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RESEARCH ARTICLE

Analytical nuclear gradients of the explicitly correlated
Møller-Plesset second-order energy

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The analytical computation of nuclear gradients has been derived and implemented for the explicitly correlated second-order Møller-Plesset method (MP2-F12). The implementation has been accomplished in the TURBOMOLE program package for ansatz MP2-F12/2*A. A Slater-type geminal expanded in six Gaussian geminals (STG-6G), a complementary auxiliary basis set (CABS), and robust density fitting approximations are used. In addition, a second-order perturbation theory correction for single excitations into the complementary auxiliary basis set (CABS singles) is included to reduce the Hartree-Fock error. Smooth convergence towards the basis set limit is observed for a selection of molecules. For computations on dimers of weakly interacting molecules in small basis sets, explicitly correlated second-order Møller-Plesset theory outperforms conventional second-order Møller-Plesset theory because basis set superposition errors are largely avoided at the MP2-F12/2*A level.

Keywords: electron correlation; second-order Møller-Plesset perturbation theory; explicitly correlated theory; analytical nuclear gradients

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1 **1. Introduction**

2
3
4 The determination of molecular equilibrium geometries and other stationary points
5 (*e.g.*, transition-state geometries) is one of the most important tasks of modern *ab*
6 *initio* quantum chemistry, for molecules in electronically excited as well as ground
7 states. For many quantum-chemical methods, analytical nuclear gradients are avail-
8 able, which is a prerequisite for computationally efficient geometry optimizations.
9 Concerning wave-function based methods that account for electron-correlation ef-
10 fects, analytical first derivatives have been derived and implemented for *general*
11 coupled-cluster and configuration-interaction models, that is, basically for all rele-
12 vant methods [1].

13 Although these methods are general in the sense that both single- and
14 multireference-type methods are included, which are able to handle wave functions
15 truncated at arbitrary excitation level or which include excitations selected via
16 a complete active space, the computation of analytical nuclear gradients thus far
17 has been restricted to coupled-cluster and configuration-interaction wave functions
18 that are expanded in terms of orbital products. The drawback of orbital-product
19 expansions, however, is the very slow convergence of the computed results (energies,
20 geometries, spectra, etc. [2–4]) to the limit of a complete basis set when the orbital
21 basis set is enlarged. In the present article, we shall be concerned with explicitly
22 correlated methods. These methods go beyond the orbital-product expansion by
23 the inclusion of additional two-electron basis functions (geminals). By virtue of
24 these geminals, it becomes possible to satisfy the electron-electron cusp condition
25 and to accelerate the basis set convergence towards the limit of a complete basis
26 set.
27

28
29 The simplest wave-function based method accounting for electron-correlation ef-
30 fects is the second-order Møller-Plesset (MP2) method. For the standard MP2
31 theory in terms of an orbital-product expansion, analytical nuclear gradients were
32 derived and implemented by Pople and co-workers already more than 30 years ago
33 [5]. In the present work, we derive and implement the computation of analytical
34 nuclear gradients of the *explicitly correlated* variant of MP2 theory, which today
35 is either denoted as MP2-R12 or MP2-F12 theory. Explicitly correlated second-
36 order Møller-Plesset theory has recently been reviewed in Ref. [6]. Here and in the
37 following, we shall refer to explicitly correlated theory as MP2-R12 method if the
38 geminal consists of an orbital product multiplied by r_{12} , the distance between the
39 two electrons in the two orbitals of the orbital product, and as MP2-F12 method
40 if the geminal is constructed from a function $f(r_{12})$ multiplied by an orbital prod-
41 uct. In particular, we shall in the present article be concerned with the MP2-F12
42 method, where $f(r_{12})$ is a Slater-type geminal (STG) of the form
43
44

45
46
$$f(r_{12}) = \gamma^{-1}\{1 - \exp(-\gamma r_{12})\}, \quad (1)$$

47
48

49 expanded in a basis of Gaussian geminals [7–10].

50 The computation of certain analytical first derivatives of the MP2-R12 and MP2-
51 F12 energies have been reported before [11–14], but a number of aspects have not
52 been accounted for thus far.

53 In our previous work [14], only the analytical first derivatives needed for the com-
54 putation of first-order molecular properties had been implemented in the TURBO-
55 MOLE program package [15]. In the present article, the implementation of Ref. [14]
56 is extended to the computation of analytical *nuclear* gradients.
57

58 In Ref. [11], Kordel et al. report the implementation of analytical nuclear gradi-
59 ents in the DALTON program package [16] at the level of MP2-R12 theory, that is,
60

1 with linear r_{12} geminals. This implementation had been accomplished for an ansatz
2 that is usually denoted as “standard approximation A” (cf. Ref. [6]). Furthermore,
3 in Ref. [11], the auxiliary basis set (ABS) used for the resolution-of-the-identity
4 (RI) approximation of explicitly correlated theory was identical with the basis set
5 of atomic orbitals (AO) used to expand the Hartree-Fock molecular orbitals (MO).
6 The latter basis is referred to as Hartree-Fock basis (HF basis) in the following.
7 In modern applications of explicitly correlated theory, not this HF basis set but
8 an especially optimized auxiliary basis set is used for the RI approximation. In
9 particular, today, researchers in the field almost exclusively use a complementary
10 auxiliary basis set (CABS) for this approximation [17]. Furthermore, only the MP2-
11 F12 method using STG’s is currently of interest.

12 In the present work, analytical nuclear gradients are derived and implemented
13 for the MP2-F12/2*A-[T+V] method. Elsewhere, we could show that applying
14 standard approximation A and the extended Brillouin condition (EBC, indicated
15 by the asterisk: 2*; cf. Ref. [6]) is sufficiently accurate for obtaining molecular
16 geometries close to those obtained at the basis set limit [14]. Therefore, we decided
17 to restrict the implementation of analytical nuclear gradients to the MP2-F12/2*A-
18 [T+V] level. Extending the work towards the MP2-F12/2B-[T+V] level does not
19 seem worth the effort [14].

20 Compared with our previous work on analytical first derivatives [11, 14], the new
21 aspects of the MP2-F12/2*A-[T+V] analytical nuclear gradients reported in the
22 present article are the following:

- 23 • Use of an complementary auxiliary basis set (CABS) [17];
- 24 • Use of the [T+V] approximation [18, 19];
- 25 • Use of density fitting [20];
- 26 • Inclusion of CABS singles [21, 22].

27 The consequences of these new aspects will be described in detail in the remainder
28 of this article. The CABS consists of basis functions that usually are centered at
29 the positions of the atoms’ nuclei in the molecule. Hence, the CABS changes when
30 the nuclei are moved when computing the nuclear gradient. This gives rise to CABS
31 related reorthonormalization terms, that is, terms related to the first derivative of
32 the CABS overlap matrix (and of overlap matrix elements between the CABS and
33 the HF basis set). These new terms are discussed in Section 2.3. The [T+V] ap-
34 proximation involves matrix elements of the kinetic energy (T) and electron-nuclear
35 attraction (V) operators, and the first derivatives of these matrices thus enter the
36 expression of the analytical MP2-F12/2*A-[T+V] nuclear gradient, see Section 2.4.
37 In the MP2-F12 implementation in TURBOMOLE, all of the two-electron integrals
38 are computed using density fitting techniques. Hence, the analytical computation
39 of the first derivatives of these integrals requires taking care of changes in the
40 density fitting approximation when nuclei are moved (Section 2.5). Finally, when
41 the MP2-F12 energy is supplemented by a correction for single excitations into
42 the CABS, then also the analytical nuclear gradient of the corresponding energy
43 contribution must be considered. This is done in Section 2.6.

44 Apart from the above mentioned sections, the present article is organized as fol-
45 lows: In Section 2, we present the MP2-F12 theory and derive its nuclear gradient.
46 Numerical issues are discussed in Section 3. Then, the performance of the MP2-
47 F12 method is assessed and compared with conventional MP2 results (Section 4).
48 Section 5 concludes the article.

2. Theory

2.1. Projection operators

In explicitly correlated MP2-F12 theory, the first-order wave function is expanded not only in a basis of double excitations containing the product of two virtual orbitals (as in standard MP2 theory) but also in a basis of two-electron basis functions

$$\hat{Q}_{12}f_{12}|xy\rangle, \quad (2)$$

where $f_{12} = f(r_{12})$ is the correlation factor which depends on the interelectronic distance r_{12} of electrons 1 and 2. In Eq. (2), $|xy\rangle = \varphi_x(1)\varphi_y(2)$ denotes a pair of ‘‘F12 geminal’’ orbitals. The projection operator \hat{Q}_{12} ensures that the new pairs are strongly orthogonal on the occupied Hartree-Fock orbitals. Throughout this article, we will use

$$\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2) - \hat{V}_1\hat{V}_2, \quad (3)$$

known as (modified) ansatz 2 in F12 theory [17, 23, 24]. The projection operators onto the one-particle spaces are given by

$$\hat{O} = \sum_m |m\rangle\langle m|, \quad (4)$$

$$\hat{V} = \sum_a |a\rangle\langle a|, \quad (5)$$

$$\hat{P} = \sum_p |p\rangle\langle p|, \quad (6)$$

$$\hat{V}' = \sum_{a'} |a'\rangle\langle a'|, \quad (7)$$

$$\hat{P}' = \sum_{p'} |p'\rangle\langle p'|. \quad (8)$$

The geminal orbitals are denoted as x, y . Often, these are active (non-frozen) occupied orbitals, denoted as i, j, k, l . All occupied orbitals (frozen as well as active) are denoted as m, n, o . Since a large number of different orbital sets are used in F12 theory, the index conventions are summarized in Table 1.

In F12 methods, an auxiliary basis set (ABS) is used for the standard approximation, that is, an approximate resolution of the identity (RI) is inserted to avoid three- and four-electron integrals [23]. Typically, in the MO basis, this RI basis set consists of the orbital basis supplemented with a complementary auxiliary basis set (CABS). Using this CABS, the projection operator \hat{Q}_{12} is approximated as

$$\hat{Q}_{12} \approx \hat{Q}_{12}^{\text{CABS}} = 1 - \hat{O}_1\hat{V}'_2 - \hat{V}'_1\hat{O}_2 - \hat{P}_1\hat{P}_2. \quad (9)$$

When computing molecular gradients, reorthonormalization terms occur since the unperturbed molecular orbitals, which are orthonormal at the reference geometry ($x = 0$), are no longer orthonormal at the new geometry ($x \neq 0$). At this new geometry, they are orthonormalized as follows to yield orthonormal molecular orbitals

(OMO) [25–28]:

$$|\tilde{p}\rangle = \sum_r |r\rangle [\mathbf{S}^{-\frac{1}{2}}]_{rp}, \quad (10)$$

where \mathbf{S} is the overlap matrix at the new geometry. The transformation to the OMO basis ensures orthonormality of the orbitals, since

$$\langle \tilde{q} | \tilde{p} \rangle = \sum_{rs} [\mathbf{S}^{-\frac{1}{2}}]_{qs} \mathbf{S}_{sr} [\mathbf{S}^{-\frac{1}{2}}]_{rp} = \delta_{qp}. \quad (11)$$

The final molecular orbitals at the new geometry are obtained by orbital rotations,

$$|p\rangle = e^{-\kappa} |\tilde{p}\rangle, \quad (12)$$

which are chosen such that $\kappa = 0$ at the reference geometry ($x = 0$). For the various projection operators, this means that we must write

$$\hat{O} = \sum_m \sum_{qr} e^{-\kappa} |q\rangle [\mathbf{S}^{-\frac{1}{2}}]_{qm} [\mathbf{S}^{-\frac{1}{2}}]_{mr} \langle r | e^{\kappa}, \quad (13)$$

$$\hat{V} = \sum_a \sum_{qr} e^{-\kappa} |q\rangle [\mathbf{S}^{-\frac{1}{2}}]_{qa} [\mathbf{S}^{-\frac{1}{2}}]_{ar} \langle r | e^{\kappa}, \quad (14)$$

$$\hat{P} = \sum_{qr} |q\rangle [\mathbf{S}^{-1}]_{qr} \langle r |, \quad (15)$$

$$\hat{V}' = \hat{P}' - \hat{P}, \quad (16)$$

$$\hat{P}' = \sum_{q'r'} |q'\rangle [\mathbf{S}^{-1}]_{q'r'} \langle r' |. \quad (17)$$

Note that the projection operators \hat{P} and \hat{P}' are invariant to orbital rotations. Furthermore, \hat{V}' is expressed as $\hat{P}' - \hat{P}$ because the complementary auxiliary basis set $\{a'\}$ must remain orthogonal on the orbital basis set $\{p\}$ for all geometries x .

2.2. The MP2-F12/2* A-[T+V] Lagrangian

For second-order Møller-Plesset perturbation theory, the inclusion of two-electron basis functions (geminals) in the F12 fashion is formulated using the Hylleraas functional, which consists of a conventional MP2 part, a pure F12 part, and a coupling term,

$$\mathcal{H}_{\text{MP2-F12}} = \mathcal{H}_{\text{MP2}} + \mathcal{H}_{\text{F12}} + \mathcal{H}_{\text{coupling}}, \quad (18)$$

where \mathcal{H}_{MP2} contains the Hartree-Fock contribution. In the following, we will only discuss the F12 contributions to the total MP2-F12 gradient in detail. The conventional MP2 gradient is considered to be available.

In the framework of molecular gradients, a Lagrange functional L is constructed that is variational with respect to both orbital rotations and amplitudes. In ansatz 2*, by virtue of the EBC, the coupling term $\mathcal{H}_{\text{coupling}}$ in Eq. (18) vanishes, and the Lagrangian consists of the conventional MP2 part, the pure F12 contributions, and

the Brillouin condition $F_{ma} = 0$ as constraint,

$$L = \mathcal{H}_{\text{MP2}} + \sum_{ma} \bar{\kappa}_{ma} F_{ma} + \sum_{Ij} \bar{\kappa}_{Ij} F_{Ij} + 2 \sum_{ij} \sum_{xy} d_{ij}^{xy} \langle \tilde{x}\tilde{y} | e^{\kappa} f_{12} \hat{Q}_{12} g_{12} e^{-\kappa} | \tilde{i}\tilde{j} \rangle + \sum_{vw} \sum_{xy} e_{xy}^{vw} \hat{P}_{xy,vw} \langle \tilde{x}\tilde{y} | e^{\kappa} f_{12} \hat{Q}_{12} [\hat{T}_{12}, f_{12}] e^{-\kappa} | \tilde{v}\tilde{w} \rangle, \quad (19)$$

where \hat{T}_{12} denotes the sum of the operators of kinetic energy of electrons 1 and 2. The operator $\hat{P}_{xy,vw}$ symmetrizes an arbitrary four-index object $E(x, y, v, w)$ as

$$\hat{P}_{xy,vw} E(x, y, v, w) = \frac{1}{2} \{ E(x, y, v, w) + E(v, w, x, y) \}. \quad (20)$$

$g_{12} = 1/r_{12}$ is the operator of interelectronic repulsion. With c_{ij}^{xy} being the F12 amplitudes, let us introduce the quantities:

$$d_{ij}^{xy} = 2c_{ij}^{xy} - c_{ij}^{yx}, \quad (21)$$

$$e_{xy}^{vw} = \sum_{ij} c_{ij}^{xy} d_{ij}^{vw}. \quad (22)$$

Inserting the projection operators into Eq. (19) yields different types of integrals. Except for integrals over the interelectronic distance, g_{12} , integrals over the correlation factor f_{12} have to be evaluated. Additionally, integrals over the product $f_{12}g_{12}$ have to be computed, as well as $f_{12}^2 r_{12}^2$, arising from the kinetic energy operator acting on the correlation factor. These will be denoted fg and $f^2 r^2$ integrals, respectively. Furthermore, the integral over the commutator

$$\hat{t}_{12} = [\hat{T}_{12}, f_{12}] \quad (23)$$

needs to be computed. Although it can be calculated analytically, we introduce an additional RI approximation (using ABS) to avoid the calculation of these integrals [18]. This RI approximation is most easily invoked using the transformed orbitals

$$|\check{p}\rangle = \hat{P}' \hat{h} |p\rangle = \sum_{r'} |r'\rangle \langle r' | \hat{h} |p\rangle, \quad (24)$$

where \hat{h} denotes the sum of kinetic energy and electron-nuclear attraction. The inclusion of the latter has turned out to increase numerical stability (using \hat{h} is denoted as [T+V] approximation) [29]. Using these transformed orbitals, an integral over the commutator can be expressed as

$$\langle pq | [\hat{T}_{12}, f_{12}] | rs \rangle \approx \check{X}_{pq,rs} \langle pq | f_{12} | rs \rangle, \quad (25)$$

where the operator $\check{X}_{pq,rs}$ carries out the appropriate transformations,

$$\check{X}_{pq,rs} E(p, q, r, s) = E(\check{p}, q, r, s) + E(p, \check{q}, r, s) - E(p, q, \check{r}, s) - E(p, q, r, \check{s}). \quad (26)$$

Here, E is an arbitrary four-index object.

As for all gradients, there are three types of contributions for MP2-F12 gradients: Differentiated one- and two-electron integrals, orbital response, and change of metric. In the framework of density fitting, differentiated two-electron integrals

are not computed explicitly but rather split into their two- and three-index contributions (*vide infra*). Hence, analytical first derivatives with respect to x can be calculated as (cf. Ref. [30])

$$\begin{aligned}
 L_{\text{F12}}^{[x]} &= \sum_{\mu'\nu'} H_{\mu'\nu'}^{\text{ao}} h_{\mu'\nu'}^{[x]} - \sum_{\mu'\nu'} F_{\mu'\nu'}^{\text{eff,ao}} S_{\mu'\nu'}^{[x]} \\
 &+ \sum_{\mu\nu P} \sum_{\mathfrak{f}}^{fg, f^2 r^2} \mathfrak{f} \Delta_{\mu\nu}^{P, \text{ao}} (\mu\nu | \mathfrak{f}_{12} | P)^{[x]} - \sum_{PQ} \sum_{\mathfrak{f}}^{g, f, fg, f^2 r^2} \mathfrak{f} \gamma_{PQ} (P | \mathfrak{f}_{12} | Q)^{[x]} \\
 &+ \sum_{\mu'\nu' P} \sum_{\mathfrak{f}}^{g, f} \mathfrak{f} \Delta_{\mu'\nu'}^{P, \text{ao}} (\mu'\nu' | \mathfrak{f}_{12} | P)^{[x]}, \tag{27}
 \end{aligned}$$

where the upper index $^{[x]}$ denotes the *partial* derivative according to Lagrange's method, and where $\mathbf{F}^{\text{eff,ao}}$ is the effective Fock matrix taking care of the reorthonormalization of the united basis (HF + CA basis). The differentiated one-electron integrals arising from the [T+V] approximation are contracted with the density \mathbf{H}^{ao} . Greek letters indicate atomic orbitals while the superscript "ao" labels the contravariant quantities that transform as the MO's. In the following, we will derive expressions for the various contributions. The computation of the orbital rotation multipliers $\bar{\kappa}$ has been described elsewhere [14].

2.3. New terms due to the CABS

We are now in the position to take derivatives of the projection operators including the operator $\hat{Q}_{12}^{\text{CABS}}$. Let us first consider \hat{O} , for which we write

$$\left. \frac{\partial \hat{O}}{\partial x} \right|_{x=0} = \left. \frac{\partial \hat{O}}{\partial x} \right|_{x=0, \text{reorth}} + \left. \frac{\partial \hat{O}}{\partial x} \right|_{x=0, \text{other}}. \tag{28}$$

The first term on the r.h.s. collects all terms in which the differentiated overlap matrix $\mathbf{S}^{[x]}$ appears, where it is understood that only the overlap matrix elements in the AO basis are differentiated with respect to x , not the molecular orbitals. Since

$$\left. \frac{\partial \mathbf{S}^{-1/2}}{\partial x} \right|_{x=0} = -\frac{1}{2} \mathbf{S}^{[x]}, \tag{29}$$

we obtain

$$\left. \frac{\partial \hat{O}}{\partial x} \right|_{x=0, \text{reorth}} = -\frac{1}{2} \sum_{mr} \left(|r\rangle S_{rm}^{[x]} \langle m| + |m\rangle S_{mr}^{[x]} \langle r| \right), \quad (30)$$

$$\left. \frac{\partial \hat{V}}{\partial x} \right|_{x=0, \text{reorth}} = -\frac{1}{2} \sum_{ar} \left(|r\rangle S_{ra}^{[x]} \langle a| + |a\rangle S_{ar}^{[x]} \langle r| \right), \quad (31)$$

$$\left. \frac{\partial \hat{P}}{\partial x} \right|_{x=0, \text{reorth}} = -\sum_{qr} |q\rangle S_{qr}^{[x]} \langle r|, \quad (32)$$

$$\left. \frac{\partial \hat{P}'}{\partial x} \right|_{x=0, \text{reorth}} = -\sum_{q'r'} |q'\rangle S_{q'r'}^{[x]} \langle r'|, \quad (33)$$

$$\begin{aligned} \left. \frac{\partial \hat{V}'}{\partial x} \right|_{x=0, \text{reorth}} &= -\sum_{q'r'} |q'\rangle S_{q'r'}^{[x]} \langle r'| + \sum_{qr} |q\rangle S_{qr}^{[x]} \langle r| \\ &= -\sum_{a'b'} |a'\rangle S_{a'b'}^{[x]} \langle b'| - \sum_{a'r} |a'\rangle S_{a'r}^{[x]} \langle r| - \sum_{qb'} |q\rangle S_{qb'}^{[x]} \langle b'|. \end{aligned} \quad (34)$$

Note that $\kappa = 0$ at the reference geometry ($x=0$). For the strong-orthogonality projection operator $\hat{Q}_{12}^{\text{CABS}}$, we obtain

$$\begin{aligned} \left. \frac{\partial \hat{Q}_{12}^{\text{CABS}}}{\partial x} \right|_{x=0, \text{reorth}} &= \sum_{pqr} S_{qr}^{[x]} (|pq\rangle \langle pr| + |qp\rangle \langle rp|) \\ &+ \frac{1}{2} \sum_{mra'} S_{rm}^{[x]} (|ra'\rangle \langle ma'| + |a'r\rangle \langle a'm|) \\ &+ \frac{1}{2} \sum_{mra'} S_{mr}^{[x]} (|ma'\rangle \langle ra'| + |a'm\rangle \langle a'r|) \\ &+ \sum_{ma'b'} S_{a'b'}^{[x]} (|ma'\rangle \langle mb'| + |a'm\rangle \langle b'm|) \\ &+ \sum_{ma'r} S_{a'r}^{[x]} (|ia'\rangle \langle mr| + |a'm\rangle \langle rm|) \\ &+ \sum_{mqb'} S_{qb'}^{[x]} (|mq\rangle \langle mb'| + |qm\rangle \langle b'm|). \end{aligned} \quad (35)$$

It is obvious how these derivatives contribute to the renormalization term $-\sum_{\mu'\nu'} F_{\mu'\nu'}^{\text{eff,ao}} S_{\mu'\nu'}^{[x]}$. The fourth term on the r.h.s. of Eq. (35), for example, yields the following contribution to the CABS-CABS block of $F_{\mu'\nu'}^{\text{eff,ao}}$:

$$\begin{aligned} F_{a'b'}^{\text{eff,ao}} &\leftarrow -4 \sum_m \sum_{ij} \sum_{xy} d_{ij}^{xy} \langle xy|f_{12}|ma'\rangle \langle mb'|g_{12}|ij\rangle \\ &- 2 \sum_m \sum_{vw} \sum_{xy} e_{xy}^{vw} \hat{P}_{xy,vw} \langle xy|f_{12}|ma'\rangle \langle mb'|[\hat{T}_{12}, f_{12}]|vw\rangle. \end{aligned} \quad (36)$$

Of course, the $[\hat{T}_{12}, f_{12}]$ integrals in Eq. (36) are evaluated using the [T+V] approximation. The other terms on the r.h.s. of Eq. (35) contribute accordingly to other parts of $F_{\mu'\nu'}^{\text{eff,ao}}$.

2.4. New terms due to the [T+V] approximation

In the [T+V] approximation, the integrals over the commutator $\hat{t}_{12} = [\hat{T}_{12}, f_{12}]$ are computed using the matrix representation of the one-electron Hamiltonian \hat{h} in the united basis set $\{p'\}$ (HF + CA basis) and two-electron integrals over f_{12} . Hence, apart from differentiated two-electron f_{12} integrals, renormalization terms occur with respect to the united basis set $\{p'\}$. Moreover, differentiated integrals of the one-electron Hamiltonian must be accounted for.

Let us first consider the renormalization terms arising from the RI approximation in $\check{X}_{pq,vw}\langle pq|f_{12}|vw\rangle$, that is, from the projection operator \hat{P}' ,

$$\begin{aligned} \left. \frac{\partial \check{X}_{pq,vw}\langle pq|f_{12}|vw\rangle}{\partial x} \right|_{x=0, \text{reorth}} &= - \sum_{q'r'} S_{q'r'}^{[x]} \{ h_{pq'}\langle r'q|f_{12}|vw\rangle \\ &+ h_{qq'}\langle pr'|f_{12}|vw\rangle - h_{q'v}\langle pq|f_{12}|r'w\rangle - h_{q'w}\langle pq|f_{12}|vr'\rangle \} \\ &+ \text{other terms.} \end{aligned} \quad (37)$$

The “other terms” refer to renormalization terms arising from the orbitals p, q, v, w . From this derivative of \hat{P}' , we obtain the following contribution to the matrix elements $F_{\mu'\nu'}^{\text{eff,ao}}$,

$$\begin{aligned} F_{\mu'\nu'}^{\text{eff,ao}} &\leftarrow -2 \sum_{vw} \sum_{xy} e_{xy}^{vw} \hat{P}_{xy,vw} \\ &\times \{ \sum_{pq} \langle xy|f_{12}|pq\rangle [h_{pq'}\langle r'q|f_{12}|vw\rangle - h_{q'v}\langle pq|f_{12}|r'w\rangle] \\ &+ \sum_{mb'} \langle xy|f_{12}|mb'\rangle [h_{mq'}\langle r'b'|f_{12}|vw\rangle + h_{b'q'}\langle mr'|f_{12}|vw\rangle \\ &- h_{q'v}\langle mb'|f_{12}|r'w\rangle - h_{q'w}\langle mb'|f_{12}|vr'\rangle] \}. \end{aligned} \quad (38)$$

Next, we consider the contributions in which the differentiated one-electron Hamiltonian integrals occur,

$$\begin{aligned} \left. \frac{\partial \check{X}_{pq,vw}\langle pq|f_{12}|vw\rangle}{\partial x} \right|_{x=0, \mathbf{h}^{[x]}} &= \sum_{r'} \{ h_{pr'}^{[x]}\langle r'q|f_{12}|vw\rangle + h_{qr'}^{[x]}\langle pr'|f_{12}|vw\rangle \\ &- h_{r'v}^{[x]}\langle pq|f_{12}|r'w\rangle - h_{r'w}^{[x]}\langle pq|f_{12}|vr'\rangle \} \end{aligned} \quad (39)$$

This leads to the following contributions to the density matrix elements $H_{pr'}$, $H_{mr'}$,

$H_{b'r'}$, and $H_{r'v}$, respectively:

$$\begin{aligned}
 H_{pr'} &\leftarrow -2 \sum_{vw} \sum_{xy} e_{xy}^{vw} \hat{P}_{xy,vw} \sum_q \langle xy|f_{12}|pq\rangle \langle r'q|f_{12}|vw\rangle, \\
 H_{mr'} &\leftarrow -2 \sum_{vw} \sum_{xy} e_{xy}^{vw} \hat{P}_{xy,vw} \sum_{b'} \langle xy|f_{12}|mb'\rangle \langle r'b'|f_{12}|vw\rangle, \\
 H_{b'r'} &\leftarrow -2 \sum_{vw} \sum_{xy} e_{xy}^{vw} \hat{P}_{xy,vw} \sum_m \langle xy|f_{12}|mb'\rangle \langle mr'|f_{12}|vw\rangle, \\
 H_{r'v} &\leftarrow \sum_w \sum_{xy} (e_{xy}^{vw} + e_{vw}^{xy}) \left(\sum_{pq} \langle xy|f_{12}|pq\rangle \langle pq|f_{12}|r'w\rangle \right. \\
 &\left. + \sum_{mb'} [\langle xy|f_{12}|mb'\rangle \langle mb'|f_{12}|r'w\rangle + \langle xy|f_{12}|b'm\rangle \langle b'm|f_{12}|r'w\rangle] \right). \quad (40)
 \end{aligned}$$

2.5. New terms due to density fitting

Let us introduce the following intermediate densities:

$$d_{xy,ij}^{fg} = 2d_{ij}^{xy} \quad (41)$$

$$d_{xy,vw}^{f^2r^2} = e_{vw}^{xy} \quad (42)$$

$$d_{xy,b'm}^f = -4 \sum_{ij} d_{ij}^{xy} \langle b'm|g_{12}|ij\rangle - \sum_{vw} (e_{vw}^{xy} + e_{xy}^{vw}) \langle b'm|t_{12}|vw\rangle \quad (43)$$

$$d_{xy,pq}^f = -2 \sum_{ij} d_{ij}^{xy} \langle pq|g_{12}|ij\rangle - \frac{1}{2} \sum_{vw} (e_{vw}^{xy} + e_{xy}^{vw}) \langle pq|t_{12}|vw\rangle \quad (44)$$

$$d_{ij,b'm}^g = -4 \sum_{xy} d_{ij}^{xy} \langle b'm|f_{12}|xy\rangle \quad (45)$$

$$d_{ij,pq}^g = -2 \sum_{xy} d_{ij}^{xy} \langle pq|f_{12}|xy\rangle \quad (46)$$

$$d_{vw,b'm}^t = - \sum_{xy} (e_{vw}^{xy} + e_{xy}^{vw}) \langle xy|f_{12}|b'm\rangle \quad (47)$$

$$d_{vw,pq}^t = -\frac{1}{2} \sum_{xy} (e_{vw}^{xy} + e_{xy}^{vw}) \langle xy|f_{12}|pq\rangle \quad (48)$$

Using these intermediates, the gradient contribution from differentiated two-electron integrals can be written as

$$\begin{aligned}
 E_{F12}^{[x]} \leftarrow & \sum_{ij} \sum_{xy} d_{xy,ij}^{fg} \langle xy | f_{12} g_{12} | ij \rangle^{[x]} + \sum_{xy,vw} d_{xy,vw}^{f^2 r^2} \langle xy | f_{12}^2 r_{12}^2 | vw \rangle^{[x]} \\
 & + \sum_{xy} \sum_{b'm} d_{xy,b'm}^f \langle xy | f_{12} | b'm \rangle^{[x]} + \sum_{xy} \sum_{pq} d_{xy,pq}^f \langle xy | f_{12} | pq \rangle^{[x]} \\
 & + \sum_{ij} \sum_{b'm} d_{ij,b'm}^g \langle b'm | g_{12} | ij \rangle^{[x]} + \sum_{ij} \sum_{pq} d_{ij,pq}^g \langle pq | g_{12} | ij \rangle^{[x]} \\
 & + \sum_{vw} \sum_{b'm} d_{vw,b'm}^t \langle b'm | t_{12} | vw \rangle^{[x]} + \sum_{vw} \sum_{pq} d_{vw,pq}^t \langle pq | t_{12} | vw \rangle^{[x]}. \quad (49)
 \end{aligned}$$

The two-electron integrals over the Coulomb operator g_{12} are evaluated using “standard” density fitting, whereas all other integrals are computed using *robust* density fitting. When computed by means of robust density fitting, the general structure of a differentiated integral is for all integrals $\mathfrak{x} = fg, f^2 r^2, f$:

$$\begin{aligned}
 & (\mu\nu | \mathfrak{x}_{12} | \kappa\lambda)_{DF}^{[x]} \\
 = & \sum_P (\mu\nu | \mathfrak{x}_{12} | P)^{[x]} g_{\kappa\lambda}^P + \sum_P g_{\mu\nu}^P (P | \mathfrak{x}_{12} | \kappa\lambda)^{[x]} \\
 & + \sum_P [\mathfrak{x} \Gamma_{\mu\nu}^P + \mathfrak{x} \tilde{\Gamma}_{\mu\nu}^P] (P | g_{12} | \kappa\lambda)^{[x]} + \sum_P (\mu\nu | g_{12} | P)^{[x]} [\mathfrak{x} \Gamma_{\kappa\lambda}^P + \mathfrak{x} \tilde{\Gamma}_{\kappa\lambda}^P] \\
 & - \sum_{PQ} [g_{\mu\nu}^P \mathfrak{x} \tilde{\Gamma}_{\kappa\lambda}^Q + g_{\kappa\lambda}^P \mathfrak{x} \tilde{\Gamma}_{\mu\nu}^Q + \mathfrak{x} \Gamma_{\mu\nu}^P g_{\kappa\lambda}^Q + g_{\mu\nu}^Q \mathfrak{x} \Gamma_{\kappa\lambda}^P] (P | g_{12} | Q)^{[x]} \\
 & - \sum_{PQ} g_{\mu\nu}^P (P | \mathfrak{x}_{12} | Q)^{[x]} g_{\kappa\lambda}^Q, \quad (50)
 \end{aligned}$$

where we have used the abbreviation for (*e.g.*, for instance $\mathfrak{x} = f$),

$$f \Gamma_{\kappa\lambda}^P = \sum_Q (P | g_{12} | Q)^{-1} (Q | f_{12} | \kappa\lambda) = \sum_Q (P | g_{12} | Q)^{-1/2} F_{\kappa\lambda}^Q, \quad (51)$$

$$f \tilde{\Gamma}_{\kappa\lambda}^P = - \sum_{QR} (P | g_{12} | Q)^{-1/2} U_{QR}^f G_{\kappa\lambda}^R, \quad (52)$$

and

$$\frac{\partial}{\partial x} \mathbf{M}^{-1} = -\mathbf{M}^{-1} \mathbf{M}^{[x]} \mathbf{M}^{-1}. \quad (53)$$

Note that the differentiated two-electron integrals are not evaluated explicitly. Rather, they are contracted on the fly with appropriate two- and three-index densities, respectively.

In the following two sections, we present the gradient expressions involving the differentiated two- and three-index integrals arising from the density fitting approximation.

2.5.1. Differentiated two-index integrals

According to Eq. (27), the contributions from the differentiated two-index integrals have the structure

$$E^{[x]} \leftarrow \sum_{PQ} (P|f_{12}|Q)^{[x]} \cdot f \gamma_{PQ} \quad (54)$$

for various two-electron operators f . Collecting all terms from Eq. (49) yields

$$f^g \gamma_{PQ} = - \sum_{xy} \sum_{ij} d_{xy,ij}^{fg} g_{\Gamma_{xi}^P} g_{\Gamma_{yj}^Q}, \quad (55)$$

$$f^2 r^2 \gamma_{PQ} = - \sum_{xyvw} d_{xy,vw}^{f^2 r^2} g_{\Gamma_{xv}^P} g_{\Gamma_{yw}^Q}, \quad (56)$$

$$\begin{aligned} f \gamma_{PQ} = & + \sum_{xy} \left\{ \sum_{b'm} d_{xy,b'm}^f g_{\Gamma_{xb'}^P} g_{\Gamma_{ym}^Q} + \sum_{pq} d_{xy,pq}^f g_{\Gamma_{xp}^P} g_{\Gamma_{yq}^Q} \right\} \\ & + \sum_{vw} \left\{ \sum_{b'm} d_{vw,b'm}^t (g_{\check{\Gamma}_{vb'}^P} g_{\Gamma_{wm}^Q} + g_{\Gamma_{vb'}^P} g_{\check{\Gamma}_{wm}^Q}) \right. \\ & \left. + \sum_{pq} d_{vw,pq}^t (g_{\check{\Gamma}_{vp}^P} g_{\Gamma_{wq}^Q} + g_{\Gamma_{vp}^P} g_{\check{\Gamma}_{wq}^Q}) \right\}. \quad (57) \end{aligned}$$

The corresponding expression for $g \gamma_{PQ}$ (*i.e.*, the density to be contracted with the differentiated two-index Coulomb integrals) is

$$\begin{aligned} g \gamma_{PQ} = & - \sum_{xyvw} d_{xy,vw}^{f^2 r^2} \left\{ g_{\Gamma_{xv}^P} f^2 r^2 \check{\Gamma}_{yw}^Q + g_{\Gamma_{yw}^P} f^2 r^2 \check{\Gamma}_{xv}^Q + f^2 r^2 \Gamma_{xv}^P g_{\Gamma_{yw}^Q} + g_{\Gamma_{xv}^Q} f^2 r^2 \Gamma_{yw}^P \right\} \\ & - \sum_{xy} \sum_{ij} d_{xy,ij}^{fg} \left\{ g_{\Gamma_{xi}^P} f g_{\check{\Gamma}_{yj}^Q} + g_{\Gamma_{yj}^P} f g_{\check{\Gamma}_{xi}^Q} + f g_{\Gamma_{xi}^P} g_{\Gamma_{yj}^Q} + g_{\Gamma_{xi}^Q} f g_{\Gamma_{yj}^P} \right\} \\ & - \sum_{xy} \sum_{pq} d_{xy,pq}^f \left\{ g_{\Gamma_{xp}^P} f \check{\Gamma}_{yq}^Q + g_{\Gamma_{yq}^P} f \check{\Gamma}_{xp}^Q + f \Gamma_{xp}^P g_{\Gamma_{yq}^Q} + g_{\Gamma_{xp}^Q} f \Gamma_{yq}^P \right\} \\ & - \sum_{xy} \sum_{b'm} d_{xy,b'm}^f \left\{ g_{\Gamma_{xb'}^P} f \check{\Gamma}_{ym}^Q + g_{\Gamma_{ym}^P} f \check{\Gamma}_{xb'}^Q + f \Gamma_{xb'}^P g_{\Gamma_{ym}^Q} + g_{\Gamma_{xb'}^Q} f \Gamma_{ym}^P \right\} \\ & - \sum_{vw} \sum_{pq} d_{vw,pq}^t \check{X}_{vw pq} \left\{ g_{\Gamma_{vp}^P} f \check{\Gamma}_{wq}^Q + g_{\Gamma_{wq}^P} f \check{\Gamma}_{vp}^Q + f \Gamma_{vp}^P g_{\Gamma_{wq}^Q} + g_{\Gamma_{vp}^Q} f \Gamma_{wq}^P \right\} \\ & - \sum_{vw} \sum_{b'm} d_{vw,b'm}^t \check{X}_{vwb'm} \left\{ g_{\Gamma_{vb'}^P} f \check{\Gamma}_{wm}^Q + g_{\Gamma_{wm}^P} f \check{\Gamma}_{vb'}^Q + f \Gamma_{vb'}^P g_{\Gamma_{wm}^Q} + g_{\Gamma_{vb'}^Q} f \Gamma_{wm}^P \right\} \\ & - \sum_{ij} \left\{ \sum_{b'm} d_{ij,b'm}^g g_{\Gamma_{ib'}^P} g_{\Gamma_{jm}^Q} + \sum_{pq} d_{ij,pq}^g g_{\Gamma_{ip}^P} g_{\Gamma_{jq}^Q} \right\}. \quad (58) \end{aligned}$$

2.5.2. Differentiated three-index integrals

In analogy to the previous section, three-index quantities contribute to the gradient as

$$E^{[x]} \leftarrow \sum_{\mu\nu P} (\mu\nu | f_{12} | P)^{[x]} \cdot f \Delta_{\mu\nu}^{P,ao}. \quad (59)$$

Note that for convenience, the three-index contributions are expressed using a back transformation,

$$fg \Delta_{\mu\nu}^{P,ao} = \sum_{xy} \sum_{ij} d_{xy,ij}^{fg} \{ C_{x\mu} C_{i\nu} {}^g \Gamma_{yj}^P + C_{y\mu} C_{j\nu} {}^g \Gamma_{xi}^P \} \quad (60)$$

$$f^2 r^2 \Delta_{\mu\nu}^{P,ao} = \sum_{xyvw} d_{xy,vw}^{f^2 r^2} \{ C_{x\mu} C_{v\nu} {}^g \Gamma_{yw}^P + C_{y\mu} C_{w\nu} {}^g \Gamma_{xv}^P \}$$

$$\begin{aligned} f \Delta_{\mu'\nu'}^{P,ao} = & - \sum_{xy} \sum_{b'm} d_{xy,b'm}^f \{ C_{x\mu'} C_{b'\nu'} {}^g \Gamma_{ym}^P + C_{y\mu} C_{m\nu} {}^g \Gamma_{x'b'}^P \} \\ & - \sum_{vw} \sum_{b'm} d_{vw,b'm}^t \check{X}_{vwb'm} \{ C_{v\mu'} C_{b'\nu'} {}^g \Gamma_{wm}^P + C_{w\mu} C_{m\nu} {}^g \Gamma_{v'b'}^P \} \\ & - \sum_{xy} \sum_{pq} d_{xy,pq}^f \{ C_{x\mu'} C_{p\nu'} {}^g \Gamma_{yq}^P + C_{y\mu'} C_{q\nu'} {}^g \Gamma_{xp}^P \} \end{aligned} \quad (61)$$

$$- \sum_{vw} \sum_{pq} d_{vw,pq}^t \check{X}_{vw,pq} \{ C_{v\mu'} C_{p\nu'} {}^g \Gamma_{wq}^P + C_{w\mu'} C_{q\nu'} {}^g \Gamma_{vp}^P \}. \quad (62)$$

Note that for the operators f_{12} and g_{12} , the back transformation must be carried out in the united basis due to the [T+V] transformation.

$$\begin{aligned} g \Delta_{\mu'\nu'}^{P,ao} = & \sum_{xy} \sum_{ij} d_{xy,ij}^{fg} \{ C_{x\mu'} C_{i\nu'} [{}^f g \Gamma_{yj}^P + {}^f g \tilde{\Gamma}_{yj}^P] + C_{y\mu'} C_{j\nu'} [{}^f g \Gamma_{xi}^P + {}^f g \tilde{\Gamma}_{xi}^P] \} \\ & + \sum_{xy} \sum_{vw} d_{xy,vw}^{f^2 r^2} \{ C_{x\mu'} C_{v\nu'} [{}^{f^2 r^2} \Gamma_{yw}^P + {}^{f^2 r^2} \tilde{\Gamma}_{yw}^P] + C_{y\mu'} C_{w\nu'} [{}^{f^2 r^2} \Gamma_{xv}^P + {}^{f^2 r^2} \tilde{\Gamma}_{xv}^P] \} \\ & + \sum_{ijpq} d_{pq,ij}^g \{ C_{i\mu'} C_{p\nu'} {}^g \Gamma_{ip}^P + C_{j\mu'} C_{q\nu'} {}^g \Gamma_{jq}^P \} \\ & + \sum_{ijb'm} d_{b'm,ij}^g \{ C_{i\mu'} C_{b'\nu'} {}^g \Gamma_{ip}^P + C_{j\mu'} C_{m\nu'} {}^g \Gamma_{jm}^P \} \\ & + \sum_{xy} \sum_{pq} d_{xy,pq}^f \{ C_{x\mu'} C_{p\nu'} [{}^f \Gamma_{yq}^P + {}^f \tilde{\Gamma}_{yq}^P] + C_{y\mu'} C_{q\nu'} [{}^f \Gamma_{xp}^P + {}^f \tilde{\Gamma}_{xp}^P] \} \\ & + \sum_{xy} \sum_{b'm} d_{xy,b'm}^f \{ C_{x\mu'} C_{b'\nu'} [{}^f \Gamma_{ym}^P + {}^f \tilde{\Gamma}_{ym}^P] + C_{y\mu'} C_{m\nu'} [{}^f \Gamma_{x'b'}^P + {}^f \tilde{\Gamma}_{x'b'}^P] \} \\ & + \sum_{vw} \sum_{pq} d_{vw,pq}^t \check{X}_{vw,pq} \{ C_{v\mu'} C_{p\nu'} [{}^f \Gamma_{wq}^P + {}^f \tilde{\Gamma}_{wq}^P] + C_{w\mu'} C_{q\nu'} [{}^f \Gamma_{vp}^P + {}^f \tilde{\Gamma}_{vp}^P] \} \\ & + \sum_{vw} \sum_{b'm} d_{vw,b'm}^t \check{X}_{vwb'm} \{ C_{v\mu'} C_{b'\nu'} [{}^f \Gamma_{wm}^P + {}^f \tilde{\Gamma}_{wm}^P] \\ & + C_{w\mu'} C_{m\nu'} [{}^f \Gamma_{v'b'}^P + {}^f \tilde{\Gamma}_{v'b'}^P] \} \end{aligned} \quad (63)$$

2.6. New terms due to CABS singles

When computing the CABS singles energy, we correct for the Hartree-Fock basis set error by means of second-order perturbation theory,

$$\mathcal{H}_S = \sum_{mn} \sum_{a'b'} c_m^{a'} \langle a' | \hat{Q} (S_{mn} \hat{F} - F_{mn}) \hat{Q} | b' \rangle c_n^{b'} + 2 \sum_m \sum_{a'} c_m^{a'} \langle a' | \hat{Q} \hat{F} | m \rangle, \quad (64)$$

with $\hat{Q} = 1 - \hat{P}$. Note that this expression does not account for single excitations into the HF basis, since we work within the EBC ($f_a^{a'} \approx 0$).

In the original implementation, when computing the CABS singles energy, we used an approximated RI-*JK* Fock matrix whenever one index is in the CABS but the exact Fock matrix for the occupied-occupied matrix elements F_{mn} . Due to these matrix elements, which depend on exact four-index two-electron integrals, differentiated four-index integrals would have entered the expression for the analytical nuclear gradient. To avoid the calculation of differentiated four-index integrals, we here invoke the RI-*JK* approximation also when computing the occupied-occupied matrix elements F_{mn} . Numerical tests showed that the change in energy due to invoking the RI-*JK* approximation for the occupied-occupied matrix elements is completely negligible compared with the remaining basis set errors.

2.6.1. Differentiated integrals

We obtain for the derivatives of the one-electron integrals

$$E_S^{[x]} \leftarrow \sum_{mn} \left(\sum_{a'b'} c_m^{a'} (\delta_{mn} h_{a'b'}^{[x]} - \delta_{a'b'} h_{mn}^{[x]}) c_n^{b'} + 2 \sum_{a'} c_m^{a'} h_{ma'}^{[x]} \right). \quad (65)$$

Furthermore, also the differentiated two-electron integrals are taken into account

$$E_S^{[x]} \leftarrow \sum_{mn} \left(\sum_{a'b'} c_m^{a'} (\delta_{mn} G_{a'b'}^{[x]} - \delta_{a'b'} G_{mn}^{[x]}) c_n^{b'} + 2 \sum_{a'} c_m^{a'} G_{ma'}^{[x]} \right), \quad (66)$$

where $G_{p'q'}$ denotes the sum of Coulomb and exchange contributions in the RI-*JK* approximation.

2.6.2. Contributions to the effective Fock matrix

For the effective Fock matrix, we obtain contributions from the outer orbitals

$$\begin{aligned} E_S^{[x]} \leftarrow & - \sum_{a'm} d_{a'm} \left(\sum_{c'} S_{a'c'}^{[x]} F_{c'm} + \sum_o S_{om}^{[x]} F_{a'o} + 2 \sum_r S_{a'r}^{[x]} F_{rm} \right) \\ & - \frac{1}{2} \sum_{a'b'} d_{a'b'} \left(\sum_{c'} S_{a'c'}^{[x]} F_{c'b'} + \sum_{c'} S_{b'c'}^{[x]} F_{c'a'} + 4 \sum_o S_{a'o}^{[x]} F_{ob'} \right) \\ & + \frac{1}{2} \sum_{mn} d_{mn} \left(S_{mr}^{[x]} F_{rn} + S_{nr}^{[x]} F_{rm} \right). \end{aligned} \quad (67)$$

with

$$d_{mn} = \sum_{a'} c_m^{a'} c_n^{a'}, \quad d_{a'b'} = \sum_m c_m^{a'} c_m^{b'}, \quad d_{a'm} = d_{ma'} = c_m^{a'}. \quad (68)$$

From the Coulomb and exchange operators, we obtain

$$\begin{aligned}
 F_{or}^{\text{eff},S} \leftarrow & -\frac{1}{2} \sum_{a'b'} d_{a'b'} (1 + \hat{P}_{ro}) (2(a'b'|g_{12}|ro) - (a'r|g_{12}|b'o)) \\
 & + \frac{1}{2} \sum_{mn} d_{mn} (1 + \hat{P}_{ro}) (2(mn|g_{12}|ro) - (mr|g_{12}|no)) \\
 & - \sum_{a'm} d_{a'm} (1 + \hat{P}_{ro}) (2(ma'|g_{12}|ro) - (mr|g_{12}|a'o)) , \quad (69)
 \end{aligned}$$

where $\hat{P}_{ro}E(r, o) = E(r, o) + E(o, r)$.

3. Computational details

3.1. General remarks

We have used Dunning's orbital basis sets aug-cc-pVXZ with $X = D, T, Q, 5$ [31, 32] together with the MP2 fitting basis sets C-aug-cc-pwCV{T,Q,5}Z for $X = D, T, Q$. For the aug-cc-pV5Z orbital basis, due to the lack of a C-aug-cc-pwCV6Z MP2 fitting basis, we used the C-aug-cc-pV6Z MP2 fitting basis [33, 34]. Note that also for the standard MP2 calculations, we have used the C-aug-cc-pwCV(X+1)Z MP2 fitting basis, that is, one cardinal number higher than what is usually done. For the RI-*JK* approximation, we have applied the auxiliary basis sets JK-aug-cc-pVXZ [35]. For the intrinsic RI approximation of F12 theory, we have used the CABS of Yousaf and Peterson [36].

The convergence criterion for the density-matrix norm was set to 10^{-9} . The geometries were considered to be optimized when a change less than $10^{-8} E_h$ in the energy and less than $10^{-4} E_h/a_0$ in the gradient was reached. Tightening the convergence criteria did not affect the significant digits reported. The frozen-core approximation was applied in all of the calculations.

For conventional methods using density fitting, the HF basis and the level of correlation treatment should be the factors that limit accuracy, whereas errors due to integral screening or density fitting should be negligible. With respect to the CABS, one has to distinguish between CABS as auxiliary basis for the MP2-F12 method and as basis for the computation of the CABS singles energy correction. Concerning the use as auxiliary basis, we note that the total basis for the RI approximation of MP2-F12 theory consists of the HF basis supplemented with the CABS. Hence the importance of the CABS decreases with increasing HF basis, because then the HF basis already becomes sufficiently large.

3.2. Density fitting error

As pointed out in Section 2, robust density fitting is applied to all two-electron integrals in our explicitly correlated methods. Since thus far no density fitting auxiliary basis sets have been optimized especially for the F12 methods, it is not *a priori* clear, which (non-optimized) auxiliary basis sets one should select. Typically, as a default, when using an aug-cc-pVXZ orbital basis in conjunction with F12 geminals, we use the C-aug-cc-pwCV(X+1)Z MP2 fitting basis for the density fitting approximation. This large MP2 fitting basis is selected to be on the safe side. It is taken with increased cardinal number, and furthermore, it is a fitting basis that would allow for correlating the core electrons.

1 The effect of the MP2 fitting basis is investigated by performing calculations on
2 C_2H_4 and one of its dimer structures. Selected results are summarized in Table 2. It
3 is observed for the C_2H_4 molecule that different density fitting basis sets yield the
4 same geometry when the explicitly correlated amplitudes are optimized (*var*-MP2-
5 F12 approach). This is not true for its dimer. Using the *var*-MP2-F12 approach,
6 the differences in the optimized dimer geometries are significant. When the C-aug-
7 cc-pwCVTZ is used as MP2 fitting basis, the intermolecular distance is 4 pm longer
8 than when the C-aug-cc-pwCVQZ or C-aug-cc-pwCV5Z MP2 fitting basis sets are
9 used. Fortunately, we find no differences in the optimized dimer geometries when
10 the explicitly correlated amplitudes are kept fixed (*fix*-MP2-F12 approach) [37].
11 Hence, it seems that in particular the nondiagonal elements of the matrices \mathbf{B} and
12 \mathbf{V} of F12 theory are sensitive to the MP2 fitting basis in this weakly interacting
13 system. Further investigations of the requirements on the MP2 fitting basis set
14 appear to be needed, but treating a weakly interacting system with the *var*-MP2-
15 F12 approach is certainly a special and challenging case.
16
17
18
19

20 4. Results

21 4.1. Molecules

22 Table 3 shows the convergence of the geometries of selected molecules using the
23 *var*-MP2-F12/2*A-[T+V] method. The geometries exhibit a smooth and fast con-
24 vergence to the basis set limit. Even for the small double- ζ basis set, reasonable
25 results are obtained both in terms of energies and geometrical parameters (*i.e.*,
26 bond lengths and angles). See also Ref. [38]. The geometries are improved, that
27 is, brought closer to the corresponding basis set limit geometries, by including the
28 CABS singles energy corrections. By accounting for CABS singles in a given aug-cc-
29 pVXZ basis, the optimized geometries are close to those obtained in the next larger
30 aug-cc-pV(X+1)Z basis without CABS singles. Basis set convergence is practically
31 reached at the quadruple- ζ level. Calculations with fixed F12 amplitudes yield very
32 similar results.
33

34 In Table 3, the row denoted as “CABS” displays the results obtained with the
35 larger C-aug-cc-pwCV(X+2)Z MP2 fitting basis. The effect of taking this larger
36 fitting basis appears to be negligible.
37
38
39
40

41 4.2. Hydrogen-bonded complexes

42 We have first used the *fix*-MP2-F12/2*A-[T+V] approach for the hydrogen-bonded
43 complexes, that is, the approach with fixed F12 amplitudes. Results of geometry op-
44 timizations of HF..H₂O and NH₃..H₂O are summarized in Table 4. The geometries
45 of the individual molecules and their dimers have been optimized independently,
46 and hence, the reported energy differences are equilibrium binding energies ($-D_e$).
47

48 We observe that basis sets larger than double- ζ provide a smooth and rapid
49 convergence to the basis set limit both for binding energies and intermolecular
50 distances. At the aug-cc-pV5Z level, the inclusion of CABS singles has little effect,
51 and we expect that we have approached the basis set limit closely at this level.
52

53 Next, we assess the performance of the *var*-MP2-F12/2*A-[T+V] approach (Ta-
54 ble 5). When using the *var* approach, in which all F12 amplitudes are optimized,
55 the results may be slightly corrupted by the so-called “geminal basis set superpo-
56 sition error” (geminal BSSE) [39]. This error may occur because pairs of occupied
57 orbitals located on one fragment may be correlated by geminals consisting of a
58 Slater-type geminal multiplied by geminal orbitals that are located on the other
59
60

1 fragment. To investigate this geminal BSSE, we decided to use a large MP2 fitting
2 basis (aug-cc-pwCV(X+2)Z in place of aug-cc-pwCV(X+1)Z) to avoid density fit-
3 ting errors. Indeed, when comparing the results of Tables 4 and 5, we observe that in
4 the aug-cc-pVDZ and aug-cc-pVTZ basis sets, the binding energies obtained from
5 the *var*-MP2-F12 approach are more negative than those obtained from the *fix*-
6 MP2-F12 approach. In fact, the latter approach yields results closer to the basis set
7 limit. Considering that the *fix*-MP2-F12 approach is computationally less involved
8 than the *var*-MP2-F12 approach, and considering that the *var*-MP2-F12 approach
9 requires a larger MP2 fitting basis, it is clear that the *fix*-MP2-F12 approach is the
10 method of choice for studies of weakly interacting complexes.

11
12 Increasing the CABS in the *fix*-MP2-F12 approach (Table 4) leads to increased
13 intermolecular distances of 0.23 pm and 0.12 pm, respectively, for HF..H₂O and
14 NH₃..H₂O in the double- ζ orbital basis (cf. row denoted "CABS"). Thus, the
15 double- ζ CABS appears to be slightly too small. However, in the larger orbital
16 basis sets, the effect of the CABS is much smaller, of the order of only 0.05 pm or
17 less.
18

19 20 21 4.3. Comparison with standard MP2 results

22 In this section, we shall compare our MP2-F12 results with the standard MP2
23 approach. We shall consider the same two dimers as in the previous section as well
24 as the water molecule.
25

26 Table 6 shows the convergence of the bond length and bond angle of the water
27 molecule, as obtained from geometry optimizations. The correlation energy as well
28 as the geometrical parameters converge smoothly to their basis set limits. Concern-
29 ing the geometry, one may consider the geometry being converged with respect to
30 the basis set at the aug-cc-pV5Z level. However, even at this level, the error in
31 the second-order correlation energy is of the order of 7.5 mE_h. When perform-
32 ing a single-point MP2-F12/aug-cc-pV5Z calculation at the standard MP2/aug-
33 cc-pV5Z geometry, however, the basis set limit second-order correlation energy is
34 obtained. In this respect, it seems legitimate to optimize equilibrium geometries
35 at the standard MP2 level in conjunction with MP2-F12 computations of the final
36 total energy.
37

38 A slightly different picture is observed for the dimers (Table 7). A fortuitous
39 error compensation occurs at the standard MP2 level when the dimer geometries
40 are optimized without correction for the basis set superposition error (BSSE) by
41 means of a function counterpoise (CP) correction. This error compensation occurs
42 since the basis set truncation error of the orbital-product approach partially cancels
43 the BSSE. It is most pronounced for the calculations in the aug-cc-pVDZ basis.
44 Without CP correction, the intermolecular bond lengths are ca. 0.7 pm longer than
45 the basis set limit value for both complexes. A geometry optimization including
46 CP corrections, however, yields much larger bond lengths, ca. 5–6 pm longer. The
47 interaction energies are too large in magnitude without CP correction while they
48 are too small when the CP correction is applied.
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52 53 4.4. Comparison with literature data

54 For the dimers studied here, only few calculations at the basis set limit are known,
55 see Table 8. Concerning the HF..H₂O complex, a good agreement is obtained when
56 comparing our results with literature data. For example, in Ref. [40], an intermolec-
57 ular distance of 171.44 pm was computed using a quintuple- ζ orbital basis, which
58 may be compared with our standard MP2/aug-cc-pV5Z value of 171.43 pm (Ta-
59
60

ble 7). The fact that we use density fitting may explain the difference of 0.01 pm. In Ref. [40], the authors emphasize that a counterpoise correction has to be carried out for every HF basis. Moreover, it is unclear whether Q5 extrapolations or sextuple- ζ results exhibit higher accuracy (both corrected for BSSE) [41]. Compared with the basis set limit computed in this work, the MP2/aug-cc-pV5Z intermolecular distance is about 0.6 pm too long when corrected for BSSE (0.1 pm too short without correcting).

The large counterpoise corrections show that the standard MP2 results converge only slowly to the basis set limit. In contrast, the MP2-F12 method provides results much closer to the basis set limit (Table 4). We expect that our MP2-F12 results for the water..ammonia complex are similarly accurate.

5. Conclusions

In the present article, we have reported the implementation of analytical nuclear gradients of the explicitly correlated Møller-Plesset second-order energy. In particular, the implementation has been accomplished for the MP2-F12/2*A-[T+V] model as implemented in the TURBOMOLE program package. Equilibrium geometries close to the limit of a complete basis are obtained at the MP2-F12/2*A-[T+V] level already in relatively small basis sets. Concerning weakly (hydrogen-bonded) complexes, it is strongly recommended to use the MP2-F12/2*A-[T+V] method in the fashion, in which the geminal amplitudes are kept fixed (*fix*-MP2-F12 approach). The *fix*-MP2-F12 approach appears less amenable to shortcomings in the MP2 fitting basis for the density fitting approximation, and the *fix*-MP2-F12 approach is free of geminal BSSE.

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Table 1. Summary of index conventions.

p, q, r, \dots	orbitals in HF basis
i, j, k, l	active occupied orbitals
I, J, K, L	frozen occupied orbitals
m, n, o	active and frozen occupied orbitals
a, b, c, \dots	active virtual orbitals in finite basis
$\alpha', \beta', \gamma', \dots$	complementary virtual orbitals in formally complete basis
a', b', c', \dots	CABS representation of complementary virtual orbitals
p', q', r', \dots	orbitals in HF plus CA basis
v, w, x, \dots	orbitals in the F12 geminals basis
μ, ν, ρ, \dots	atomic orbitals in finite basis
μ', ν', ρ', \dots	atomic orbitals in finite plus CA basis
P, Q	density fitting basis

Table 2. Investigations concerning the density fitting error using aug-cc-pVDZ as orbital basis set. CABS singles were not included. Different auxiliary basis sets of the type C-aug-cc-pwCVYZ have been used. $\|\nabla\|$ denotes the norm of the gradient for the initial geometry in E_h/a_0 . Convergence criteria are described in the text. $R_{\text{Et-Et}}$ denotes the intermolecular distance in the dimer. Energies E are given in mE_h, distances R in pm, and angles \sphericalangle in degrees.

		Y=T ($\cong X+1$)	DF basis: Y=Q ($\cong X+2$)	Y=5 ($\cong X+3$)
C ₂ H ₄		<i>var</i> -MP2-F12/2* A-[T+V]		
1st Iteration	$\ \nabla\ $	27.11	27.10	27.10
	E_{F12}	-97.03	-97.02	-97.02
Optimized	$R_{\text{C-C}}$	133.77	133.77	133.77
	$R_{\text{C-H}}$	108.69	108.69	108.69
	$\sphericalangle_{\text{H-C-H}}$	117.53	117.53	117.53
(C ₂ H ₄) ₂		<i>var</i> -MP2-F12/2* A-[T+V]		
1st Iteration	$\ \nabla\ $	20.97	20.51	20.50
	E_{F12}	-192.45	-192.20	-192.20
Optimized	$R_{\text{C-C}}$	133.80	133.82	133.82
	$R_{\text{C-H}}$	108.75	108.75	108.76
	$\sphericalangle_{\text{H-C-H}}$	117.33	117.44	117.44
	$R_{\text{Et-Et}}$	370.00	366.42	366.36
(C ₂ H ₄) ₂		<i>fix</i> -MP2-F12/2* A-[T+V]		
1. Iteration	$\ \nabla\ $	20.21	20.21	20.21
	E_{F12}	-181.08	-181.06	-181.06
Optimized	$R_{\text{C-C}}$	133.84	133.84	133.84
	$R_{\text{C-H}}$	108.72	108.71	108.71
	$\sphericalangle_{\text{H-C-H}}$	117.43	117.43	117.43
	$R_{\text{Et-Et}}$	369.69	369.69	369.69

Table 3. Geometry optimization of different molecules using *var*-MP2-F12 and the [T+V] commutator approximation. Bond lengths R are given in pm, angles \sphericalangle in degrees.

Basis	CABS singles	H ₂ O		NH ₃		HF
		$R_{\text{O-H}}$	$\sphericalangle_{\text{H-O-H}}$	$R_{\text{N-H}}$	$\sphericalangle_{\text{H-N-H}}$	$R_{\text{H-F}}$
aVDZ	yes	96.02	104.32	101.08	106.85	92.01
	no	96.24	104.08	101.50	106.42	92.21
	CABS ^a	96.24	104.07	101.49	106.44	92.21
aVTZ	yes	95.86	104.39	100.98	106.94	91.87
	no	95.97	104.39	101.03	106.94	92.05
	CABS ^a	95.97	104.39	101.03	106.94	92.05
aVQZ	no	95.85	104.39	100.97	106.98	91.87
	yes	95.84	104.39	100.96	106.97	91.84
aV5Z	no	95.84	104.39	100.96	106.99	91.85
	yes	95.84	104.39	100.95	106.99	91.85

^aCABS was increased by one cardinal number.

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Table 4. Geometry optimizations at the *fix*-MP2-F12 level without counterpoise correction. aVXZ is a shorthand notation for the aug-cc-pVXZ orbital basis set.

Orbital basis	CABS singles		Bond length / pm		Binding energy / mE_h	
			HF..H ₂ O	NH ₃ ..H ₂ O	HF..H ₂ O	NH ₃ ..H ₂ O
aVDZ	yes		171.38	196.56	-13.35	-10.10
		limit ^a			-13.88	-10.40
	no		171.72	196.00	-13.58	-10.54
aVTZ		CABS ^b	<i>171.95</i>	<i>196.12</i>	<i>-13.44</i>	<i>-10.49</i>
	yes		170.82	195.96	-13.86	-10.40
		limit ^a			-13.89	-10.37
aVQZ	no		170.25	195.45	-14.05	-10.51
		CABS ^b	<i>170.29</i>	<i>195.50</i>	<i>-14.02</i>	<i>-10.50</i>
	yes		170.81	196.07	-13.91	-10.41
aV5Z ^c	no		170.72	196.01	-13.97	-10.44
	yes		170.84	196.09	-13.90	-10.40
	no		170.82	196.08	-13.90	-10.40

^aBasis set limit for binding energies using MP2-F12 at given geometry (basis: aug-cc-pV5Z).

^bCABS was increased by one cardinal number.

^cUsed as basis set limit in the following.

Table 5. Geometry optimizations at the *var*-MP2-F12 level without counterpoise correction. aVXZ is a shorthand notation for the aug-cc-pVXZ orbital basis set. Auxiliary basis sets of the type C-aug-cc-pwCV(X+2)Z were used for density fitting.

Orbital basis	CABS singles		Bond length / pm		Binding energy / mE_h	
			HF..H ₂ O	NH ₃ ..H ₂ O	HF..H ₂ O	NH ₃ ..H ₂ O
aVDZ	yes		171.09	196.24	-13.63	-10.40
		limit ^a			-13.89	-10.41
	no		171.46	195.69	-13.85	-10.83
aVTZ		CABS ^b	<i>171.73</i>	<i>195.83</i>	<i>-13.75</i>	<i>-10.79</i>
	yes		170.69	195.79	-13.98	-10.51
		limit ^a			-13.90	-10.41
Limit ^c	no		170.13	195.28	-14.17	-10.62
		CABS ^b	<i>170.18</i>	<i>195.33</i>	<i>-14.13</i>	<i>-10.60</i>
	yes		170.84	196.09	-13.90	-10.90

^aSingle-point MP2-F12 energy calculation (orbital basis: aug-cc-pV5Z).

^bCABS was increased by one cardinal number.

^cSee Table 4.

Table 6. MP2 optimized geometry of H₂O.

	R_{O-H} / pm	\angle_{H-O-H} / °	$E^{(2)}$ / mE_h
aVDZ	96.59	103.87	-220.143
aVTZ	96.14	104.11	-268.704
aVQZ	95.89	104.27	-286.052
aV5Z	95.84	104.34	-293.002
			-300.587 ^a
aV6Z	95.84	104.37	-296.048
Limit ^b	95.84	104.39	-300.586

^aSingle-point MP2-F12/aug-cc-pV5Z energy.

^bAt the MP2-F12/aug-cc-pV5Z level.

Table 7. MP2 geometry optimizations.

Basis	CP correction	Bond length / pm		Binding energy / mE_h	
		HF..H ₂ O	NH ₃ ..H ₂ O	HF..H ₂ O	NH ₃ ..H ₂ O
aVDZ	yes	176.07	201.98	-12.59	-9.31
	no	171.52	196.78	-14.39	-11.07
	limit ^a			-13.89	-10.44
aVTZ	no	170.39	195.74	-14.28	-10.69
	limit ^a			-14.02	-10.53
aVQZ	no	170.37	195.83	-14.17	-10.55
	limit ^a			-13.89	-10.40
aV5Z	yes	171.43	196.74	-13.69	-10.26
	no	170.76	196.01	-14.02	-10.45
	limit ^a			-13.89	-10.40
aV6Z	no	170.79	196.03	-13.95	-10.42
Limit ^b		170.84	196.09	-13.90	-10.40

^aSingle-point MP2-F12/aug-cc-pV5Z energy.

^bSee Table 4.

Table 8. Comparison with literatur data.

Method	Basis	Reference	Bond length / pm		Binding energy / mE_h	
			HF..H ₂ O	NH ₃ ..H ₂ O	HF..H ₂ O	NH ₃ ..H ₂ O
MP2	daV5Z	[40]	170.78			
MP2 (CP) ^a	aV5Z	[40]	171.44		-14.37	
MP2 (CP) ^a	Q5 ^b	[40]	171.02			
MP2 (CP) ^a	aVTZ	[42]				-9.94
MP2	aV6Z		170.79		-13.95	
MP2-F12 ^c	aV5Z		170.84	196.09	-13.90	-10.40

^aCP corrected results.

^bExtrapolated results.

^cSee Table 4.