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Analytic Calculation of First-order Molecular Properties at the Explicitly-correlated Second-order Møller-Plesset Level

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Formulae are derived and implemented for the analytic calculation of first-order molecular properties at the level of explicitly-correlated second-order Møller-Plesset perturbation theory. In this theory, which is denoted as MP2-F12 theory, Slater-type geminals are used to expand the first-order wave function. A second-order perturbation theory correction for single excitations into a complementary auxliary basis set is also included. At the MP2-F12 level, it seems sufficient to restrict the analytic calculation of energy derivatives to the level of standard approximation A of MP2-F12 theory and to assume the extended Brillouin condition to hold. Smooth and rapid convergence towards the basis-set limit is observed for the dipole moments of a selection of small closed- and open-shell molecules when calculated at the RI-MP2-F12/$2A^*$[T+V] + CABS singles level in augmented correlation-consistent polarized valence double-, triple-, and quadruple-zeta basis sets that have been optimized especially for use in MP2-F12 theory.

1. Introduction

Over the past 50 years, the numerical methods of quantum chemistry have developed into what can be said to be a "quantitative quantum chemistry", that is, a tool for providing quantitative data about chemistry, sufficiently accurate to reliably predict, confirm, or reject experimental observations and measurements [1].

Important components of this quantitative tool are the coupled-cluster theory since the early 1980s and the correlation-consistent cc-pVXZ basis sets devel-

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oped by Dunning and others since the late 1980s [2]. However, although very successful, coupled-cluster calculations in cc-pVXZ basis sets suffer from a notoriously slow basis-set convergence, that is, slow convergence with the cardinal number X = 2, 3, 4, ... towards the basis-set limit obtained for X = ∞.

This slow convergence can be traced back to the inability of Slater determinants build from one-electron functions to appropriately describe the Coulomb hole around the electron-electron coalescence point. The basis-set convergence can, however, be accelerated significantly by using explicitly-correlated coupled-cluster wave functions that account for the electron-electron cusp and describe the Coulomb hole in an accurate manner.

It is the purpose of the present article to briefly review the recent advances in explicitly-correlated theory (R12 and F12 approaches, *vide infra*) and to summarize the achievents made in this field with respect to the analytic calculation of molecular properties including nuclear gradients. We begin by discussing the early R12 theory of Kutzelnigg and proceed by reviewing the more recent F12 theory and the calculation of analytic derivatives.

1.1 Early R12 theory

In 1985, Kutzelnigg [3] suggested to supplement conventional configuration-interaction wave functions with two-electron basis functions of the type $r_{12}\phi_i(1)\phi_j(2)$, where r_{12} is the distance between the electrons 1 and 2, and where ϕ_i and ϕ_j are occupied orbitals of the Hartree-Fock reference determinant. For molecular many-electron systems, this approach was first implemented at the level of second-order Møller-Plesset perturbation theory and was denoted as MP2-R12 theory [4]. Similar implementations at the configuration-interaction, coupled-electron-pair approximation [5], and coupled-cluster levels (CC-R12) followed shortly thereafter [6,7].

Using linear r_{12} terms in the many-electron wave function dramatically improved the convergence towards the limit of a complete one-electron basis. In Dunning's [8] correlation-consistent cc-pVXZ basis, for example, the basis-set error had been reduced from $\propto \mathrm{X}^{-3}$ for conventional expansions [9] to $\propto \mathrm{X}^{-7}$ for R12-type wave functions [10].

Until 2002, the R12 approaches had employed linear r_{12} terms and a single set of atomic basis functions, that is, Gaussians. This basis set was used both for expanding the Hartree-Fock orbitals and for the approximate resolution of the identity (RI) that was inserted into the three- and four-electron integrals to factorize these into sums of products of two-electron integrals. This required the use of very large basis sets. Nevertheless, highly accurate correlation energies of benchmark quality were obtained for small systems, that is, for few-electron atoms and molecules [11].

The R12 methods were used mainly to obtain MP2 and coupled-cluster energies close to the limit of a complete basis set. On a few occasions, static electric properties such as dipole moments, polarizabilities, and first and second hyperpo-

larizabilities were computed by numerical differentiation, for example for the four-electron systems Be [12], LiH [13], and He_2 [14]. Other examples include the numerical calculation of the dipole moments of BH and HF [15] and the relativistic two-electron Darwin energies of Ne and HF [16]. Molecular geometries were usually kept fixed, but Refs. [17] and [18] provide examples of partial geometry optimizations of the (protonated) water dimer by means of point-wise energy calculations. More recently, but still using R12 wave functions, such a point-wise numerical approach was applied to obtain the basis-set-limit equilibrium geometries [19] of a series of closed- and open-shell molecules as well as their harmonic vibrational frequencies [20].

1.2 Modern F12 theory

The introduction of an auxiliary basis set (ABS) for the intrinsic RI approximation in 2002 [10] revolutionized the R12 approach. This new ABS approach was soon further improved by switching to a complementary auxiliary basis set (CABS) [21]. Density-fitting (DF) techniques were developed for the two-electron integrals that occur in R12 theory [22], the linear r_{12} terms were replaced by much more efficient Slater-type geminals (STGs) of the form $\exp(-\zeta r_{12})$ [23], an approximation was introduced to avoid two-electron integrals over the commutator between the operators of kinetic energy and r_{12} [24], and it was proposed to keep the amplitudes of the R12 geminals fixed at values that follow from Kato's cusp condition [25].

When using STGs or other functions of r_{12}, Møller-Plesset perturbation theory is referred to as MP2-F12 theory (in place of MP2-R12 theory) to highlight the fact that the function $f(r_{12})$ is used in place of r_{12} itself. Today, MP2-F12 theory is applied using the aforementioned techniques and approximations that have become available since about 2003. These include STGs, CABS, DF, the commutator approximation, and fixed amplitudes [26–32]. The MP2-R12 and MP2-F12 theories have recently been reviewed in Ref. [33].

Although the focus of the present article is on MP2-F12 theory, we notice that explicitly-correlated coupled-cluster theory, for example CCSD-F12, has developed in a similar manner as MP2-F12 theory since about 2004. With respect to coupled-cluster theory, we refer the reader to Refs. [34–48] and the references therein.

Not only at the R12 level but also at the F12 level, equilibrium geometries and harmonic vibrational frequencies have been obtained by means of point-wise energy calculations [49–52].

1.3 Analytic gradients

Recently, Kordel *et al.* implemented the analytic calculation of the density matrix for relaxed first-order molecular properties at the level of MP2-R12 theory [53]. Also the analytic calculation of nuclear gradients was accomplished at the MP2-

R12 level [54], however without using an auxiliary basis set (neither ABS nor CABS).

In these previous works by Kordel and co-workers, [53,54] only Ansatz 1 of MP2-R12 theory was considered. Nuclear gradients were implemented using standard approximation A, that is, at the MP2-R12/1A level. Furthermore, the same basis of atomic orbitals used to expand the Hartree-Fock orbitals was used for the RI approximation to simplify the theory. And finally, whereas Kordel *et al.* conducted their implementation in the Dalton program [55] at the MP2-R12 level, the present article addresses the implementation of the analytic calculation of nuclear gradients of density-fitted RI-MP2-F12 theory in the Turbomole program [56].

2. Theory

2.1 The MP2-F12 Hylleraas functional

In terms of spin orbitals from an unrestricted Hartree-Fock (UHF) reference determinant, the Ansatz for the first-order wave function is

$$\begin{aligned} |\Psi^{(1)}\rangle &= \left(\hat{\mathcal{T}}_2^{(1)} + \hat{\mathcal{T}}_{2'}^{(1)}\right)|\mathrm{HF}\rangle \\ &= \sum_{i>j}\sum_{a>b} t_{ij}^{ab}|_{ij}^{ab}\rangle + \sum_{i>j}\sum_{\mathbf{k}>\mathbf{l}} c_{ij}^{\mathbf{kl}} \sum_{\alpha\beta} \bar{F}_{\mathbf{kl}}^{\alpha\beta}|_{ij}^{\alpha\beta}\rangle, \end{aligned} \tag{1}$$

with $\bar{F}_{\mathbf{kl}}^{\alpha\beta} = \langle \mathbf{kl}|f_{12}\hat{Q}_{12}|\alpha\beta\rangle$, $f_{12} = \exp(-\zeta r_{12})$, and $\hat{Q}_{12}$ is the projection operator that ensures strong orthogonality. In the following, $|xy\rangle$ denotes an antisymmetrized product of spin orbitals. The lower-case indices $i,j,k,...$ denote active occupied orbitals. Bold letters refer to the F12 excitations, usually into a geminal constructed from a pair of occupied orbitals

$$\hat{Q}_{12} f_{12}|\mathbf{kl}\rangle. \tag{2}$$

Capital letters indicate all occupied orbitals (frozen + active). $c_{ij}^{\mathbf{kl}}$ are the amplitudes of the F12 excitations, which can be determined either variationally or held fixed according to Ten-no's rational generator approach [25].

Throughout this article, we use Ansatz 2 for the projection operator,

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

where $\hat{O} = \Sigma_I\, |I\rangle\langle I|$ is the projector onto all occupied orbitals and $\hat{V} = \Sigma_a\, |a\rangle\langle a|$ the projector onto all virtual orbitals. Inserting the Ansatz for $\Psi^{(1)}$ into the Hylleraas functional yields

$$\begin{aligned}\mathcal{H}_{\text{MP2-F12}} &= \sum_{i>j}\sum_{a>b} t_{ij}^{ab}\left[2\bar{g}_{ab}^{ij} + (\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j)t_{ij}^{ab}\right] \\ &+ \sum_{i>j}\sum_{\mathbf{k}>\mathbf{l}} c_{ij}^{\mathbf{kl}}\left[2\bar{V}_{\mathbf{kl}}^{ij} + \sum_{\mathbf{m}>\mathbf{n}} \bar{B}_{\mathbf{kl},\mathbf{mn}}^{(ij)} c_{ij}^{\mathbf{mn}}\right] \\ &+ 2\sum_{i>j}\sum_{a>b} t_{ij}^{ab}\sum_{\mathbf{k}>\mathbf{l}} \bar{C}_{\mathbf{kl}}^{ab} c_{ij}^{\mathbf{kl}},\end{aligned} \tag{4}$$

with the antisymmetrized (indicated by a bar) integrals

$$\bar{g}_{ab}^{ij} = \langle ab|r_{12}^{-1}|ij\rangle, \tag{5}$$

$$\bar{C}_{\mathbf{kl}}^{ab} = \langle \mathbf{kl}|f_{12}\hat{Q}_{12}(\hat{F}_1 + \hat{F}_2)|ab\rangle \overset{\text{EBC}}{\approx} 0, \tag{6}$$

$$\bar{V}_{\mathbf{kl}}^{ij} = \langle \mathbf{kl}|f_{12}\hat{Q}_{12}r_{12}^{-1}|ij\rangle, \tag{7}$$

$$\begin{aligned}\bar{B}_{\mathbf{kl},\mathbf{mn}}^{(ij)} &= \langle \mathbf{kl}|f_{12}\hat{Q}_{12}(\hat{F}_1 + \hat{F}_2 - \epsilon_i - \epsilon_j)\hat{Q}_{12}f_{12}|\mathbf{mn}\rangle \\ &\overset{A}{\approx} \frac{1}{2}\langle \mathbf{kl}|\left(f_{12}\hat{Q}_{12}[\hat{T}_{12}, f_{12}] + [f_{12}, \hat{T}_{12}]\hat{Q}_{12}f_{12}\right)|\mathbf{mn}\rangle.\end{aligned} \tag{8}$$

$\hat{F}_1$ and $\hat{F}_2$ are the Fock operators for electrons 1 and 2, and $\hat{T}_{12}$ is the sum of the operators of kinetic energy for electrons 1 and 2. The MP2-F12 energy is obtained by minimizing $\mathcal{H}_{\text{MP2-F12}}$ with respect to the amplitudes t_{ij}^{ab} and $c_{ij}^{\mathbf{kl}}$.

The off-diagonal block Eq. (6) of the Fock matrix vanishes ($C_{\mathbf{kl}}^{ab} = 0$) if we assume that the extended Brillouin condition (EBC) [33] holds. This is equivalent with assuming that the canonical virtual orbitals are exact eigenfunctions of the Fock operator. We attach an asterisk to the method's acronym if the EBC is assumed (here: 2*).

In approximation A [33], terms with the exchange operator involved are neglected, including the orbital energies. The remaining contributions are shown in Eq. (8). Considerable amounts of computation time are saved by computing the integrals over the operator $[\hat{T}_{12}, f_{12}]$ in Eq. (8) using the approach proposed by Kedžuch [24]. In this approach, the exact operator is approximated with for example the matrix representation of $\hat{T} + \hat{V}$ (the bare nuclear Hamiltonian), which we use by default in our MP2-F12 calculations with Turbomole.

In addition to improving the description of elecron correlation, we also include a correction to the Hartree-Fock energy obtained from treating single excitations into the CABS by perturbation theory,

$$E_{\text{CABS}} = \sum_{I,p'} c_I^{p'} F_{Ip'} = \sum_{I,p'} \frac{F_{Ip'}^2}{\epsilon_I - \epsilon_{p'}}, \tag{9}$$

where the CABS is denoted as $\{p'\}$. It is understood that the Hartree-Fock basis functions as well as the CABS have been rotated among themselves in such a manner that the Hartree-Fock...Hartree-Fock and CABS...CABS blocks of the Fock matrix $\mathbf{F}$ are diagonal, and the diagonal elements are given by the orbital

energies ε_I and $\varepsilon_{p'}$. This provides a balanced description (in terms of accuracy) of the Hartree-Fock reference and the correlation part. The $F_{ap'}$ off-diagonal elements, which give rise to certain coupling terms [35,46,57], have so far been neglected in our work.

2.2 Level of approximation

With respect to the implementation of analytic nuclear gradients in Turbomole, we aim at the MP2-F12/2^*A [T+V] level. Despite the many approximations that are involved to allow for efficient calculations, this level captures all main effects for both properties and geometries, as explained in the following.

The most important improvement is obtained by switching from Ansatz 1 to 2 and from R12 to F12 theory. In terms of basis-set quality, it has been shown that quintuple-zeta quality results are obtained using Ansatz 2 of F12 theory in just a triple-zeta basis [34].

Table 1 demonstrates that the differences between the equilibrium geometries obtained with the Ansätze 2 and 2^* are very small, for both approximations A and B. Note that the effects of changing the basis set from cc-pVTZ-F12 to cc-pVQZ-F12 are larger than the differences between the four MP2-F12 Ansätze. The results furthermore show that in basis sets of cc-pVTZ-F12 quality and better, the differences between approximations A and B are insignificant, such that it seems sufficient to only consider standard approximation A.

Table 2 indicates that the CABS singles term should be included when considering the calculation of nuclear gradients, especially in comparably small (*e.g.*, cc-pVDZ-F12) basis sets. The CABS singles effects are an order of magnitude larger than the effects of using one of the Ansätze 2A, 2A*, 2B, or 2B*. When including the CABS singles correction, the first derivative of the MP2-F12 energy with respect to a perturbation α to the one-electron Hamiltonian can be written as

$$\left.\frac{\mathrm{d}E_{\text{MP2-F12}}}{\mathrm{d}\alpha}\right|_{\alpha=0} = \sum_{\mu\nu}\left(z_{\mu\nu} + d_{\mu\nu}^{\text{MP2}} + d_{\mu\nu}^{\text{F12}} + d_{\mu\nu}^{\text{CABS}}\right)\left.\frac{\partial h_{\mu\nu}}{\partial\alpha}\right|_{\alpha=0} . \tag{10}$$

$\mathbf{d}^{\text{MP2}}$ is the unrelaxed density matrix of standard MP2 theory. Because we restrict our implementation to standard approximation A, the F12-part of the unrelaxed density matrix vanishes, $\mathbf{d}^{\text{F12}} = \mathbf{0}$ [53]. The CABS singles part of the unrelaxed density matrix, however, is nonzero,

$$d_{IJ}^{\text{CABS}} = -\sum_{p'} c_I^{p'} c_J^{p'} ,\; d_{p'q'}^{\text{CABS}} = \sum_I c_I^{p'} c_I^{q'} ,\; d_{Ip'}^{\text{CABS}} = d_{p'I}^{\text{CABS}} = c_I^{p'} . \tag{11}$$

For simplicity, the density matrix is given in the MO basis. Note that the basis set $\{\mu\}$ in Eq. (10) is the union of the orbital basis and CABS.

To calculate relaxed first-order properties, the response of the Hartree-Fock orbitals has to be taken into account. This is achieved via the Lagrangian multipliers $\mathbf{z}$, which are obtained when solving the linear z-vector equation [53]

Table 1. Effect of the Ansatz (2A, 2A*, 2B, or 2B*) of MP2-F12 theory on the equilibrium geometry of a few selected molecules. The CABS singles contribution is not included.

Basis	Molecule	Parameter	2A	2A*	2B	2B*
cc-pVDZ-F12	CH_2 ($^1A_1$)	R_{CH}/pm	110.38	110.36	110.35	110.33
		$\angle_{HCH}$/°	102.03	102.02	102.02	102.02
	CO	R_{CO}/pm	113.79	113.82	113.80	113.81
	H_2O	R_{OH}/pm	96.11	96.12	96.10	96.11
		$\angle_{HOH}$/°	104.16	104.16	104.18	104.18
	HF	R_{FH}/pm	92.14	92.15	92.14	92.14
	NH_3	R_{NH}/pm	101.25	101.26	101.22	101.22
		$\angle_{HNH}$/°	106.39	106.34	106.47	106.43
	OH	R_{OH}/pm	96.92	96.92	96.91	96.91
cc-pVTZ-F12	CH_2 ($^1A_1$)	R_{CH}/pm	110.25	110.25	110.26	110.26
		$\angle_{HCH}$/°	102.24	102.24	102.22	102.22
	CO	R_{CO}/pm	113.41	113.40	113.42	113.41
	H_2O	R_{OH}/pm	95.90	95.90	95.90	95.90
		$\angle_{HOH}$/°	104.36	104.35	104.35	104.34
	HF	R_{FH}/pm	91.94	91.95	91.95	91.95
	NH_3	R_{NH}/pm	101.00	100.99	101.00	101.00
		$\angle_{HNH}$/°	106.97	106.96	106.97	106.96
	OH	R_{OH}/pm	96.71	96.71	96.72	96.71
cc-pVQZ-F12	CH_2 ($^1A_1$)	R_{CH}/pm	110.22	110.21	110.22	110.22
		$\angle_{HCH}$/°	102.29	102.28	102.28	102.28
	CO	R_{CO}/pm	113.38	113.37	113.39	113.38
	H_2O	R_{OH}/pm	95.85	95.85	95.85	95.85
		$\angle_{HOH}$/°	104.39	104.39	104.39	104.38
	HF	R_{FH}/pm	91.86	91.86	91.86	91.86
	NH_3	R_{NH}/pm	100.96	100.97	100.97	100.97
		$\angle_{HNH}$/°	107.00	107.00	106.99	106.99
	OH	R_{OH}/pm	96.67	96.66	96.67	96.67

$$\sum_{b,J} z_{bJ} \left(2\delta_{ab}\delta_{IJ}(\epsilon_b - \epsilon_J) + A_{bJaI}\right) = A_{aI}, \tag{12}$$

where A_{bJaI} is the coupled-perturbed Hartree-Fock (CPHF) matrix. We proceed by discussing the contributions to the right-hand side A_{aI}.

2.3 Orbital-relaxed first-order properties

In Ref. [53], only Ansatz 1 of MP2-F12 theory was considered, because the projection operator in this Ansatz is not effected by changes in the Hartree-Fock orbitals. In Ansatz 2, however, the projection operator of Eq. (3) is approximated as

$$\hat{Q}_{12} \approx \hat{Q}_{12}^{\mathrm{RI}} = 1 - \hat{P}_1\hat{P}_2 - \hat{O}_1\hat{P}'_2 - \hat{P}'_1\hat{O}_2. \tag{13}$$

Table 2. Equilibrium geometries of selected molecules optimized at the MP2-F12/2A and MP2-F12/2B levels including the CABS singles contribution.

Basis	Molecule	Parameter	2A	2B
cc-pVDZ-F12	CH_2 ($^1A_1$)	R_{CH}/pm	110.31	110.28
		$\angle_{HCH}$/°	102.16	102.15
	CO	R_{CO}/pm	113.48	113.49
	H_2O	R_{OH}/pm	95.89	95.88
		$\angle_{HOH}$/°	104.29	104.31
	HF	R_{FH}/pm	91.89	91.89
	NH_3	R_{NH}/pm	101.04	101.01
		$\angle_{HNH}$/°	106.84	106.92
	OH	R_{OH}/pm	96.70	96.69

Whereas the projector $\hat{P}'$ onto the CABS is invariant under orbital rotations, the projector $\hat{O}$ onto the space spanned by the occupied Hartree-Fock orbitals is not.

In the following, we shall distinguish beween inner and outer derivatives, where the outer derivatives are those with respect to the orbital indices of the matrices **B** and **V** and the inner derivatives those with respect to the projection operator $\hat{O}$. For simplicity, we only consider (active) occupied orbitals for the F12 excitations. Bold letters are thus omitted in the following.

In approximation A, we can write the F12 part of the Hylleraas functional of Eq. (4) as

$$\begin{aligned} \mathcal{H}_{\mathrm{F12}} &= \sum_{k>l}\sum_{m>n} D_{kl,mn}\bar{B}_{kl,mn} + 2\sum_{k>l}\sum_{m>n} c_{kl}^{mn}\bar{V}_{mn}^{kl}, \\ D_{kl,mn} &= \sum_{i>j} c_{ij}^{kl}c_{ij}^{mn}. \end{aligned} \tag{14}$$

The outer derivatives lead to the contribution [53]

$$A_{ai}^{\mathrm{outer}} = 2\sum_{l}\sum_{m>n}\left(D_{il,mn}\bar{B}_{al,mn} + c_{il}^{mn}\bar{V}_{mn}^{al} + c_{mn}^{il}\bar{V}_{al}^{mn}\right). \tag{15}$$

Inner derivatives arise from the contribution

$$-\langle mn|f_{12}\left(\hat{O}_1\hat{P}_2' + \hat{P}_1'\hat{O}_2\right)r_{12}^{-1}|kl\rangle \tag{16}$$

to the matrix element $\bar{V}_{mn}^{kl}$ from which we obtain

$$A_{aI}^{\mathrm{inner,V}} = -2\sum_{k>l}\sum_{m>n} c_{kl}^{mn}\sum_{p'}\left(\bar{f}_{mn}^{Ip'}\bar{g}_{ap'}^{kl} + \bar{f}_{mn}^{ap'}\bar{g}_{Ip'}^{kl}\right), \tag{17}$$

with $\bar{f}_{pq}^{rs} = \langle pq|f_{12}|rs\rangle$. The corresponding contribution from the projection operators $\hat{O}_1$ and $\hat{O}_2$ in the matrix element $\bar{B}_{kl,mn}$ is

$$A_{aI}^{\mathrm{inner,B}} = -\sum_{k>l}\sum_{m>n} D_{kl,mn}\sum_{p'}\left(\bar{f}_{mn}^{Ip'}\bar{t}_{ap'}^{kl} + \bar{f}_{mn}^{ap'}\bar{t}_{Ip'}^{kl}\right), \tag{18}$$

with $\bar{t}_{pq}^{rs} = \langle pq|[\hat{T}_{12}, f_{12}]|rs\rangle$. Note that in our implementation, the integrals $\bar{t}_{pq}^{rs}$ are evaluated using the matrix representation of the bare nuclear Hamiltonian (*cf.* Section 2.2).

Table 3. Basis-set combinations used in the present work. MP2-fitting basis sets (cbas) are labeled with 'C-'.

Notation	X	Basis-set name	CABS	cbas
aVXZ	D, T, Q, 5	aug-cc-pVXZ	C-aug-cc-pVQZ	C-aug-cc-pV5Z
aV6Z		aug-cc-pV6Z	C-aug-cc-pVQZ	C-aug-cc-pV6Z
aVXZ-F12[a]	D, T, Q	aug-cc-pVXZ-F12	cc-pVXZ-F12	C-aug-cc-pwCV5Z

[a] The aVXZ-F12 basis was obtained by adding the diffuse functions of the aug-cc-pVXZ basis to the cc-pVXZ-F12 basis.

The final contribution to A_{aI} comes from the CABS singles correction,

$$\begin{aligned} A_{aI}^{\mathrm{CABS}} &= 2\sum_{p',q'} d_{p'q'}\,\bar{g}_{Ip'}^{aq'} - 2\sum_{K,L} d_{KL}\,\bar{g}_{IK}^{aL} + 2\sum_{p'} d_{Ip'}F_{p'a} \\ &+ 2\sum_{K,p'} d_{Kp'}\left(\bar{g}_{Ip'}^{aK} + \bar{g}_{ap'}^{IK}\right). \end{aligned} \tag{19}$$

Inactive occupied-active occupied orbital rotations must be taken into account in the frozen-core approximation. The corresponding equation is analogous to Eq. (15) and is obtained by replacing the virtual index a by a frozen-occupied index (*cf.* Ref. [53]).

3. Example calculations

3.1 Computational details

The analytic calculation of relaxed first-order properties has been implemented in the Ricc2 module [58,59] of the Turbomole package [56]. The geometries of CH_2 ($^1A_1$), H_2O, NH_3, HF, and CO were taken from Ref. [60] while R_{ClO} = 155.60 pm and R_{OH} = 97.00 pm were used for ClO and OH, respectively. Dunning's aug-cc-pVXZ basis sets [8,61] were used with X = D, T, Q, 5, 6. As CABS, we used the MP2-fitting C-aug-cc-pVQZ [62] basis. For the density-fitting approximation, we used the MP2-fitting C-aug-cc-pVXZ (X = 5, 6) and C-aug-cc-pwCV5Z basis sets [63] (cbas). We have also used Peterson's cc-pVXZ-F12 basis set with X = D, T, Q [64], to which we added additional diffuse functions (aug-cc-pVXZ-F12) taken from Dunning's correlation consistent sets [61] (since the cc-pVXZ-F12 sets are already rather diffuse, the additional diffuse functions were sometimes strongly overlapping with existing functions, but this did not lead to numerical problems). The MP2-F12 calculations in the aug-cc-pVXZ-F12 basis sets were carried out with the corresponding optimized cc-pVXZ-F12 CABS [65]. Table 3 summarizes the basis-set combinations used.

Depending on the Ansatz and approximations, Fock matrix elements of the type $F_{pq'}$ are needed in MP2-F12 theory. Such matrix elements are computed invoking the RI-*JK* approximation using an exchange-fitting basis [66] (note that this approximation is not used in the underlying Hartree-Fock calculation, in

which only elements F_{pq} are needed). No exchange-fitting basis (jkbas) is needed for standard approximation A of MP2-F12 theory, but on a few occasions, we have computed first-order properties at the MP2-F12/2B level by numerical differentiation. In these calculations, we used the corresponding exchange-fitting basis set of Weigend [66] to represent the exchange operator for the extended Fock matrix.

A linear combination of six Gaussian geminals was used to represent the STG, with coefficients and exponents taken from Ref. [67]. The STG exponent was 1.4 a_0^{-1} except for the calculations in Peterson's (aug-)cc-pVXZ-F12 F12 basis sets, where we used the exponents recommended by Peterson [64] (0.9, 1.0, and 1.1 a_0^{-1} for X = D, T, and Q, respectively).

With respect to numerical differentiation, results were obtained from calculations in finite electric fields of strength $F = \pm 0.0005\ E_\mathrm{h}/(ea_0)$. The dipole moment was in this case obtained from a central-differences formula. Furthermore, the convergency criteria for the Hartree-Fock calculation were tightened to $10^{-10}\ E_\mathrm{h}$ change in energy (scfconv). The convergence criterion for the density matrix norm was also set to 10^{-10} (denconv).

Open-shell molecules were treated in a fully unrestricted formalism for both the Hartree-Fock (UHF) and correlation part (UMP2-F12).

Although the inclusion of spin-flipped geminals is necessary to fulfill the cusp conditions for *s* and *p* waves [68,69], we have used the diag option as described in Ref. [70] at the UMP2-F12 level for fixed amplitudes, since this was the only method available at the time of writing this article. Spin-flipped geminals are currently being implement in Turbomole for fixed as well as optimized amplitudes, using contracted geminals for the latter [71]. All calculations were carried out in the frozen-core approximation.

3.2 Results and discussion

From the orbital-relaxed one-electron density matrix, we have computed the dipole moments for a selection of closed- and open-shell molecules (Table 4) in the aVXZ-F12 basis sets of Peterson [64]. In the present work, we are interested in the performance of the MP2-F12 method with respect to the convergence of the calculated dipole moment to the basis set limit of valence-shell MP2 theory. We therefore compare our computed dipole moments with the basis set limit of MP2 theory, but not with experimental values. For such a comparison between theory and experiment, high-order correlation and vibrational effects should be taken into account [72]. To estimate the basis set limits, we have performed various calculations in large basis sets for closed- and open-shell molecules (Table 5). Applying the X^{-3} extrapolation of Helgaker *et al.* [9] to the aV5Z and aV6Z correlation contributions to the dipole moment yields values that are probably within $0.5\times10^{-3}\ ea_0$ of the basis-set limit. Our best estimates are obtained at the MP2-F12/2A* [T+V] + CABS singles level. Based on the excellent agreement with the MP2-F12/2B values, we assume that these estimates are accurate

Table 4. Dipole moments (in ea_0) obtained at the valence-shell MP2-F12/2A* level for a few selected closed-shell and open-shell molecules.

Basis	CABS singles	Amp.[a]	H_2O	NH_3	OH	ClO
aVDZ-F12	No	Opt.	0.74572	0.61631	0.66716	0.49248
	No	Fix.	0.74538	0.61620	0.66611	0.49291
	Yes	Opt.	0.74144	0.61543	0.66400	0.48890
	Yes	Fix.	0.74110	0.61532	0.66294	0.48933
aVTZ-F12	No	Opt.	0.73765	0.61167	0.66175	0.49018
	No	Fix.	0.73756	0.61159	0.66153	0.49045
	Yes	Opt.	0.73674	0.61129	0.66113	0.48952
	Yes	Fix.	0.73665	0.61122	0.66091	0.48981
aVQZ-F12	No	Opt.	0.73575	0.61047	0.66048	0.48819
	No	Fix.	0.73573	0.61044	0.66042	0.48827
	Yes	Opt.	0.73570	0.61044	0.66046	0.48824
	Yes	Fix.	0.73567	0.61041	0.66040	0.48832
Limit			0.7353	0.6102	0.6603	0.4884

[a] The F12 amplitudes are either optimized (Opt.) or kept fixed (Fix.).

Table 5. Estimates of the valence-shell MP2 basis-set limits for dipole moments (in ea_0) of a few selected closed-shell and open-shell molecules.

Method	Basis	H_2O	NH_3	OH	ClO
MP2	aV(56)Z[a]	0.73504	0.61000	0.65993	0.48845
MP2-F12/2B[b]	aV5Z	0.73534	0.61020	0.66031	0.48877
MP2-F12/2A*	aV6Z	0.73536	0.61024	0.66028	0.48829
MP2-F12/2A*+CABS[c]	aV6Z	0.73534	0.61023	0.66026	0.48845

[a] The Hartree-Fock contribution was calculated in the aV6Z basis while the correlation contribution was X^{-3} extrapolated from the aV5Z and aV6Z results as described in Ref. [15].
[b] From numerical differentiation.
[c] CABS singles included.

to within 1×10^{-4} ea_0. In the large aV6Z Basis, the CABS singles contribute only little to the dipole moments, from which we conclude that the underlying Hartree-Fock limit has been approached closely ($\approx 5\times10^{-5}$ ea_0).

Table 4 shows that with the aVXZ-F12 (X = D, T, Q) basis sets, the results converge smoothly and rapidly to the basis-set limit. Including CABS singles, the MP2-F12/2A*/aVDZ-F12 level yields results to within ca. 0.004 ea_0 of the basis-set limit. In this basis, the CABS singles contribution is significant. It is of the same order of magnitude as the remaining basis-set error at this level.

In the aVTZ-F12 basis, the CABS singles contributions are an order of magnitude smaller than in the aVDZ-F12 basis. Also the differences between the results obtained with optimized and fixed F12 amplitudes are an order of magnitude smaller than in the aVDZ-F12 basis.

Table 6. Dipole moment (in ea_0) of HBr obtained at the valence-shell MP2 level[a,b].

Method	MP2	MP2-F12	MP2-F12 + CABS singles
aVDZ	0.35349	0.36836	0.34976
aVTZ	0.33133	0.34539	0.34308
aVQZ	0.33647	0.34363	0.34256
aV5Z	0.33892	0.34305	0.34232

[a] At internuclear distance R_{HBr} = 140.75 pm.
[b] MP2-F12 refers to the MP2-F12/2A* [T+V] level.

The aVQZ-F12 basis yields converged results, that is, with remaining basis-set errors of $O(10^{-4})$ ea_0. Neither the CABS singles nor the optimized–fixed differences are significant at this level.

Finally, Table 6 shows results for the HBr molecule in the standard aVXZ basis sets with X = D, T, Q and 5. Obviously, the basis-set convergence of the MP2 dipole moments is much accellerated by the F12 terms. Whereas the basis-set error at the MP2/aVTZ level is of the order of 0.01 ea_0, this error is reduced to about 0.001 ea_0 at the MP2-F12/2A* level. In the aVTZ basis, the MP2-F12 approach benefits from the CABS singles contribution, which becomes less important in the aVQZ and aV5Z basis sets. Futhermore, whereas the MP2-F12+CABS approach yields very satifactory results in the aVTZ, aVQZ, and aV5Z basis sets, the aVDZ basis appears to be inadequate (note that at the MP2/aVDZ level, the calculated dipole moment is larger than the anticipated basis-set limit of ca. 0.342 ea_0).

Concerning computation times, we note that the analytic calculation of first-order properties is *m* times more involved than a single-point energy calculation, where *m* depends on the one-particle basis set. For a molecule such as methanol, the factor *m* is roughly 9, 7, and 5 for the basis sets aVDZ-F12, aVTZ-F12, and aVQZ-F12, respectively.

4. Conclusions

Numerical geometry optimizations at various levels of MP2-F12 theory have shown that it seems legitimate to assume the extended Brillouin condition to simplify the analytic calculation of energy derivatives while it is worthwhile to account for single excitations into the complementary auxiliary basis. Furthermore, it seems sufficient to restrict this analytic calculation to standard approximation A of MP2-F12 theory. Smooth and rapid convergence towards the basis-set limit is observed for the dipole moments of a selection of small molecules when calculated at the MP2-F12/2A* level in augmented cc-pVXZ-F12 basis sets (aVXZ-F12).

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References

1. T. Helgaker, W. Klopper, D. P. Tew, Mol. Phys. **106** (2008) 2107.
2. T. H. Dunning Jr, K. A. Peterson, D. E. Woon, in *Encyclopedia of Computational Chemistry*, edited by P.v.R. Schleyer, *et al.* (Wiley, New York, 1998), Vol. 1, p. 88.
3. W. Kutzelnigg, Theor. Chim. Acta **68** (1985) 445.
4. W. Klopper, W. Kutzelnigg, Chem. Phys. Lett. **134** (1987) 17.
5. W. Klopper, R. Röhse, W. Kutzelnigg, Chem. Phys. Lett. **178** (1991) 455.
6. J. Noga, W. Kutzelnigg, W. Klopper, Chem. Phys. Lett. **199** (1992) 497.
7. J. Noga, W. Kutzelnigg, J. Chem. Phys. **101** (1994) 7738.
8. T. H. Dunning Jr., J. Chem. Phys. **90** (1989) 1007.
9. T. Helgaker, W. Klopper, H. Koch, J. Noga, J. Chem. Phys. **106** (1997) 9639.
10. W. Klopper, C. C. M. Samson, J. Chem. Phys. **116** (2002) 6397.
11. J. Noga, P. Valiron, W. Klopper, J. Chem. Phys. **115** (2001) 2022; *ibid.* **115** (2001) 5690 (Erratum); *ibid.* **117** (2002) 2989 (Erratum).
12. D. Tunega, J. Noga, W. Klopper, Chem. Phys. Lett. **269** (1997) 435.
13. D. Tunega, J. Noga, Theor. Chem. Acc. **100** (1998) 78.
14. M. Jaszuński, W. Klopper, J. Noga, J. Chem. Phys. **113** (2000) 71.
15. A. Halkier, W. Klopper, T. Helgaker, P. Jørgensen, J. Chem. Phys. **111** (1999) 4424.
16. A. Halkier, T. Helgaker, W. Klopper, J. Olsen, Chem. Phys. Lett. **319** (2000) 287.
17. A. A. Auer, T. Helgaker, W. Klopper, Phys. Chem. Chem. Phys. **2** (2000) 2235.
18. W. Klopper, J. G. C. M. van Duijneveldt-van de Rijdt, F. B. van Duijneveldt, Phys. Chem. Chem. Phys. **2** (2000) 2227.
19. M. Heckert, M. Kállay, D. P. Tew, W. Klopper, J. Gauss, J. Chem. Phys. **125** (2006) 044108.
20. D. P. Tew, W. Klopper, M. Heckert, J. Gauss, J. Phys. Chem. A **111** (2007) 11242.
21. E. F. Valeev, Chem. Phys. Lett. **395** (2004) 190.
22. F. R. Manby, J. Chem. Phys. **119** (2003) 4607.
23. S. Ten-no, Chem. Phys. Lett. **398** (2004) 56.
24. S. Kedžuch, M. Milko, J. Noga, Int. J. Quantum Chem. **105** (2005) 929.
25. S. Ten-no, J. Chem. Phys. **121** (2004) 117.
26. H.-J. Werner, T. B. Adler, F. R. Manby, J. Chem. Phys. **126** (2007) 164102.
27. H.-J. Werner, F. R. Manby, J. Chem. Phys. **124** (2006) 054114.
28. F. R. Manby, H.-J. Werner, T. B. Adler, A. J. May, J. Chem. Phys. **124** (2006) 094103.
29. S. Höfener, F. A. Bischoff, A. Glöß, W. Klopper, Phys. Chem. Chem. Phys. **10** (2008) 3390.
30. F. A. Bischoff, S. Höfener, A. Glöß, W. Klopper, Theor. Chem. Acc. **121** (2008) 11.
31. T. B. Adler, H.-J. Werner, F. R. Manby, J. Chem. Phys. **130** (2009) 054106.
32. F. A. Bischoff, S. Wolfsegger, D. P. Tew, W. Klopper, Mol. Phys. **107** (2009) 963.
33. W. Klopper, F. R. Manby, S. Ten-no, E. F. Valeev, Int. Rev. Phys. Chem. **25** (2006) 427.

34. D. P. Tew, W. Klopper, C. Neiss, C. Hättig, Phys. Chem. Chem. Phys. **9** (2007) 1921; *ibid.* **10** (2008) 6325 (Erratum).
35. T. B. Adler, G. Knizia, H.-J. Werner, J. Chem. Phys. **127** (2007) 221106.
36. D. P. Tew, W. Klopper, C. Hättig, Chem. Phys. Lett. **452** (2008) 326.
37. A. Köhn, G. W. Richings, D. P. Tew, J. Chem. Phys. **129** (2008) 201103.
38. E. F. Valeev, Phys. Chem. Chem. Phys. **10** (2008) 106.
39. M. Torheyden and E. F. Valeev, Phys. Chem. Chem. Phys. **10** (2008) 3410.
40. J. Noga, S. Kedžuch, J. Šimunek, S. Ten-no, J. Chem. Phys. **128** (2008) 174103; *ibid.* **130** (2009) 029901 (Erratum).
41. E. F. Valeev and T. D. Crawford, J. Chem. Phys. **128** (2008) 244113.
42. T. Shiozaki, M. Kamiya, S. Hirata, E. F. Valeev, Phys. Chem. Chem. Phys. **10** (2008) 3358.
43. T. Shiozaki, M. Kamiya, S. Hirata, E. F. Valeev, J. Chem. Phys. **129** (2008) 071101.
44. D. Bokhan, S. Bernadotte, S. Ten-no, Chem. Phys. Lett. **469** (2009) 214.
45. T. Shiozaki, M. Kamiya, S. Hirata, E. F. Valeev, J. Chem. Phys. **130** (2009) 054101.
46. G. Knizia, T. B. Adler, and H.-J. Werner, J. Chem. Phys. **130** (2009) 054104.
47. A. Köhn, J. Chem. Phys. **130** (2009) 131101.
48. T. B. Adler, H.-J. Werner, J. Chem. Phys. **130** (2009) 241101.
49. J. J. Lee, S. Höfener, W. Klopper, T. N. Wassermann, M. A. Suhm, J. Phys. Chem. C **113** (2009) 10929.
50. G. Rauhut, G. Knizia, H.-J. Werner, J. Chem. Phys. **120** (2009) 054105.
51. P. Botschwina, R. Oswald, G. Knizia, H.-J. Werner, Z. Phys. Chem. **223** (2009) 447.
52. D. P. Tew, W. Klopper, R. A. Bachorz, C. Hättig, in *Handbook of High-Resolution Spectroscopies.* F. Merkt, M. Quack (Eds.), Wiley, Chichester (in press).
53. E. Kordel, C. Villani, W. Klopper, J. Chem. Phys. **122** (2005) 214306.
54. E. Kordel, C. Villani, W. Klopper, Mol. Phys. **105** (2007) 2565.
55. Dalton, a molecular electronic structure program, release 2.0, 2005; available from: http://www.kjemi.uio.no/software/dalton/dalton.html.
56. TURBOMOLE V6.0 2009, a development of Universität Karlsruhe (TH) and Forschungszentrum Karlsruhe GmbH, 1989–2007, Turbomole GmbH, since 2007; available from http://www.turbomole.com.
57. G. Knizia, H.-J. Werner, J. Chem. Phys. **128** (2008) 154103.
58. C. Hättig, F. Weigend, J. Chem. Phys. **113** (2000) 5154.
59. C. Hättig, J. Chem. Phys. **118** (2003) 7751.
60. W. Kopper, J. Chem. Phys. **120** (2004) 10890.
61. R. A. Kendall, T. H. Dunning Jr., R. J. Harrison, J. Chem. Phys. **96** (1992) 6796.
62. F. Weigend, A. Köhn, C. Hättig, J. Chem. Phys. **116** (2002) 3175.
63. C. Hättig, Phys. Chem. Chem. Phys. **7** (2005) 59.
64. K. A. Peterson, T. B. Adler, H.-J. Werner, J. Chem. Phys. **128** (2008) 084102.
65. K. E. Yousaf, K. A. Peterson, J. Chem. Phys. **129** (2008) 184108.
66. F. Weigend, J. Comput. Chem. **29** (2007) 167.
67. D. P. Tew, W. Klopper, J. Chem. Phys. **123** (2005) 074101.
68. D. Bokhan, S. Ten-no, J. Noga, Phys. Chem. Chem. Phys. **10** (2008) 3320.
69. D. Bokhan, S. Bernadotte, S. Ten-no, J. Chem. Phys. **131** (2009) 084105.
70. TURBOMOLE V6.0 2009, User's Manuel, Turbomole GmbH, Karlsruhe, 2009, Section 9.5.
71. D. P. Tew, W. Klopper, Mol. Phys. **108** (2010) 315.
72. K. L. Bak, J. Gauss, T. Helgaker, P. Jørgensen, J. Olsen, Chem. Phys. Lett. **319** (2000) 563.