum_{a}^{\mathrm{vact}}\sum_{b}^{\mathrm{vact}} \frac{[2(ia|kb) - (ib|ka)]}{D_{ik}^{ab}} \frac{(ja|kb)}{D_{jk}^{ab}} \ . \tag{143}$$

A closed-shell amplitude may be defined as

$$T_{ik}^{ab} = \frac{[2(ia|kb) - (ib|ka)]}{D_{ik}^{ab}} \ . \tag{144}$$

Thus, the active–active density matrix contribution may be written as

$$P_{ij}^{\mathrm{CS}(2)} = -2\sum_{k}^{\mathrm{act}}\sum_{a}^{\mathrm{vact}}\sum_{b}^{\mathrm{vact}} T_{ik}^{ab} \frac{(ja|kb)}{D_{jk}^{ab}} \ . \tag{145}$$

Next, the simplification of the A terms must be considered. With $\alpha = \beta$, Eqs. (91, 92, 93, 94) become

$$A_{p^\alpha q^\alpha r^\alpha s^\alpha} = 2(pq|rs) - (pr|qs) - (ps|qr) \ , \tag{146}$$

$$A_{p^\alpha q^\alpha r^\beta s^\beta} = 2(pq|rs) \ , \tag{147}$$

$$A_{p^\beta q^\beta r^\alpha s^\alpha} = 2(pq|rs) \ , \tag{148}$$

$$A_{p^\beta q^\beta r^\beta s^\beta} = 2(pq|rs) - (pr|qs) - (ps|qr) \ . \tag{149}$$

Now, the closed-shell energy-weighted matrix contribution, $W_{ij}^{\mathrm{CS}(2)}[III]$, may be written as

$$W_{ij}^{\mathrm{cs}(2)}[III] = 2W_{i^\alpha j^\alpha}^{(2)}[III] \tag{150}$$

$$\begin{aligned} &= -2\sum_{p^\alpha q^\alpha}^{\mathrm{all}^\alpha} P_{p^\alpha q^\alpha}^{(2)}[(p^\alpha q^\alpha|i^\alpha j^\alpha) - (p^\alpha i^\alpha|q^\alpha j^\alpha)] \\ &\quad -2\sum_{p^\alpha q^\alpha}^{\mathrm{all}^\alpha} P_{p^\alpha q^\alpha}^{(2)}(p^\alpha q^\alpha|i^\alpha j^\alpha) \end{aligned} \tag{151}$$

$$= -2\sum_{p^\alpha q^\alpha}^{\mathrm{all}^\alpha} P_{p^\alpha q^\alpha}^{(2)}[2(pq|ij) - (pi|qj)] \tag{152}$$

$$= -\sum_{pq}^{\mathrm{all}} P_{pq}^{\mathrm{CS}(2)}[2(pq|ij) - (pi|qj)] \ . \tag{153}$$

These techniques may be used to simplify the other closed-shell one-particle density matrix and one-particle energy-weighted density matrix blocks, which are summarized in Sect. 5.5.

5.2 Lagrangian

The closed-shell Lagrangian is

$$L_{ai}^{\mathrm{CS}(2)} = 2L_{a^\alpha i^\alpha}^{(2)} \tag{154}$$

$$\begin{aligned} &= 2\sum_{j^\alpha k^\alpha}^{\mathrm{occ}^\alpha} P_{j^\alpha k^\alpha}^{(2)}[2(ai|jk) - (aj|ik) - (ak|ij)] + 2\sum_{j^\alpha k^\alpha}^{\mathrm{occ}^\alpha} P_{j^\alpha k^\alpha}^{(2)}[2(ai|jk)] \\ &\quad +2\sum_{b^\alpha c^\alpha}^{\mathrm{vall}^\alpha} P_{b^\alpha c^\alpha}^{(2)}[2(ai|bc) - (ab|ic) - (ac|ib)] \\ &\quad +2\sum_{b^\alpha c^\alpha}^{\mathrm{vall}^\alpha} P_{b^\alpha c^\alpha}^{(2)}[2(ai|bc)] - 4N_a\sum_{jk}^{\mathrm{act}}\sum_{b}^{\mathrm{vact}} \frac{[(ja|kb) - (jb|ka)]}{D_{jk}^{ab}}(ij|bk) \\ &\quad -4N_a\sum_{jk}^{\mathrm{act}}\sum_{b}^{\mathrm{vact}} \frac{(ja|kb)}{D_{jk}^{ab}}(ij|bk) \end{aligned}$$

$$+4N_i\sum_{j}^{\text{act}}\sum_{bc}^{\text{vact}}\frac{[(ib|jc)-(ic|jb)]}{D_{ij}^{bc}}(ab|jc)$$

$$+4N_i\sum_{j}^{\text{act}}\sum_{bc}^{\text{vact}}\frac{(ib|jc)}{D_{ij}^{bc}}(ab|jc) \tag{155}$$

$$=2\sum_{j^\alpha k^\alpha}^{\text{occ}^\alpha}P_{j^\alpha k^\alpha}^{(2)}[4(ai|jk)-(aj|ik)-(ak|ij)]$$

$$+2\sum_{b^\alpha c^\alpha}^{\text{vall}^\alpha}P_{b^\alpha c^\alpha}^{(2)}[4(ai|bc)-(ab|ic)-(ac|ib)]$$

$$-4N_a\sum_{jk}^{\text{act}}\sum_{b}^{\text{vact}}\frac{[2(ja|kb)-(jb|ka)]}{D_{jk}^{ab}}(ij|bk)$$

$$+4N_i\sum_{j}^{\text{act}}\sum_{bc}^{\text{vact}}\frac{[2(ib|jc)-(ic|jb)]}{D_{ij}^{bc}}(ab|jc) \tag{156}$$

$$=\sum_{jk}^{\text{occ}}P_{jk}^{\text{CS}(2)}[4(ai|jk)-(aj|ik)-(ak|ij)]$$

$$+\sum_{bc}^{\text{vall}}P_{bc}^{\text{CS}(2)}[4(ai|bc)-(ab|ic)-(ac|ib)]$$

$$-4N_a\sum_{jk}^{\text{act}}\sum_{b}^{\text{vact}}\frac{[2(ja|kb)-(jb|ka)]}{D_{jk}^{ab}}(ij|bk)$$

$$+4N_i\sum_{j}^{\text{act}}\sum_{bc}^{\text{vact}}\frac{[2(ib|jc)-(ic|jb)]}{D_{ij}^{bc}}(ab|jc)\ . \tag{157}$$

Now, if the closed-shell A term is defined as

$$A_{pqrs}^{\text{CS}}=4(pq|rs)-(pr|qs)-(ps|qr), \tag{158}$$

then the closed-shell Lagrangian can be written more simply as

$$L_{ai}^{\text{CS}(2)}=\sum_{jk}^{\text{occ}}P_{jk}^{CS(2)}A_{aijk}^{CS}+\sum_{bc}^{\text{vall}}P_{bc}^{CS(2)}A_{aibc}^{CS}$$

$$-4N_a\sum_{jk}^{\text{act}}\sum_{b}^{\text{vact}}T_{jk}^{ab}(ij|bk)+4N_i\sum_{j}^{\text{act}}\sum_{bc}^{\text{vact}}T_{ij}^{bc}(ab|jc)\ . \tag{159}$$

5.3 CPHF equations

For closed-shell systems, Eq. (101) becomes

$$-L_{a^\alpha i^\alpha}=\sum_{b^\alpha}^{\text{vall}^\alpha}\sum_{j^\alpha}^{\text{occ}^\alpha}\{2[(ai|bj)-(ab|ij)-(aj|bi)]$$

$$+\delta_{ab}\delta_{ij}(\varepsilon_b^\alpha-\varepsilon_j^\alpha)\}P_{b^\alpha j^\alpha}^{(2)}+\sum_{\text{b}^\alpha}^{\text{vall}^\alpha}\sum_{j^\alpha}^{\text{occ}^\alpha}[2(ai|bj)]P_{b^\alpha j^\alpha}^{(2)} \tag{160}$$

$$=\sum_{b^\alpha}^{\text{vall}^\alpha}\sum_{j^\alpha}^{\text{occ}^\alpha}\left\{4[(ai|bj)-(ab|ij)-(aj|bi)]+\delta_{ab}\delta_{ij}\left(\varepsilon_b-\varepsilon_j\right)\right\}P_{b^\alpha j^\alpha}^{(2)}. \tag{161}$$

Since the off-diagonal closed-shell density is

$$P_{bj}^{\text{CS}(2)}=2P_{b^\alpha j^\alpha}^{(2)}\ , \tag{162}$$

substitution of the closed-shell A term (Eq. 158), density matrix (Eq. 162), and Lagrangian (Eq. 157) in Eq. (161) yields

$$-L_{ai}^{\text{CS}}=\sum_{b}^{\text{vall}}\sum_{j}^{\text{occ}}\left[A_{aibj}^{\text{CS}}+\delta_{ab}\delta_{ij}\left(\varepsilon_b-\varepsilon_j\right)\right]P_{bj}^{\text{CS}(2)}\ . \tag{163}$$

Equation (163) represents the linear equations that must be solved to find the virtual-occupied block of the density. The contribution to the gradient equation is

$$\sum_{ai}B_{ai}^{x(\text{CS})}P_{ai}^{\text{CS}(2)}\ . \tag{164}$$

The closed-shell equations for $B_{pq}^{x(\text{CS})}$ may be written

$$B_{p^\alpha q^\alpha}^{x(\text{CS})}=F_{p^\alpha q^\alpha}^{(x)}-S_{p^\alpha q^\alpha}^{(x)}\varepsilon_q^\alpha-\sum_{k^\alpha l^\alpha}^{\text{occ}^\alpha}S_{k^\alpha l^\alpha}^{(x)}[(p^\alpha q^\alpha|k^\alpha l^\alpha)$$

$$-(p^\alpha k^\alpha|q^\alpha l^\alpha)]-\sum_{k^\alpha l^\alpha}^{\text{occ}^\alpha}S_{k^\alpha l^\alpha}^{(x)}(p^\alpha q^\alpha|k^\alpha l^\alpha)\ , \tag{165}$$

$$B_{pq}^{x(\text{CS})}=F_{pq}^{(x)}-S_{pq}^{(x)}\varepsilon_q$$

$$-\sum_{kl}^{\text{occ}}S_{kl}^{(x)}[2(pq|kl)-(pk|ql)]\ , \tag{166}$$

where

$$F_{p^\alpha q^\alpha}^{(x)}=H_{p^\alpha q^\alpha}^{(x)}+\sum_{k^\alpha}^{\text{occ}^\alpha}[(p^\alpha q^\alpha|k^\alpha k^\alpha)^{(x)}-(p^\alpha k^\alpha|q^\alpha k^\alpha)^{(x)}]$$

$$+\sum_{k^\alpha}^{\text{occ}^\alpha}(p^\alpha q^\alpha|k^\alpha k^\alpha)^{(x)}\ , \tag{167}$$

$$F_{pq}^{(x)}=H_{pq}^{(x)}+\sum_{k}^{\text{occ}}\left[2(pq|kk)^{(x)}-(pk|qk)^{(x)}\right]\ . \tag{168}$$

5.4 Two-particle density matrices

Next, the closed-shell versions of the nonseparable two-particle density and the separable two-particle density must be derived from the unrestricted versions. If $\alpha=\beta$ is substituted in the nonseparable density,

$$\Gamma^{\mathrm{NS}}_{\mu\nu\lambda\sigma} = \sum_{ij}^{\mathrm{act}}\sum_{ab}^{\mathrm{vact}}\frac{[(ia|jb)-(ib|ja)]}{\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b}C_{\mu i}C_{\nu a}C_{\lambda j}C_{\sigma b} + 2\sum_{ij}^{\mathrm{act}}\sum_{ab}^{\mathrm{vact}}\frac{(ia|jb)}{\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b}C_{\mu i}C_{\nu a}C_{\lambda j}C_{\sigma b} + \sum_{ij}^{\mathrm{act}}\sum_{ab}^{\mathrm{vact}}\frac{[(ia|jb)-(ib|ja)]}{\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b}C_{\mu i}C_{\nu a}C_{\lambda j}C_{\sigma b} \quad (169)$$

Since the first and third terms are the same and the second term is equal to the first part of the first term, Eq. (169) can be simplified to

$$\Gamma^{\mathrm{NS}}_{\mu\nu\lambda\sigma} = 2\sum_{ij}^{\mathrm{act}}\sum_{ab}^{\mathrm{vact}}\frac{[2(ia|jb)-(ib|ja)]}{\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b}C_{\mu i}C_{\nu a}C_{\lambda j}C_{\sigma b}\ . \quad (170)$$

Substitution of the form of the closed-shell amplitude (Eq. 144) yields

$$\Gamma^{\mathrm{NS}}_{\mu\nu\lambda\sigma} = 2\sum_{ij}^{\mathrm{act}}\sum_{ab}^{\mathrm{vact}}T^{ab}_{ij}C_{\mu i}C_{\nu a}C_{\lambda j}C_{\sigma b}\ , \quad (171)$$

which corresponds to a back-transformation of the closed-shell MP2 amplitudes.

If $\alpha = \beta$ is substituted in the separable density, this term becomes

$$\Gamma^{\mathrm{S}}_{\mu\nu\lambda\sigma} = P^{(2)}_{\mu\nu}(\alpha\alpha)P^{\alpha\mathrm{SCF}}_{\lambda\sigma} - P^{(2)}_{\mu\lambda}(\alpha\alpha)P^{\alpha\mathrm{SCF}}_{\nu\sigma} + P^{(2)}_{\mu\nu}(\alpha\alpha)P^{\alpha\mathrm{SCF}}_{\lambda\sigma} + P^{(2)}_{\mu\nu}(\alpha\alpha)P^{\alpha\mathrm{SCF}}_{\lambda\sigma} - P^{(2)}_{\mu\lambda}(\alpha\alpha)P^{\alpha\mathrm{SCF}}_{\nu\sigma} + P^{(2)}_{\mu\nu}(\alpha\alpha)P^{\alpha\mathrm{SCF}}_{\lambda\sigma}, \quad (172)$$

$$\Gamma^{\mathrm{S}}_{\mu\nu\lambda\sigma} = 4P^{(2)}_{\mu\nu}(\alpha\alpha)P^{\alpha\mathrm{SCF}}_{\lambda\sigma} - 2P^{(2)}_{\mu\lambda}(\alpha\alpha)P^{\alpha\mathrm{SCF}}_{\nu\sigma}\ . \quad (173)$$

Now, since $P^{\mathrm{CS}(2)}_{\mu\nu} = 2P^{(2)}_{\mu\nu}(\alpha\alpha)$ and $P^{\mathrm{SCF}}_{\lambda\sigma} = 2P^{\alpha\mathrm{SCF}}_{\lambda\sigma}$, Eq. (173) becomes

$$\Gamma^{\mathrm{S}}_{\mu\nu\lambda\sigma} = P^{\mathrm{CS}(2)}_{\mu\nu}P^{\mathrm{SCF}}_{\lambda\sigma} - \frac{1}{2}P^{\mathrm{CS}(2)}_{\mu\lambda}P^{\mathrm{SCF}}_{\nu\sigma}\ . \quad (174)$$

5.5 One-particle gradient summary

The one-particle density matrices for the closed-shell basis are summarized here.

MP2 density correction terms

$KJ = \mathrm{core} - \mathrm{core}$

$$P^{\mathrm{CS}(2)}_{KJ} = 0 \quad (175)$$

$Ki = \mathrm{core} - \mathrm{act}$

$$P^{\mathrm{CS}(2)}_{Ki} = P^{\mathrm{CS}(2)}_{iK} = \frac{2}{(\varepsilon_i-\varepsilon_K)}\sum_{j}^{\mathrm{act}}\sum_{ab}^{\mathrm{vact}}T^{ab}_{ij}(Ka|jb) \quad (176)$$

$ij = \mathrm{act} - \mathrm{act}$

$$P^{\mathrm{CS}(2)}_{ij} = -2\sum_{k}^{\mathrm{act}}\sum_{ab}^{\mathrm{vact}}T^{ab}_{ik}(ja|kb)\Big/D^{ab}_{jk} \quad (177)$$

$ab = \mathrm{vact} - \mathrm{vact}$

$$P^{\mathrm{CS}(2)}_{ab} = 2\sum_{ij}^{\mathrm{act}}\sum_{c}^{\mathrm{vact}}T^{ac}_{ij}(ib|jc)\Big/D^{bc}_{ij} \quad (178)$$

$Ca = \mathrm{vf} - \mathrm{vact}$

$$P^{\mathrm{CS}(2)}_{Ca} = P^{\mathrm{CS}(2)}_{aC} = \frac{2}{(\varepsilon_a-\varepsilon_C)}\sum_{ij}^{\mathrm{act}}\sum_{b}^{\mathrm{vact}}T^{ab}_{ij}(iC|jb) \quad (179)$$

$ai = \mathrm{vall} - \mathrm{occ}$

$$P^{\mathrm{CS}(2)}_{ai} = Z^{\mathrm{CS}}_{ai} \quad (180)$$

MP2 energy-weighted density correction terms

[*I*] terms:

$$ij = \mathrm{act} - \mathrm{occ} \quad W^{\mathrm{CS}(2)}_{ij}[I] = -2\sum_{k}^{\mathrm{act}}\sum_{ab}^{\mathrm{vact}}T^{ab}_{ik}(ja|kb) \quad (181)$$

$$ab = \mathrm{vact} - \mathrm{vall} \quad W^{\mathrm{CS}(2)}_{ab}[I] = -2\sum_{ij}^{\mathrm{act}}\sum_{c}^{\mathrm{vact}}T^{ac}_{ij}(ib|jc) \quad (182)$$

$$ai = \mathrm{vact} - \mathrm{occ} \quad W^{\mathrm{CS}(2)}_{ai}[I] = -4\sum_{jk}^{\mathrm{act}}\sum_{b}^{\mathrm{vact}}T^{ab}_{jk}(ij|bk) \quad (183)$$

[*II*] terms:

$$ij = \mathrm{act} - \mathrm{occ} \quad W^{\mathrm{CS}(2)}_{ij}[II] = -\frac{1}{2}P^{\mathrm{CS}(2)}_{ij}\left(\varepsilon_i+\varepsilon_j\right) \quad (184)$$

$$ab = \mathrm{vact} - \mathrm{vall} \quad W^{\mathrm{CS}(2)}_{ab}[II] = -\frac{1}{2}P^{\mathrm{CS}(2)}_{ab}(\varepsilon_a+\varepsilon_b) \quad (185)$$

$$ai = \mathrm{vall} - \mathrm{occ} \quad W^{\mathrm{CS}(2)}_{ai}[II] = -P^{\mathrm{CS}(2)}_{ai}\varepsilon_i \quad (186)$$

[*III*] terms:

$$ij = \mathrm{occ} - \mathrm{occ} \quad W^{\mathrm{CS}(2)}_{ij}[III] = -\sum_{pq}^{\mathrm{all}}P^{\mathrm{CS}(2)}_{pq}[2(pq|ij)-(pi|qj)] \quad (187)$$

5.6 Two-particle gradient summary

The two-electron density can be expressed as a sum of the nonseparable two-particle density and the separable two-particle density:

$$\Gamma^{(2)}_{\mu\nu\lambda\sigma} = \Gamma^{\mathrm{NS}}_{\mu\nu\lambda\sigma} + \Gamma^{\mathrm{S}}_{\mu\nu\lambda\sigma}. \quad (188)$$

Nonseparable density:

$$\Gamma^{\mathrm{NS}}_{\mu\nu\lambda\sigma} = 2\sum_{ij}^{\mathrm{act}}\sum_{ab}^{\mathrm{vact}} T_{ij}^{ab} C_{\mu i} C_{\nu a} C_{\lambda j} C_{\sigma b}. \tag{189}$$

Separable density:

$$\Gamma^{\mathrm{S}}_{\mu\nu\lambda\sigma} = P^{\mathrm{CS}(2)}_{\mu\nu} P^{\mathrm{SCF}}_{\lambda\sigma} - \frac{1}{2} P^{\mathrm{CS}(2)}_{\mu\lambda} P^{\mathrm{SCF}}_{\nu\sigma} \quad . \tag{190}$$

6 Implementation considerations

A brief summary of the significant computational steps is presented. Some of the important implementation aspects are considered in more detail, including the back-transformation, symmetrization, and contraction of the one- and two-particle density matrices.

6.1 Computational procedure

An outline of the computational procedure used to calculate MP2 gradients is presented here.

1. Follow the SCF procedure to obtain orbital energies, coefficients, and the $\mathbf{P}^{\mathrm{SCF}}$, $\mathbf{W}^{\mathrm{SCF}}$, and $\mathbf{\Gamma}^{\mathrm{SCF}}$ matrices.
2. Transform ERIs from the AO to the MO basis (see Sect. 7.1).
3. Determine contributions to the $\mathbf{P}^{(2)}$, $\mathbf{W}^{(2)}$, and $\mathbf{L}$ matrices according to the relevant equations (Sects. 4.2, 4.5, 5.2, 5.5).
4. Calculate the MP2 energy.
5. Form the last two terms in the Lagrangian in the AO basis (Sect. 7.3).
6. Iteratively solve the CPHF equations in the AO basis to determine P_{ai} (Sects. 4.3, 5.3).
7. Calculate the contribution to $\mathbf{W}$ from the $\mathbf{W}$[II] terms (Sects. 4.5, 5.5).
8. Form $\mathbf{W}$[III] in the AO basis (Sect. 7.3) and transform to the MO basis.
9. Calculate the nonseparable contribution to $\mathbf{\Gamma}$. (Sects. 4.6 and 5.6)
10. Back-transform the completed $\mathbf{P}^{(2)}$ and $\mathbf{W}^{(2)}$ matrices to the AO basis and add to the SCF density matrices to yield $\mathbf{P}^{\mathrm{MP2}}$ and $\mathbf{W}^{\mathrm{MP2}}$ (Sects. 6.2, 6.3).
11. Contract the $\mathbf{P}^{\mathrm{MP2}}$ and $\mathbf{W}^{\mathrm{MP2}}$ matrices with appropriate one-electron Hamiltonian and overlap derivative integrals.
12. Complete $\mathbf{\Gamma}$ and contract with appropriate $(\mu\nu|\lambda\sigma)^x$ integrals.

6.2 Back-transformation and symmetrization of density matrices

The total one-particle energy gradient is obtained by first back-transforming the complete MP2 density correction $P^{(2)}_{pq}$ and energy-weighted density correction $W^{(2)}_{pq}$ to the AO basis. Note that only the virtual–occupied contributions to $P^{(2)}_{pq}$ (Eq. 127 or Eq. 180) and $W^{(2)}_{pq}$ (Eqs. 130, 133 or Eqs. 183, 186) appear from this derivation. The corresponding occupied–virtual blocks are zero. Thus, symmetrization of $P^{(2)}_{pq}$ and $W^{(2)}_{pq}$ is customary prior to the back-transformation. $P^{(2)}_{pq}$ must be symmetrized before Eq. (134) or Eq. (187) can be applied.

For the closed-shell case, the back-transformation is done as follows:

$$P^{(2)}_{\mu\nu} = \sum_{pq}^{\mathrm{all}} C_{\mu p} C_{\nu q} P^{\mathrm{CS}(2)}_{pq} \quad , \tag{191}$$

$$W^{(2)}_{\mu\nu} = \sum_{pq}^{\mathrm{all}} C_{\mu p} C_{\nu q} W^{\mathrm{CS}(2)}_{pq} \quad . \tag{192}$$

For the unrestricted open-shell case, the back-transformation is

$$P^{(2)}_{\mu\nu}(\alpha\alpha) = \sum_{p^\alpha q^\alpha}^{\mathrm{all}^\alpha} C^{\alpha}_{\mu p} C^{\alpha}_{\nu q} P^{(2)}_{p^\alpha q^\alpha} \quad , \tag{193}$$

$$W^{(2)}_{\mu\nu}(\alpha\alpha) = \sum_{p^\alpha q^\alpha}^{\mathrm{all}^\alpha} C^{\alpha}_{\mu p} C^{\alpha}_{\nu q} W^{(2)}_{p^\alpha q^\alpha} \quad , \tag{194}$$

with corresponding equations for the $(\beta\beta)$ matrices.

The nonseparable and separable density matrix corrections are already in the AO basis (Eqs. 136, 137 or Eqs. 189, 190). They must be symmetrized according to the particular ERI permutational symmetries used in a given algorithm.

6.3 Contraction of MP2 density matrices

The second-order corrections must be added to the corresponding SCF densities. For the closed-shell case, these equations are

$$P^{\mathrm{MP2}}_{\mu\nu} = P^{\mathrm{SCF}}_{\mu\nu} + P^{\mathrm{CS}(2)}_{\mu\nu} \quad , \tag{195}$$

$$W^{\mathrm{MP2}}_{\mu\nu} = 2W^{\mathrm{SCF}}_{\mu\nu} + W^{\mathrm{CS}(2)}_{\mu\nu} \quad , \tag{196}$$

where

$$P^{\mathrm{SCF}}_{\mu\nu} = 2\sum_{k}^{\mathrm{occ}} C_{\mu k} C_{\nu k} \quad , \tag{197}$$

$$W^{\mathrm{SCF}}_{\mu\nu} = \sum_{k}^{\mathrm{occ}} C_{\mu k} C_{\nu k} \varepsilon_k \quad . \tag{198}$$

For the unrestricted open-shell case, these equations are

$$P^{\mathrm{MP2}}_{\mu\nu} = P^{\alpha\mathrm{SCF}}_{\mu\nu} + P^{\beta\mathrm{SCF}}_{\mu\nu} + P^{(2)}_{\mu\nu}(\alpha\alpha) + P^{(2)}_{\mu\nu}(\beta\beta) \quad , \tag{199}$$

$$W^{\mathrm{MP2}}_{\mu\nu} = W^{\alpha\mathrm{SCF}}_{\mu\nu} + W^{\beta\mathrm{SCF}}_{\mu\nu} + W^{(2)}_{\mu\nu}(\alpha\alpha) + W^{(2)}_{\mu\nu}(\beta\beta) \quad , \tag{200}$$

where

$$P^{\alpha\mathrm{SCF}}_{\mu\nu} = \sum_{k^\alpha}^{\mathrm{occ}^\alpha} C^\alpha_{\mu k} C^\alpha_{\nu k} \ , \tag{201}$$

$$W^{\alpha SCF}_{\mu\nu} = \sum_{k^\alpha}^{\mathrm{occ}^\alpha} C^\alpha_{\mu k} C^\alpha_{\nu k} \varepsilon^\alpha_k \ , \tag{202}$$

with corresponding equations for the β SCF matrices. The final MP2 densities $P^{\mathrm{MP2}}_{\mu\nu}$ and $W^{\mathrm{MP2}}_{\mu\nu}$ are contracted with the one-electron Hamiltonian derivatives $H^{(x)}_{\mu\nu}$ and overlap derivatives $S^{(x)}_{\mu\nu}$, respectively.

The total frozen-core two-particle density matrix is evaluated by adding the two-particle density correction to the SCF two-particle density,

$$\Gamma^{\mathrm{MP2}}_{\mu\nu\lambda\sigma} = \Gamma^{(2)}_{\mu\nu\lambda\sigma} + \Gamma^{\mathrm{SCF}}_{\mu\nu\lambda\sigma} \ , \tag{203}$$

where

$$\Gamma^{\mathrm{SCF}}_{\mu\nu\lambda\sigma} = \frac{1}{2} P^{\mathrm{SCF}}_{\mu\nu} P^{\mathrm{SCF}}_{\lambda\sigma} - \frac{1}{4} P^{\mathrm{SCF}}_{\mu\lambda} P^{\mathrm{SCF}}_{\nu\sigma} \tag{204}$$

for the closed-shell case, and

$$\begin{aligned}\Gamma^{\mathrm{SCF}}_{\mu\nu\lambda\sigma} = \frac{1}{2}\Big(& P^{\alpha\mathrm{SCF}}_{\mu\nu} P^{\alpha\mathrm{SCF}}_{\lambda\sigma} - P^{\alpha\mathrm{SCF}}_{\mu\lambda} P^{\alpha\mathrm{SCF}}_{\nu\sigma} + P^{\alpha\mathrm{SCF}}_{\mu\nu} P^{\beta\mathrm{SCF}}_{\lambda\sigma} \\ & + P^{\beta\mathrm{SCF}}_{\mu\nu} P^{\beta\mathrm{SCF}}_{\lambda\sigma} - P^{\beta\mathrm{SCF}}_{\mu\lambda} P^{\beta\mathrm{SCF}}_{\nu\sigma} + P^{\beta\mathrm{SCF}}_{\mu\nu} P^{\alpha\mathrm{SCF}}_{\lambda\sigma} \Big)\end{aligned} \tag{205}$$

for the unrestricted case. $\Gamma^{\mathrm{MP2}}_{\mu\nu\lambda\sigma}$ is then contracted with the two-electron AO derivatives.

This finishes all the terms necessary for the evaluation of the closed-shell frozen-orbital MP2 gradient (Eq. 24).

7 Reduction in computational effort

Having identified the summation ranges, the computational effort required for the frozen-orbital MP2 gradient computation compared to that required in the full MP2 gradient computation may be examined.

7.1 Time savings in the two-electron transformation

Inspection of the last two terms in the closed-shell MP2 Lagrangian (Eq. 159), the diagonal blocks of the MP2 density correction (Eqs. 176, 177, 178, 179), and all the MP2 energy-weighted density correction [*I*] terms (Eqs. 181, 182, 183) reveals that their formation requires a subset of the transformed integrals required for the corresponding full MP2 terms,

$$\begin{aligned}&(\mu\nu|\lambda\sigma) \rightarrow (jp|qr)\ \mathrm{full\,MP2}: j = \mathrm{occ}, p = \mathrm{vall}, q = \mathrm{all}, r = \mathrm{all}\\ &\mathrm{frozen-core\ MP2}: \qquad j = \mathrm{act}, p = \mathrm{vact}, q = \mathrm{all}, r = \mathrm{all}\,.\end{aligned}$$

The transformations may be carried out by first performing a one-index transformation producing integrals of the type $(j\nu|\lambda\sigma)$, with the remaining indices transformed stepwise to produce the full set [21].

If $\lambda\sigma$ is treated as a combined index, the memory required to hold all $(j\nu|\lambda\sigma)$ integrals is $N^2(N+1)n/2$, where N is the number of basis functions, and n is the number of active orbitals (for full MP2, n is all occupied orbitals). The reduction in memory requirements on going from full MP2 to frozen-core MP2, then, is $N^2(N+1)C/2$, where C is the number of frozen cores. Usually, even with such a reduction, an inadequate amount of memory is available and the transformation is carried out in batches. So, more important than the memory reduction is the time saving that accrues as a consequence of the reduction in the number of batches of integrals that one needs to transform for frozen-core MP2 relative to full MP2.

The available memory determines the number of active orbitals j transformed in each batch. The minimum memory requirement is then $N^2(N+1)/2$ for one orbital to be transformed per batch (this is the same for the full and frozen-core cases). This requires n batches for the full transformation. Clearly, then, by reducing n from all occupied orbitals in the full MP2 to only active occupied orbitals in the frozen-core MP2, the number of batches required is reduced (by C in the minimum memory case). This can result in substantial time savings. A similar analysis of the time savings may be done for the unrestricted case.

7.2 Time savings in the two-particle gradient

The nonseparable term of the two-particle gradient (Eq. 136 or Eq. 189) corresponds to a back-transformation of the MP2 amplitudes. As in the two-electron transformation described earlier, this back-transformation usually requires a batched scheme. As the occupied summation in Eq. (136) or Eq. (189) only goes over active occupied orbitals, the frozen-core scheme again results in fewer batches and therefore substantial time savings.

7.3 Terms that must be determined in the AO basis

Inspection of the closed-shell CPHF equations (Eq. 163), the first two terms in the MP2 Lagrangian (Eq. 159), and the energy-weighted density [*III*] correction term (Eq. 187) reveals that MO integrals of the type

$$(jp|qr),\ \mathrm{where}\ j = \mathrm{occ},\ p = \mathrm{all},\ q = \mathrm{all},\ r = \mathrm{all},$$

are required in the frozen-core MP2 as well as the full MP2. If one wishes to take advantage of the savings in computational effort discussed previously, these terms must be evaluated in the AO basis.

Both Frisch et al. [2] and Dupuis et al. [22] have described the formation of the first two terms of the closed-shell MP2 Lagrangian (Eq. 159) in the AO basis. The first two terms {1,2} of Eq. (159) are formed in either a direct or conventional fashion by constructing a Fock-like matrix,

$$L^{1,2}_{\mu\nu} = \sum_{\lambda\sigma}^{\mathrm{AO}} D_{\lambda\sigma}\{2(\mu\nu|\lambda\sigma) - (\mu\lambda|\nu\sigma)\} \ , \tag{206}$$

where

$$D_{\lambda\sigma} = -\sum_{jk}^{\text{occ}} C_{\lambda j} C_{\sigma k} P_{jk}^{\text{CS}(2)} - \sum_{bc}^{\text{vall}} C_{\lambda b} C_{\sigma c} P_{bc}^{\text{CS}(2)} \ . \tag{207}$$

Frisch et al. [2] also described how to solve the CPHF equations in the AO basis. Equation (163) is rewritten as

$$\sum_{b}^{\text{vall}} \sum_{j}^{\text{occ}} A_{aibj}^{\text{CS}} P_{bj}^{\text{CS}(2)} + (\varepsilon_a - \varepsilon_i) P_{ai}^{\text{CS}(2)} = L_{ai}^{\text{CS}}, \tag{208}$$

and the first term is evaluated with a trial $P_{bj}^{(2)}$ again by forming a Fock-like matrix. The resulting $P_{ai}^{(2)}$ is used as the next trial $P_{bj}^{(2)}$, and the process is repeated until the matrices are self-consistent. Once the solution is obtained and $P_{pq}^{(2)}$ is completed, the energy-weighted density [*III*] term (Eq. 187) may be formed in the AO basis, again by formation of a Fock-like matrix.

For the unrestricted case, the $(\alpha\alpha)$ and $(\beta\beta)$ MP2 Lagrangian contributions (see Eq. 98) may be formed in the AO basis. This is done similarly to the closed-shell case by forming the Fock-like matrices

$$\begin{aligned} L_{\mu\nu}(\alpha\alpha) = &\sum_{\lambda\sigma}^{\text{AO}} D_{\lambda\sigma}(\alpha\alpha)\{2(\mu\nu|\lambda\sigma) - (\mu\lambda|\nu\sigma) - (\mu\sigma|\nu\lambda)\} \\ &+ \sum_{\lambda\sigma}^{\text{AO}} D_{\lambda\sigma}(\beta\beta)\{2(\mu\nu|\lambda\sigma)\} \ , \end{aligned} \tag{209}$$

$$\begin{aligned} L_{\mu\nu}(\beta\beta) = &\sum_{\lambda\sigma}^{\text{AO}} D_{\lambda\sigma}(\beta\beta)\{2(\mu\nu|\lambda\sigma) - (\mu\lambda|\nu\sigma) - (\mu\sigma|\nu\lambda)\} \\ &+ \sum_{\lambda\sigma}^{\text{AO}} D_{\lambda\sigma}(\alpha\alpha)\{2(\mu\nu|\lambda\sigma)\} \ , \end{aligned} \tag{210}$$

where

$$D_{\lambda\sigma}(\alpha\alpha) = -\sum_{j^\alpha k^\alpha}^{\text{occ}^\alpha} C_{\lambda j}^{\alpha} C_{\sigma k}^{\alpha} P_{j^\alpha k^\alpha}^{(2)} - \sum_{b^\alpha c^\alpha}^{\text{vall}^\alpha} C_{\lambda b}^{\alpha} C_{\sigma c}^{\alpha} P_{b^\alpha c^\alpha}^{(2)} \ , \tag{211}$$

$$D_{\lambda\sigma}(\beta\beta) = -\sum_{j^\beta k^\beta}^{\text{occ}^\beta} C_{\lambda j}^{\beta} C_{\sigma k}^{\beta} P_{j^\beta k^\beta}^{(2)} - \sum_{b^\beta c^\beta}^{\text{vall}^\beta} C_{\lambda b}^{\beta} C_{\sigma c}^{\beta} P_{b^\beta c^\beta}^{(2)} \ . \tag{212}$$

The unrestricted CPHF equations may be solved similarly to the closed-shell case described previously. However, Eqs. (101) and (102) each contain contributions from $P_{b^\alpha j^\alpha}^{(2)}$ and $P_{b^\beta j^\beta}^{(2)}$, so the equations must be solved simultaneously until self-consistency is achieved.

8 Timings

The C_{2v} isomer of the molecule silicocene (Fig. 3) was chosen as a test case to demonstrate the reduction in computational effort due to the frozen-core approximation. Silicocene is a group 14 analog of ferrocene, and its molecular and electronic structure, as well as its reactivity, have been studied by many researchers [23, 24, 25, 26, 27, 28, 29, 30, 31]. In the timing calculations reported here, a triple-zeta plus polarization basis set was employed. For carbon and hydrogen, the 6-311G basis set of Krishnan et al. [32] was utilized; for silicon, the McLean and Chandler basis set was used [33]. The d and p polarization functions added are the default values in GAMESS. This basis set gives rise to 277 basis functions. Calculations were carried out on the ground singlet state of silicocene using the closed-shell MP2 code in GAMESS. Triplet state calculations were carried out using the UMP2 code in GAMESS. One full MP2 single-point gradient calculation and one frozen-core MP2 single-point gradient calculation were carried out for each state. The number of core orbitals is 15. For the closed-shell calculation, there are 27 valence orbitals; therefore, the full MP2 closed-shell calculation involves 42 active occupied orbitals, while the frozen-core calculation involves 27 active occupied orbitals. For the triplet calculation, there are 28 α and 26 β valence orbitals; thus, the full UMP2 calculation requires 43 α and 41 β active occupied orbitals, while the frozen-core UMP2 calculation involves 28 α and 26 β active occupied orbitals. The minimum amount of memory required for the full UMP2 calculation on the triplet is about 43 Mwords. Fifty Mwords were used, so only one α and one β orbital could be transformed per batch. The minimum amount of memory required for the transformation of one closed-shell orbital is about 11 Mwords, so four orbitals could be transformed per batch for this calculation.

The timings for the calculations are shown in Table 1. All calculations were performed on an ultra SPARC2 300 MHz processor using 50 Mwords of memory. The overall speedup of 1.4–1.7 is mainly due to the decrease in the number of batches required in the transformation step. The time required for an unrestricted open-shell

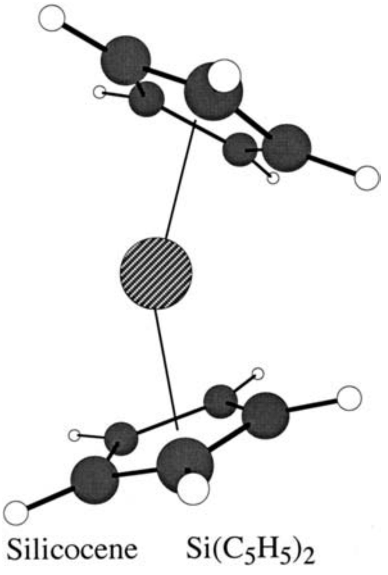

Fig. 3. The C_{2v} isomer of silicocene

Table 1. The total and a breakdown of the computation time for the full and frozen-core second-order perturbation theory (*MP2*) single-point gradient calculations on silicocene [$Si(C_5H_5)_2$]. There are 277 basis functions. All calculations were carried out using an ultra SPARC2 300 MHz processor using 50 M words of memory

Step in algorithm	Computation time (s)			
	Two-electron transformation and MP2 energy	Coupled perturbed Hartree–Fock	Two-electron gradient	Total
Full closed-shell MP2 gradient	6,703.1	749.04	4,893.89	15,173.6
Frozen-core closed-shell MP2 gradient	5,137.5	785.1	3,052.7	10,754.8
Speedup for closed-shell calculation	1.30	0.95	1.60	1.41
Full open-shell unrestricted MP2 gradient	32,441.6	1,300.6	8,349.6	51,677.1
Frozen-core open-shell unrestricted MP2 gradient	18,602.4	1,368.8	5,865.3	30,849.2
Speedup for open-shell calculation	1.74	0.95	1.42	1.68

calculation is about 3 times that for a comparable closed-shell calculation.

9 Conclusion

A detailed derivation of the frozen-orbital MP2 gradient has been presented. The density matrix contributions and CPHF equations were explicitly derived in the spin-orbital basis and reduced to the unrestricted open-shell and restricted closed-shell cases. Details of summation ranges and other modifications resulting from the frozen-orbital approximation have been presented.

Having determined the appropriate expressions and their summation ranges, the reduction in computational effort resulting from the frozen-orbital approximation has been examined. The main reduction in time is due to the decrease in the number of batches required in transformation steps. Test calculations on silicocene show that this time reduction can be considerable, especially when the memory available is close to the minimum required.

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