

Explicitly correlated RMP2 for high-spin open-shell reference states

Gerald Knizia and Hans-Joachim Werner

Citation: *J. Chem. Phys.* **128**, 154103 (2008); doi: 10.1063/1.2889388

View online: <http://dx.doi.org/10.1063/1.2889388>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v128/i15>

Published by the [American Institute of Physics](#).

Additional information on *J. Chem. Phys.*

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT

Instruments for advanced science

Gas Analysis



- dynamic measurement of reaction gas streams
- catalysis and thermal analysis
- molecular beam studies
- dissolved species probes
- fermentation, environmental and ecological studies

Surface Science



- UHV TPD
- SIMS
- end point detection in ion beam etch
- elemental imaging - surface mapping

Plasma Diagnostics



- plasma source characterization
- etch and deposition process
- reaction kinetic studies
- analysis of neutral and radical species

Vacuum Analysis



- partial pressure measurement and control of process gases
- reactive sputter process control
- vacuum diagnostics
- vacuum coating process monitoring

contact Hiden Analytical for further details

HIDEN
ANALYTICAL

info@hideninc.com
www.HidenAnalytical.com

CLICK to view our product catalogue



Explicitly correlated RMP2 for high-spin open-shell reference states

Gerald Knizia and Hans-Joachim Werner^{a)}*Institut für Theoretische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany*

(Received 11 January 2008; accepted 6 February 2008; published online 16 April 2008)

We present an explicitly correlated version of the high-spin open-shell RMP2 method. The theory is derived in a unitarily invariant form, which is suitable for the insertion of local approximations. It is demonstrated that the rapid basis set convergence of closed-shell MP2-F12 is also achieved in RMP2-F12, and similar *Ansätze* and approximations can be employed. All integrals are computed using efficient density fitting approximations, and many-electron integrals are avoided using resolution of the identity approximations. The performance of the method is demonstrated by benchmark calculations on a large set of ionization potentials, electron affinities and atomization energies. Using triple-zeta basis sets RMP2-F12 yields results that are closer to the basis set limit than standard RMP2 with augmented quintuple-zeta basis sets for all properties. Different variants of perturbative corrections for the open-shell Hartree–Fock treatment are described and tested. © 2008 American Institute of Physics. [DOI: 10.1063/1.2889388]

I. INTRODUCTION

Explicitly correlated methods^{1–7} greatly diminish the problem of basis set convergence, one of the worst bottlenecks encountered in traditional quantum chemical treatments. Such methods have seen tremendous advancements in theory and implementation recently: The introduction of auxiliary basis sets⁸ and complementary auxiliary basis sets⁹ (CABSs) for resolution of the identity (RI) approximations, density fitting (DF) approximations for the integrals,^{10,11} nonlinear correlation factors,^{12–14} fixed amplitude *Ansätze*¹² local treatments,^{15–17} systematic hierarchies of approximation for MP2-F12 (Ref. 17) as well as alternative *Ansätze* for MP2-R12,¹⁸ and simplified CC2-R12 and CCSD(T)-F12 approximations^{19–22} have been described, and results that are amazingly close to the basis set limits have been obtained with moderate basis sets such as aug-cc-pVTZ. The relation between MP2-F12 and Gaussian geminal theories has also been discussed and clarified.^{23–25}

Most of the previous work was focused on the treatment of closed-shell molecules, and important recent advancements have not yet been carried over into the open-shell regime. In particular, the only practical demonstrations of open-shell methods we are currently aware of are the MRCI-R12 calculations by Gdanitz *et al.*,^{6,26–29} CASPT2-F12 calculations by Ten-no³⁰ and UMP2-R12 as well as UHF-CCSD-R12 atomization energies and electron affinities by Noga *et al.*,^{31,32} Klopper and Noga,³³ and Tew *et al.*³⁴ These calculations were limited, however, to atoms and very small molecules. Very recently, UMP2-F12 calculations for atoms were also reported by Valeev²⁴ and UMP2-R12 calculations for the uracil anion by Bachorz *et al.*³⁵

It is well known that UMP2 based on unrestricted Hartree–Fock (UHF) reference functions may suffer severely from spin-contamination, and the results of UMP2 treatments often cannot be trusted (see, e.g., Refs. 36–40). This

problem can be avoided using the RMP2 method of Knowles *et al.*³⁹ and Lauderdale *et al.*,^{41,42} which is based on spin-restricted Hartree–Fock (RHF) reference functions. In the current work we describe an explicitly correlated version of this method in an orbital invariant form. This is an extension of the DF-MP2-F12 methods developed earlier in our group.¹⁷ The orbital invariant formulation is important for generalizations to higher-order coupled-cluster methods. It also allows for the use of localized orbitals and the later introduction of local approximations.^{15,16}

In Sec. II we will present the theory and discuss the modifications that are necessary due to the fact that for open-shell RHF reference functions the Brillouin conditions are not fulfilled. Another goal of this study is to establish the performance of F12 treatments which is to be expected for different applications involving open-shell systems. In the previous studies, both the molecular species and the properties investigated were quite limited. The basis sets and other computational details of our calculations will be summarized in Sec. III. Finally, in Sec. IV we will examine the basis set convergence for ionization potentials (IPs), electron affinities (EAs), and atomization energies (AEs) using a variety of RMP2-F12 approximations.

The presented DF-RMP2-F12 method has been implemented in the MOLPRO (Ref. 43) program package.

II. THEORY

In Sec. II A the conventional RMP2 method^{39,41,42,44} will be recapitulated briefly. We feel the need to do this due to some mathematical subtleties arising when F12 approximations are introduced.

The following notation will be used: the indices r, s denote spin-orbitals inside the molecular orbital (MO) basis, i, j, \dots, n denote occupied spin-orbitals, and the indices $\alpha, \beta, \gamma, \delta$ a formally complete set of virtual spin-orbitals. The latter orbital space can be divided into the set of virtual orbitals a, b, c, d in the MO basis and the remaining comple-

^{a)}Electronic mail: werner@theochem.uni-stuttgart.de.

mentary auxiliary (CA) space (indices x, y), so that $\{\alpha\} = \{a\} \cup \{x\}$. In certain terms of the working equations the CA orbitals occur explicitly, and then they are approximated by the union of the atomic orbital basis and an auxiliary RI basis set. All orbitals are assumed to be orthonormal. Summation over repeated dummy indices will be implied in most expressions. For any one-particle operator \hat{a} , the notation \hat{a}_n means that the operator is applied to particle n and acts as identity operator on the other particles. \hat{a}_{12} means $\hat{a}_1 + \hat{a}_2$.

A. Recapitulation of RMP2

In a complete orbital basis the Møller–Plesset zeroth-order Hamiltonian for closed-shell or spin-unrestricted open-shell Hartree–Fock reference wave functions can be written in second quantization as

$$\hat{H}^{(0)} = \sum_{ij} f_j^i \hat{e}_i^\dagger \hat{e}_j + \sum_{\alpha\beta} f_\beta^\alpha \hat{e}_\alpha^\dagger \hat{e}_\beta + \sum_{ix} f_x^i (\hat{e}_x^\dagger \hat{e}_i + \hat{e}_i^\dagger \hat{e}_x). \quad (1)$$

$f_s^r = \langle r | \hat{f} | s \rangle$ are the matrix elements of the Fock operator in the spin-orbital basis. Due to Brillouin's theorem the matrix elements f_a^i vanish for optimized orbitals. Unless the orbital basis is complete, the Hartree–Fock wave function $\Psi^{(0)} \equiv \Phi$ is not an eigenfunction of $\hat{H}^{(0)}$, and therefore, strictly speaking, Rayleigh–Schrödinger perturbation theory (RSPT) cannot be applied. However, the contributions of the terms involving the complementary auxiliary basis set are usually small and their importance decreases with increasing orbital basis. One can either assume that the matrix elements f_x^i can be neglected [generalized Brillouin condition (GBC)] or use variational perturbation theory and minimize the Hylleraas functional to obtain an approximate second-order energy.

In the spin-restricted open-shell case, however, the Brillouin theorem does not hold and the matrix elements f_a^i are nonzero. The RHF reference function is then not even an eigenfunction of $\hat{H}^{(0)}$ if the GBC is assumed. In RMP2 theory one therefore uses a *projected* Fock operator \hat{g} instead of \hat{f} ,

$$\hat{g} = \hat{\delta} \hat{f} \hat{\delta} + (1 - \hat{\delta}) \hat{f} (1 - \hat{\delta}), \quad (2)$$

where $\hat{\delta} = \sum_i |i\rangle \langle i|$ projects onto the occupied spin-orbital space. The zeroth-order Hamiltonian then takes the simpler form

$$\hat{H}^{(0)} = \sum_{ij} f_j^i \hat{e}_i^\dagger \hat{e}_j + \sum_{\alpha\beta} f_\beta^\alpha \hat{e}_\alpha^\dagger \hat{e}_\beta, \quad (3)$$

and it is easily seen that $\hat{H}^{(0)} |\Phi\rangle \propto |\Phi\rangle$ if $|\Phi\rangle$ is a single Slater determinant. As a side effect of the projection the GBC is not required anymore to make $|\Phi\rangle$ an eigenfunction of $\hat{H}^{(0)}$. Instead, the coupling between the occupied and CA orbital spaces is moved into the perturbation. As recently discussed by Noga *et al.*,¹⁸ other projections for the $\hat{H}^{(0)}$ operator are also possible, but these will not be considered further in the current work.

The original article of Knowles *et al.*³⁹ formulated the RMP2 method in terms of semicanonical orbitals block-diagonalizing semi-Fock matrices corresponding to \hat{g} projected on alpha or beta spin, respectively. If this is done,

noniterative direct formulas for the energy corrections can be obtained just like for MP2. However, since in explicitly correlated methods many more different integral classes are needed than in standard RMP2, it is advantageous to use the single set of RHF orbitals directly. Furthermore, since we aim for a localized description for large molecules and extensions to higher-order coupled-cluster methods, we require an orbital invariant formulation of the theory.

An orbital invariant formulation has already been given previously by Lauderdale *et al.*^{41,42} (see also Gauss and Bartlett⁴⁴), and has also been used by Crawford *et al.*⁴⁵ While Lauderdale *et al.* obtained their formulation by extraction of the relevant terms from the coupled cluster with singles and doubles (CCSD) equations, the invariant form can be derived more directly by simply inserting the *Ansatz* for the first-order wave function

$$|\Psi^{(1)}\rangle = \left[\sum_{k\gamma} t_\gamma^k \hat{e}_k^\gamma + \frac{1}{2} \sum_{kl\gamma\delta} T_{\gamma\delta}^{kl} \hat{e}_{kl}^{\gamma\delta} \right] |\Phi\rangle, \quad (4)$$

where $\hat{e}_{kl}^{\gamma\delta} = \hat{e}_k^\dagger \hat{e}_l^\dagger \hat{e}_\gamma \hat{e}_\delta$ are pair excitation operators, and $t_\gamma^k, T_{\gamma\delta}^{kl}$ the excitation amplitudes, into the general RSPT2 equation

$$\langle \Xi | \hat{H}^{(0)} - E^{(0)} | \Psi^{(1)} \rangle + \langle \Xi | \hat{H} | \Phi \rangle = 0. \quad (5)$$

Single excitations need to be included in the wave function because the Brillouin condition $f_i^\alpha = 0$ is not fulfilled. Inserting Eq. (4) into (5) for $\Xi \in \{\Phi_i^\alpha, \frac{1}{2} \Phi_{ij}^{\alpha\beta}\}$ and carrying out the second quantization algebra we arrive at (summations over repeated dummy indices implied)

$$r_\alpha^i = f_\alpha^i - f_k^i t_\alpha^k + t_\gamma^i f_\alpha^\gamma = 0, \quad (6)$$

$$R_{\alpha\beta}^{ij} = \frac{1}{2} [K_{\alpha\beta}^{ij} - K_{\alpha\beta}^{ji}] + f_\alpha^\gamma T_{\gamma\beta}^{ij} + T_{\alpha\gamma}^{ij} f_\beta^\gamma - f_k^i T_{\alpha\beta}^{kj} - T_{\alpha\beta}^{ik} f_j^k = 0, \quad (7)$$

where $K_{\alpha\beta}^{ij} = \langle ij | r_{12}^{-1} | \alpha\beta \rangle$. Note that here and in the following $|\alpha\beta\rangle$ and $|ij\rangle$ represent simple, nonantisymmetrized spin-orbital products. All quantities vanish unless the spins of the upper and lower labels correspond to each other. If the equations are transformed into a semicanonical basis, which block diagonalizes the alpha- and beta-spin parts of the Fock matrix in the occupied and virtual orbital subspaces, the equations fully decouple and can be solved noniteratively as described by Knowles *et al.*³⁹ and Lauderdale *et al.*^{41,42}

The second-order energy can be obtained by

$$E^{(2)} = \langle \Psi^{(1)} | \hat{H} | \Phi \rangle = t_\alpha^i f_\alpha^i + T_{\alpha\beta}^{ij} K_{\alpha\beta}^{ij} \quad (8)$$

(direct RSPT2 expression) or by evaluating the Hylleraas functional

$$E^{(2)} = \langle \Psi^{(1)} | \hat{H}^{(0)} - E^{(0)} | \Psi^{(1)} \rangle + 2 \langle \Psi^{(1)} | \hat{H} | \Phi \rangle = t_\alpha^i (f_\alpha^i + r_\alpha^i) + T_{\alpha\beta}^{ij} (K_{\alpha\beta}^{ij} + R_{\alpha\beta}^{ij}). \quad (9)$$

The latter variational expression is more stable with respect to inaccuracies in $|\Psi^{(1)}\rangle$, but both expressions are obviously identical if Eq. (5) is exactly fulfilled within the given model space.

Since $\hat{H}^{(0)}$ is not spin-free in the RMP2 case (it commutes with \hat{S}_z , but not with \hat{S}^2), the first-order wave function

can be spin-contaminated. However, since \hat{H} is spin-free and $|\Phi\rangle$ is spin-adapted, the spin-contaminations are projected out when computing the RMP2 correlation energy.

We note that it is possible to modify the residual equations so that the spin-contamination is removed and the first-order wave function becomes fully spin-adapted. This has been discussed in detail in the context of partially spin-restricted open-shell coupled-cluster theory.⁴⁶ This fully spin-adapted RMP2 (SRMP2) leads to slightly different energies than RMP2, but usually the effect is very minor and negligible.

B. Introduction of explicit correlations

In the explicitly correlated method the (exact) full space of doubly excited configurations in Eq. (4) is approximated with two subsets

$$T_{\alpha\beta}^{ij} \hat{e}_{ij}^{\alpha\beta} \approx T_{ab}^{ij} \hat{e}_{ij}^{\alpha\beta} + T_{\alpha\beta}^{ij} \hat{e}_{ij}^{\alpha\beta}, \quad (10)$$

where the first term contains conventional and the second the explicitly correlated double excitations. The additional amplitudes $T_{\alpha\beta}^{ij}$ are implicitly given by

$$T_{\alpha\beta}^{ij} = \mathcal{F}_{\alpha\beta}^{mn} T_{mn}^{ij}, \quad (11)$$

$$\mathcal{F}_{\alpha\beta}^{mn} = \langle mn | F_{12} \hat{Q}_{12} | \alpha\beta \rangle, \quad (12)$$

$$\hat{Q}_{12} = (1 - \hat{o}_1)(1 - \hat{o}_2)(1 - \hat{v}_1 \hat{v}_2), \quad (13)$$

where $\hat{v} = |a\rangle\langle a|$ projects on virtual spin-orbitals representable in the MO basis. \hat{Q}_{12} is a projector (*Ansatz 3*) ensuring strong orthogonality of the explicitly correlated configurations to the occupied and conventional virtual space ($\mathcal{F}_{rs}^{ij} = 0$). As pair correlation factor we use a Slater function, approximated by a linear combination of Gaussians

$$F(r_{12}) = -\frac{1}{\beta} \exp(-\beta r_{12}) \approx \sum c_i \exp(-\alpha_i r_{12}^2), \quad (14)$$

where β is a fixed length scale parameter. Note that for convenience in later expressions we include here the factor $-1/\beta$ in the definition of F_{12} .

The explicitly correlated configurations are short ranged and well suited to describe the correlation cusp of the pair distribution function of the wave function for $r_{12} \rightarrow 0$ and thus *dynamical* correlation. In the derivations they are conveniently treated as “externally contracted” configurations of the *complete basis set* double excitation space, as indicated above.

Equations for the explicitly correlated double excitations are obtained from Eq. (7) by contracting $R_{\alpha\beta}^{ij}$ with $\mathcal{F}_{\alpha\beta}^{kl}$,

$$R_{kl}^{ij} = \frac{1}{2}(V_{kl}^{ij} - V_{lk}^{ij}) + B_{kl,mn} T_{mn}^{ij} + C_{ab}^{kl} T_{ab}^{ij} - X_{kl,mn} (f_o^i T_{mn}^{oj} + T_{mn}^{io} f_o^j) = 0, \quad (15)$$

with the matrices

$$V_{kl}^{ij} = \langle ij | r_{12}^{-1} \hat{Q}_{12} F_{12} | kl \rangle, \quad (16)$$

$$B_{kl,mn} = \langle kl | F_{12} \hat{Q}_{12} (\hat{f}_1 + \hat{f}_2) \hat{Q}_{12} F_{12} | mn \rangle, \quad (17)$$

$$X_{kl,mn} = \langle kl | F_{12} \hat{Q}_{12} F_{12} | mn \rangle, \quad (18)$$

$$C_{ab}^{kl} = \langle kl | F_{12} \hat{Q}_{12} (\hat{f}_1 + \hat{f}_2) | ab \rangle \quad (19)$$

(all indices correspond to spin-orbitals). The contraction with $\mathcal{F}_{\alpha\beta}^{kl}$ ensures that we acquire as many equations as we have free parameters and that the externally contracted configurations are weighted in a suitable manner to focus their agreement with the perturbation equation to the cusp region.

In the R_{ab}^{ij} residuals for the conventional part an additional coupling term $+C_{ab}^{kl} T_{kl}^{ij}$ arises. Apart from that, they are given by Eq. (7) with α , β , and γ replaced by a , b , and c .

The energy expression for the explicit part is

$$E_{F12}^{(2)} = T_{kl}^{ij} (V_{kl}^{ij} + R_{kl}^{ij}). \quad (20)$$

Additionally, we consider the change of the conventional second-order energy $E_{\text{conv}}^{(2)}$ due to the effect of the F12 configurations on the conventional amplitudes as part of the F12 energy correction.

The equations and definitions given above are entirely similar to those for the closed-shell case, except that here we use a spin-orbital basis and therefore the residuals R_{kl}^{ij} and amplitudes T_{kl}^{ij} are antisymmetric with respect to exchange of the indices i, j or k, l .

In order to arrive at Eqs. (15)–(20), several *exact* complete basis set RIs in the form of

$$|\alpha\beta\rangle\langle\alpha\beta| \hat{Q}_{12} = \hat{Q}_{12} \quad (21)$$

are used, giving rise to new analytic integrals. No finite-basis expansion in the pair function space is required for these. This aspect distinguishes F12 methods from simply performing the correlation treatment in a larger basis.

Note that the explicitly correlated configurations are *not* normalized. As pointed out in the Appendix, this may lead to artificial singularities in the $B_{kl,mn}$ tensor. Even though such singularities can easily be projected out, this is undesirable, since the projection—depending on the threshold—can lead to small steps on potential energy surfaces. The problem can be avoided by using the “diagonal *Ansatz*” as described in Sec. II H.

C. Calculation of matrix elements in spin-orbitals

Various ways of evaluating the matrix elements in Eqs. (16)–(19) (in the closed-shell theory) have been suggested and used. For a systematic study of different approaches, and the approximations employed or feasible in them, see Ref. 17. Here we use the approach considered most promising in that study, namely, method 3C with CABS approximations of the projectors. The derivations closely follow Ref. 17, but for the sake of clarity and in order to point out subtle differences, they are repeated here.

The CABS is an extended basis set orthonormal in itself and orthogonal to the MO space. Its use was first suggested by Valeev.⁹ In the simplest case, the CABS orbitals (indices x, y) are explicitly calculated by projecting the MO basis out of given RI functions: $|\mu^*\rangle = (1 - |r\rangle\langle r|) |\mu\rangle$ (where $|\mu\rangle$ is a RI basis function) and orthogonalizing the $|\mu^*\rangle$ to yield $|x\rangle$. Due to the projection, $|x\rangle$ orbitals have components in both the

AO and RI bases, and in practice they are represented in the union of the orbital (AO) and the auxiliary (RI) bases sets.

In terms of CABS orbitals the projector \hat{Q}_{12} used in Eqs. (16)–(19) can be approximated as

$$\hat{Q}_{12} = 1 - \hat{P}_{12}, \quad (22)$$

$$\hat{P}_{12} \approx |ix\rangle\langle ix| + |xi\rangle\langle xi| + |rs\rangle\langle rs|. \quad (23)$$

Alternatively, if also the unit operator is approximated by a double RI,

$$\hat{Q}_{12} \approx |ax\rangle\langle ax| + |xa\rangle\langle xa| + |xy\rangle\langle xy|. \quad (24)$$

Both formulas are exact for a complete basis. For a finite RI basis the use of $\hat{Q}_{12} = 1 - \hat{P}_{12}$ is preferable, since the dominant terms $1 - |rs\rangle\langle rs|$ can be computed exactly and no double-RI is required. The alternative form in Eq. (24) is only used if the integrals arising from the unit operator cannot be evaluated analytically. Note that \hat{Q}_{12} and \hat{P}_{12} , although being spin-dependent, commute with \hat{S}_z and thus matrix elements of \hat{Q}_{12} or \hat{P}_{12} vanish unless the bra and ket vectors have equal spin-labels.

Using Eq. (23) for $X_{kl,mn}$ and V_{mn}^{kl} and Eq. (24) for C_{ab}^{kl} (method 3C), we obtain in terms of spin-orbitals:

$$X_{kl,mn} = \langle kl|F_{12}F_{12}|mn\rangle - F_{rs}^{kl}F_{rs}^{mn} - F_{xi}^{kl}F_{xi}^{mn} - F_{ix}^{kl}F_{ix}^{mn}, \quad (25)$$

$$V_{mn}^{kl} = \langle kl|r_{12}^{-1}F_{12}|mn\rangle - K_{rs}^{kl}F_{rs}^{mn} - K_{xi}^{kl}F_{xi}^{mn} - K_{ix}^{kl}F_{ix}^{mn}, \quad (26)$$

$$C_{ab}^{kl} = f_{ax}F_{xb}^{kl} + F_{ax}^{kl}f_{xb}, \quad (27)$$

where $F_{pq}^{ij} = \langle ij|F_{12}|pq\rangle$ (p, q : arbitrary orbitals). In order to calculate $B_{kl,mn}$, we notice that

$$\hat{Q}_{12}\hat{f}_{12}\hat{Q}_{12} = \hat{S}(\hat{g}_{12}\hat{Q}_{12} - \hat{P}_{12}\hat{g}_{12}\hat{Q}_{12}), \quad (28)$$

where the symmetrizing operator S is defined by $\hat{S}\hat{O} = \frac{1}{2}(\hat{O} + \hat{O}^\dagger)$ in terms of operators, which in terms of indices leads to $\hat{S}B_{kl,mn} = \frac{1}{2}(B_{kl,mn} + B_{mn,kl})$ for real matrices (bra and ket indices are swapped by the transposition). Note that $\hat{Q}_{12}\hat{f}_{12}\hat{Q}_{12} = \hat{Q}_{12}\hat{g}_{12}\hat{Q}_{12}$, but $\hat{f}_{12}\hat{Q}_{12} \neq \hat{g}_{12}\hat{Q}_{12}$. In this sense we have

$$\begin{aligned} B_{kl,mn} &= \langle kl|F_{12}[\hat{S}(\hat{g}_{12}\hat{Q}_{12} - \hat{P}_{12}\hat{g}_{12}\hat{Q}_{12})]F_{12}|mn\rangle \\ &= \hat{S}[A_{kl,mn} - Z_{kl,mn} - F_{ab}^{kl}C_{ab}^{mn}], \end{aligned} \quad (29)$$

where

$$A_{kl,mn} = \langle kl|F_{12}\hat{g}_{12}\hat{Q}_{12}F_{12}|mn\rangle, \quad (30)$$

$$Z_{kl,mn} = \langle kl|F_{12}(\hat{o}_1\hat{g}_1 + \hat{o}_2\hat{g}_2)\hat{Q}_{12}F_{12}|mn\rangle. \quad (31)$$

Due to the projected form of \hat{g} [cf. Eq. (2)], we have $\hat{o}\hat{g} = \hat{g}\hat{o}$ and thus $Z_{kl,mn} = 0$ since \hat{Q}_{12} projects out orbital pairs containing occupied orbitals.

For the A term we split \hat{g} into $\hat{g} = \hat{h} - \hat{n}$ with

$$\hat{h} = \hat{t} + \hat{v}_{\text{nuc}} + \hat{j}, \quad (32)$$

$$\hat{n} = \hat{h} - \hat{g} = \hat{k} - (2\hat{o}\hat{f}\hat{o} - \hat{o}\hat{f} - \hat{f}\hat{o}). \quad (33)$$

The Hartree operator \hat{h} contains the kinetic energy operator and the parts of \hat{g} which commute with F_{12} (here Coulomb field \hat{j} and nuclear potential \hat{v}_{nuc}), while \hat{n} contains the entire rest (here $\Delta\hat{g} = \hat{f} - \hat{g}$ and exchange \hat{k}). The A terms are then evaluated in the following way:

$$\begin{aligned} A_{kl,mn} &= \langle kl|F_{12}(\hat{h}_{12} - \hat{n}_{12})\hat{Q}_{12}F_{12}|mn\rangle = \langle kl|F_{12}\hat{h}_{12}F_{12}|kl\rangle \\ &\quad - \langle kl|F_{12}\hat{h}_{12}\hat{P}_{12}F_{12}|kl\rangle - \langle kl|F_{12}\hat{n}_{12}\hat{Q}_{12}F_{12}|mn\rangle \\ &= \langle kl|\hat{h}_{12}F_{12}F_{12}|mn\rangle - \langle kl|F_{12}\hat{h}_{12}\hat{P}_{12}F_{12}|mn\rangle \\ &\quad - \langle kl|[\hat{t}_{12}, F_{12}]F_{12}|mn\rangle - \langle kl|F_{12}\hat{n}_{12}\hat{Q}_{12}F_{12}|mn\rangle. \end{aligned} \quad (34)$$

We employ approximation 3C in which only unit operator parts of $\hat{Q}_{12} = 1 - \hat{P}_{12}$ in the matrix $A_{kl,mn}$ are approximated with the commutator approach and the remaining terms are approximated with straight RIs. The commutator trick avoids the use of double RIs for the term involving the kinetic energy operator, which is very slowly convergent.^{3,4} The expression for A then becomes

$$\begin{aligned} A_{kl,mn} &= F_{kl,mn}^2 + F_{kl,mn}^2 - \bar{F}_{ix}^{kl}F_{ix}^{mn} - \bar{F}_{xi}^{kl}F_{xi}^{mn} - \bar{F}_{rs}^{kl}F_{rs}^{mn} \\ &\quad + U_{kl,mn}^F - \bar{Y}_{kl,mn}, \end{aligned} \quad (35)$$

where Eq. (23) has been inserted and

$$\bar{F}_{pq}^{kl} = F_{pq}^{kl} + F_{p\bar{q}}^{kl}, \quad (36)$$

$$U_{kl,mn}^F = \langle kl|[F_{12}, \hat{t}_{12}]F_{12}|mn\rangle, \quad (37)$$

$$F_{kl,mn}^2 = \langle kl|F_{12}F_{12}|mn\rangle, \quad (38)$$

$$\bar{Y}_{kl,mn} = \langle kl|F_{12}\hat{n}_{12}\hat{Q}_{12}F_{12}|mn\rangle, \quad (39)$$

in which p, q denote any orbital and overlined indices refer to orbitals transformed by \hat{h} ,

$$|\bar{p}\rangle = \hat{h}|p\rangle. \quad (40)$$

The term $\bar{Y}_{kl,mn}$, which contains the exchange contribution and $\Delta\hat{g}$, i.e., $\hat{n} = \hat{k} - \Delta\hat{g}$, can be approximated by a double RI using Eq. (24) for the projector,

$$\bar{Y}_{kl,mn} = \bar{F}_{ax}^{kl}F_{ax}^{mn} + \bar{F}_{xa}^{kl}F_{xa}^{mn} + \bar{F}_{xy}^{kl}F_{xy}^{mn}, \quad (41)$$

where

$$|\bar{p}\rangle = \hat{n}|p\rangle, \quad (42)$$

$$\bar{F}_{pq}^{kl} = F_{pq}^{kl} + F_{p\bar{q}}^{kl}. \quad (43)$$

In the atomic case this double RI is known to converge very fast for the exchange term. The $\Delta\hat{g}$ term also does not pose a problem due to its specific form (33): All contributions except $\hat{o}\hat{f}$ are projected out by \hat{Q}_{12} and for the remaining expression the formal double RI is in fact only a single RI.

We note that due to the Fock-operator projection employed here, the $\tilde{Y}_{kl,mn}$ term defined in this work slightly differs from the $\tilde{Y}_{kl,mn}$ term of Ref. 17. If used in the closed-shell case, the projected 3C method suggested here closely reproduces the results of the unprojected 3C(+Z) method reported in Ref. 17. This happens since the (extremely small) effect of the $Z_{kl,mn}$ term [which is not exactly zero without the projection (2)] is handled implicitly as part of the perturbation. All other matrices with equal names have equal meaning in the closed-shell case, since the minimally projected form (2) of \hat{g} then only affects GBC terms.

D. Hybrid approximations

As in the closed-shell theory,¹⁷ it is possible to drop the last term of Eq. (41) without significant losses in accuracy [approximation 3C(HY2)]. As $\Delta g_{xy}=0$ this affects only the approximation of the exchange contributions. A more severe approximation is to neglect the matrix $\tilde{Y}_{kl,mn}$ entirely [approximation 3C(HY1)]. This approximation is similar (but not identical) to Klopper's hybrid approximation.⁴⁷ In the latter work *Ansatz 2* was used, which differs from *Ansatz 3* as used here by omission of the factor $1-\hat{v}_1\hat{v}_2$ in the projector \hat{Q}_{12} [cf. Eq. (13)]. As discussed previously¹⁷ the two *Ansätze* lead to different results if hybrid approximations are introduced.

For the hybrid approximations the storage for the transformed integrals scales only linearly with the size of the RI basis. The computational effort for some transformation steps still scales quadratically, but significant savings are possible, in particular for approximation 3C(HY1).

E. The extended Brillouin condition approximation

Another approximation that leads to some simplifications is to assume that the extended Brillouin condition (EBC) is fulfilled, i.e., $f_{xa}=0$. This leads to $C_{ab}^{kl}=0$, and therefore the conventional and explicit amplitude equations decouple. The contributions of the C matrices to the B tensor are also neglected, cf. Eq. (29). As in previous work a star in the method designation (e.g., 3*C), indicates that the EBC approximation is applied.

F. Adaption to restricted spatial orbitals

The previous equations were written in terms of spin-orbitals. Since we use a RHF reference wave function, they can easily be adapted to restricted spatial orbitals. The most favorable way to do this in our current situation is keeping the *single* orbital set of the reference function (i.e., not following the way of the original RMP2 paper of obtaining separate alpha- and beta-spin-orbitals) and obtaining the spin-orbitals as spatial RHF orbitals multiplied by either alpha (A) or beta (B) spin-functions. That means that closed-shell orbitals occur with identical spatial part as occupied A and B orbitals, active orbitals occur as occupied A and virtual B orbitals, and external orbitals occur as virtual A and B orbitals.

The residual equations (7) are fulfilled for vanishing amplitudes if the sets of spin-labels for ij and $\alpha\beta$ are different,

since then both $K_{\alpha\beta}^{ij}$ and $K_{\alpha\beta}^{ji}$ vanish. That means we need to calculate only the residuals of $R_{\alpha\beta}^{ij}$ with the spin-labels of ij being AA , BB , or AB (the BA equations are equal to the AB ones). Similarly, all matrix elements in Eqs. (25)–(27) vanish unless the spin-labels on the bras and kets are equal, since \hat{Q}_{12} , although spin-dependent, does not alter the spin-labels of particles 1 and 2. Therefore a set of AA , BB , and AB matrices of these quantities also determines the complete spin-orbital set. It is straightforward to transfer the remaining quantities into spatial expressions as well.

Although most F12 matrices and some integral matrices have to be calculated in three to four different versions, due to the use of the same spatial orbitals for the internal labels, the same half-transformed integrals can be used for all of them. This leads to DF-RMP2-F12 being only moderately more expensive than closed-shell DF-MP2-F12 in the integral evaluation step.

Furthermore, in RMP2 (but not in higher-order theories), the residual equations of AA , BB , and AB become independent. It is advisable to solve them independently because the AA and BB equations converge faster than the AB ones.

G. Integral evaluation and transformation

In our implementation all basic integrals are calculated using robust density fitting.^{10,11} As described in Ref. 17, efficient pathways for the transformation of integrals are determined recursively and reuse previously calculated intermediates.

Transformed integrals containing CABS orbital labels can be obtained by splitting the CABS transformation into its AO and RI parts (as already noted, CABS orbitals have components in both the AO and RI bases), evaluating the transformed integrals for both basis sets independently, and adding them afterwards.

H. Ansatz restrictions for T_{kl}^{ij}

The *Ansatz* for explicitly correlated configurations is not always used in the general form as given in Eq. (11). One may assume that the amplitudes T_{kl}^{ij} are only nonzero if $kl=ij$ or $kl=ji$ (diagonal *Ansatz*). And in the latter case, one can furthermore determine the amplitudes from the condition that the cusp conditions are fulfilled (fixed amplitude *Ansatz*). The advantages and disadvantages of these different *Ansätze* will be briefly discussed in the following subsections.

1. The diagonal Ansatz (3C(D))

In the diagonal *Ansatz* the T_{kl}^{ij} are only allowed to be nonzero if either $|kl\rangle=|ij\rangle$ or $|kl\rangle=|ji\rangle$, where i, j, k, l are spin-orbitals. This is the original *Ansatz* of Kutzelnigg and Klopper.^{3,4} This *Ansatz* can be interpreted in terms of excitations from occupied orbital pairs $|ij\rangle$ into short-range functions $F_{12}|ij\rangle$, thus cutting short-ranged holes into $|ij\rangle$ if the corresponding amplitudes are positive [as they usually are; note that $F_{12}(r)<0$, cf. Eq. (14)].

A formal disadvantage of this *Ansatz* is that it is not unitarily invariant. It should be applied with localized orbitals in order to obtain size consistency. However, with local-

ized orbitals the diagonal *Ansatz* has been found¹⁷ to yield more accurate results than the other variants discussed below. This is due to the avoidance of geminal basis set superposition error (BSSE) effects and of singularities in the *B* matrix.

2. The general orbital invariant Ansatz (3C)

In this case all T_{kl}^{ij} are allowed. The *Ansatz* was introduced by Klopper⁴⁸ to remove the lack of unitary invariance of the diagonal *Ansatz*. It is not easily interpreted. Despite giving the wave function more freedom, it was found to actually *worsen* the F12 treatment in certain cases (some more will be shown in Sec. IV). This can happen due to a geminal BSSE effect,^{17,49} which cannot easily be corrected for, or due to linear dependency problems as discussed in the Appendix.

More extended variants of the general *Ansatz* (e.g., also allowing *k* and/or *l* of T_{kl}^{ij} to run over virtual orbitals) may become necessary in methods dealing with excited states.⁵⁰ This is because otherwise the explicit correlations stabilize the reference state much stronger than the excited states.

3. The fixed amplitude Ansatz (3C(FIX))

This *Ansatz* was introduced by Ten-no.¹² It is based on the diagonal *Ansatz*, but the amplitudes T_{ij}^{ij} and T_{ji}^{ij} are not determined from the perturbation equation, but rather fixed to

$$T_{ii}^{ii} = t_s, \quad (44)$$

$$T_{ij}^{ij} = \frac{1}{2}(t_s + t_p) \quad (i \neq j), \quad (45)$$

$$T_{ji}^{ij} = \frac{1}{2}(t_s - t_p) \quad (i \neq j) \quad (46)$$

(all other T_{kl}^{ij} are set to zero). In the closed-shell case and for spatial orbitals, the values $t_s=1/2$ and $t_p=1/4$ are obtained from the *s*- and *p*-wave cusp conditions, respectively.^{51,52} For spin-orbitals and non spin-adapted wave functions, we formally do not have clean singlet and triplet pairs. But it can be argued that taking the same formulas as above is the most natural extension to this case (for spin *AA* and *BB* pairs $t_s=0$).

This *Ansatz* is unitarily invariant, size consistent, and free of geminal BSSE, but extensive tests have shown the results are not quite as good as with the diagonal *Ansatz*. In particular, the results are more sensitive to the choice of β . Note that, despite the fact that the amplitudes are fixed, the residual and thus all matrices it involves are still required for computing the Hylleraas functional.

In principle, one could think of employing Eq. (8) to compute the energy without using the Hylleraas functional. If the fixed amplitudes are used this would only require the integrals V_{kl}^{ij} , thus cutting most of the integral evaluations. However, the F12 treatment then is independent of the correlation method used and becomes very sensitive to the form of F_{12} (e.g., the choice of β). The error is linear in errors of the amplitudes and may become quite large. Therefore, this very cheap approximation should be considered with great

care, even though tests have shown that in most cases a significant improvement of the basis set convergence is still observed.

Despite the apparently reduced complexity of the diagonal and fixed *Ansätze* compared with the general one, the actual numerical work required to evaluate any of them does not differ much. The reason for this is that all of them require the same atomic integrals to be evaluated, which is the most time consuming step in an MP2-F12 calculation.

I. Single excitations

In RMP2, energy contributions from single excitations occur. These depend only on the *A*- and *B*-Fock matrices and do not couple to the doubles equations. In RMP2-F12 we need Fock matrices for the whole MO/MO, MO/CABS, and CABS/CABS basis sets anyway in order to calculate the transformed integrals entering in the A_{mn}^{kl} term in Eq. (35). Therefore it is cheap to calculate these single excitations not only within the normal MO basis, but within the combined MO and CABS basis (where the CABS orbitals are treated like normal virtual orbitals). Concretely, the solution of the RMP2 singles equation in Eq. (6) can be written down in closed form if it is transformed into a basis in which \hat{g} is diagonal [that means diagonalizing (f_{ij}) and $(f_{\alpha\beta})$ independently],

$$t_\alpha^i = \frac{f_\alpha^i}{g_{ii} - g_{\alpha\alpha}}, \quad (47)$$

$$E_{\text{singles}}^{(2)} = \sum_{i\alpha} \frac{(f_\alpha^i)^2}{g_{ii} - g_{\alpha\alpha}}, \quad (48)$$

where α runs over all virtual orbitals (the unoccupied MOs and the CABS).

This basis extension has two consequences: (i) The basis set convergence of the singles correlation contributions is accelerated, and (ii) the Hartree–Fock orbitals are perturbatively relaxed by the CABS. The second effect is by far dominant in magnitude, and it is very helpful in practical calculations, since it greatly diminishes the deviation of the Hartree–Fock energy from the basis set limit. This is significant because, while with conventional electron correlation calculations the accuracy of the Hartree–Fock treatment is usually not a serious issue, this changes when using explicitly correlated methods. If not corrected for, the basis limit deviation due to Hartree–Fock is often larger than the remaining MP2-F12 correlation error.

The part of the singles energy correction that corresponds purely to a spin-free relaxation of the RHF function can be isolated by solving

$$0 = \langle \bar{\Phi}_\alpha^i | \hat{H} | \Phi \rangle + \sum_{k\gamma} t_\gamma^k \langle \bar{\Phi}_\alpha^i | \hat{g} | \bar{\Phi}_\gamma^k \rangle \quad (49)$$

as perturbation equation, where $|\bar{\Phi}_\alpha^i\rangle = \hat{E}_i^\alpha |\Phi\rangle$ and $\hat{E}_i^\alpha = \hat{e}_{iA}^{\alpha A} + \hat{e}_{iB}^{\alpha B}$ are the spin-free excitation operators. The corresponding numerical equations can be obtained from the spin-orbital equation (6) by using the spin-orbital amplitudes

$$t_{\alpha A}^{iA} = t_{\alpha B}^{iB} = t_\alpha^i, \quad (50)$$

$$t_{\alpha A}^{uA} = t_{\alpha}^u \text{ and } t_{\alpha B}^{uB} = 0, \quad (51)$$

$$t_{uB}^{iB} = t_u^i \text{ and } t_{uA}^{iA} = 0, \quad (52)$$

and demanding

$$r_{\alpha A}^{iA} + r_{\alpha B}^{iB} = r_{\alpha A}^{uA} = r_{uB}^{iB} = 0, \quad (53)$$

where i denotes closed, u active, and α external spatial orbitals. The values of $t_{\alpha A}^{uA}$ and $t_{\alpha B}^{uB}$ only appear to be different, because $\hat{e}_{uB}^{\alpha B}|\Phi\rangle=0$ and thus the B configuration and corresponding residual intrinsically vanish. Due to the RHF Brillouin conditions,

$$f_{\alpha A}^{iA} + f_{\alpha B}^{iB} = f_{\alpha A}^{uA} = f_{uB}^{iB} = 0, \quad (54)$$

for optimized RHF functions no closed-to-active relaxation occurs and furthermore, the total energy correction vanishes if α and γ are constrained to the MO basis.

III. COMPUTATIONAL DETAILS

A. Basis sets

As orbital basis sets we used the aug-cc-pVnZ basis sets⁵³ for first-row elements and the aug-cc-pV(n+d)Z basis sets⁵⁴ for second-row elements. The “+d” indicates that an additional tight d shell is included. For the sake of brevity, these basis sets will be denoted “AVnZ” in the remainder of this article.

In the case of EAs we found it necessary to make the AVTZ basis sets a bit more diffuse in order to consistently reach a very high accuracy for all systems in the benchmark set. This was done by augmenting the AVTZ basis sets by one additional diffuse s and p shell each, except for the hydrogen atom, for which only one s function was added. The exponents of these additional s and p shells were obtained by dividing the most diffuse exponent already present by 1.8. The resulting (nonoptimized) basis set is called “A2VTZ” in this work. Due to these additional functions the root mean square (rms) error of the DF-RMP2-F12 EA treatments dropped by more than one-half at very moderate cost.

As auxiliary basis sets for applications in the RI and Fock-matrix DF (JK-fit), the cc-pVTZ/JKFIT basis sets of Weigend⁵⁵ were found to work well previously.¹⁶ They are used in this work for both RI and JK fitting. However, in the case of the EAs we found it necessary to augment them with one additional diffuse shell per angular momentum in order to obtain accurate Fock matrices. The exponents of these additional shells were obtained as ζ_1^2/ζ_2 , where ζ_1 denotes the smallest and ζ_2 the next larger exponent already present for the corresponding angular momentum. If only one exponent was in the shell beforehand, the new shell's exponent was obtained by dividing the present exponent by 2.5. This auxiliary basis set is called AVTZ-JK in this article.

All other integral quantities apart from the Fock matrices were obtained using robust DF with the AVTZ/MP2FIT basis sets of Weigend *et al.*⁵⁶

In the case of IPs and AEs, augmenting the orbital or fitting bases, like we did for the EAs, had noticeable but much smaller effects. Therefore the corresponding calculations are not reported here.

TABLE I. Systems in the benchmark set. EAs and IPs are adiabatic; RMP2/AVTZ geometries were used.

Electron Affinities: NO, CH ₃ , NH, O ₂ , CH ₂ , P, NH ₂ , PH, SiH ₂ , PO, CH, PH ₂ , SiH, C, SiH ₃ , Si, O, S ₂ , OH, S, SH, Cl ₂ , F, Cl, CN.
Ionization Potentials: Al, Si, B, S ₂ , PH ₃ , PH ₂ → PH ₂ ⁺ (¹ A ₁), PH, S, NH ₃ , SH, SH ₂ → SH ₂ ⁺ (² B ₁), P, C ₂ H ₄ , P ₂ , SiH ₄ , C, CS, Cl ₂ , C ₂ H ₂ , O ₂ , ClF, SH ₂ → SH ₂ ⁺ (² A ₁), HCl, H ₂ O, CH ₄ , Cl, OH, O, CO, N, N ₂ → N ₂ ⁺ (² Σ _g), HF, N ₂ → N ₂ ⁺ (² Π _u), F.
Atomization Energies: F ₂ , Cl ₂ , ClO, ClF, Si ₂ , NH, CH, HCl, OH, S ₂ , P ₂ , SiH ₂ (³ B ₁), SO, O ₂ , HF, SiH ₂ (¹ A ₁), PH ₂ , NO, HOCl, CH ₂ (¹ A ₁), CS, SH ₂ , NH ₂ , CN, CH ₂ (³ B ₁), SiO, SiH ₃ , PH ₃ , H ₂ O, N ₂ , CO, H ₂ O ₂ , SO ₂ , HCO, NH ₃ , CH ₃ , SiH ₄ , HCN, H ₂ CO, CH ₃ Cl, C ₂ H ₂ , CO ₂ , CH ₄ , N ₂ H ₄ , CH ₃ SH, CH ₃ OH, Si ₂ H ₆ , C ₂ H ₄ , C ₂ H ₆ .

B. Other calculation parameters

Diagonal methods are always applied with Pipek–Mezey localized orbitals.⁵⁷ All values in tables and figures refer to total energies, including RMP2 singles and DF-RHF. For DF-RMP2-F12, the RMP2 single excitations are evaluated in the combined MO and CA basis, as described in the first part of Sec. III.

The frozen core approximation is used throughout, except for DF-RMP2-F12 single excitations which are always calculated including excitations from core electrons. This is done since their defining feature is a relaxation of the RHF orbitals (see also Sec. IV E).

IV. RESULTS

A. Benchmark systems

In order to assess the basis set convergence of the RMP2-F12 method for a wide variety of systems, we used a subset of the quantities tested in the original G2 benchmark set.⁵⁸ Namely, all EAs, IPs, and AEs from the set have been chosen, except for compounds containing alkali or alkali earth elements. The groups 1 and 2 elements had to be excluded because we do not have suitable augmented orbital and JK-fitting basis sets for them at the moment. The IPs and AEs are adiabatic; i.e., the geometry of the ions is relaxed.

This set of atoms and very small molecules has been chosen in order to admit accurate reference calculations which allow for a systematic study of different possible error sources (e.g., from DF or RI approximations). All reference values used for G2-set molecules are obtained at the full RMP2/CBS[56] level without any DF approximations. The

TABLE II. Basis set rms deviations of conventional RMP2 methods relative to the RMP2/CBS[56] reference values.

Method	ΔEA (meV)	ΔIP (meV)	ΔAE (kJ/mol)
RMP2/AVTZ	104.60	122.62	29.58
RMP2/AVQZ	52.46	61.18	12.11
RMP2/AV5Z	29.24	33.24	6.10
RMP2/AV6Z	16.99	19.40	3.43
RMP2/CBS[45]	4.41	3.27	0.51

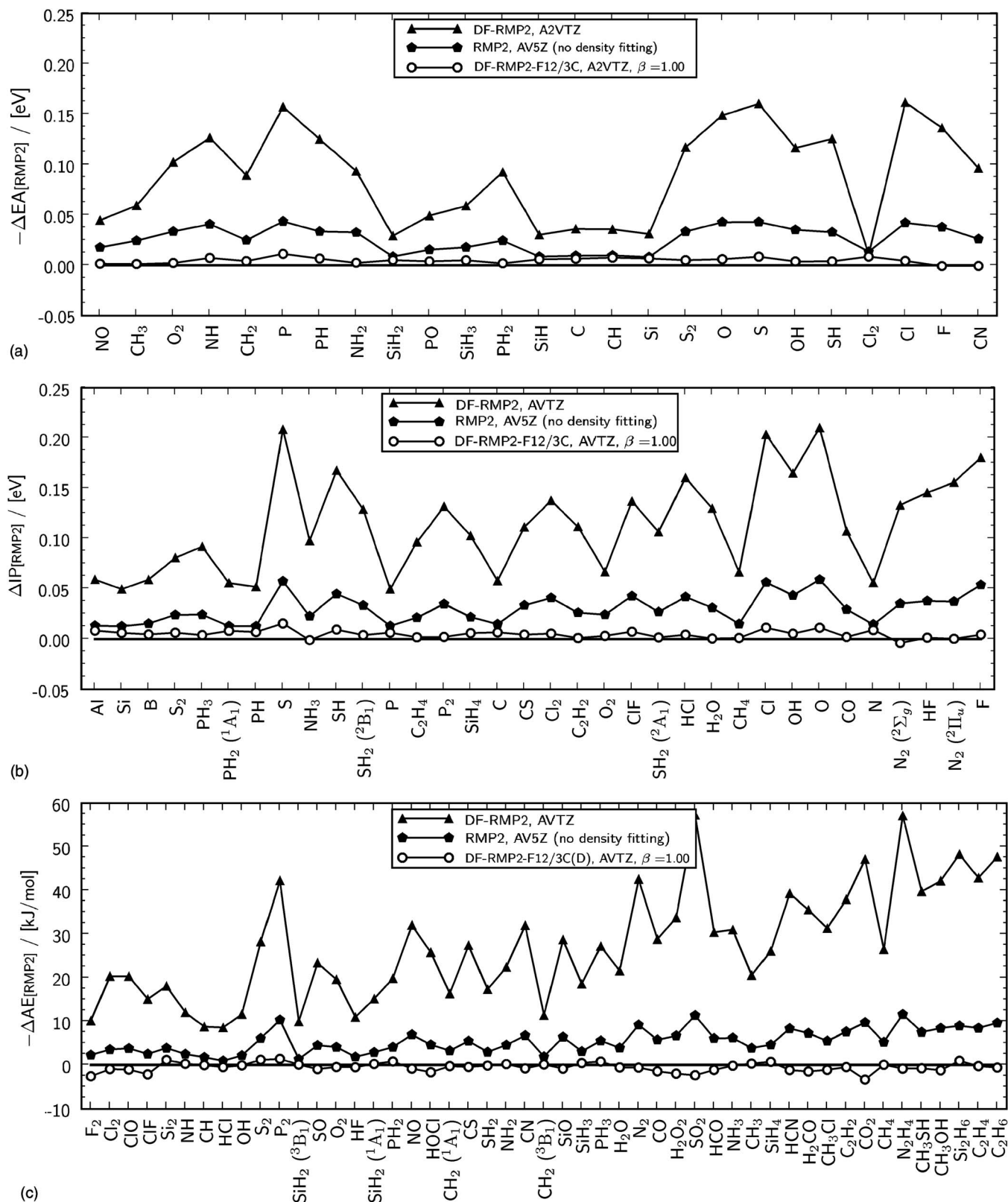


FIG. 1. Total deviation of DF-RMP2/A(2)VTZ, RMP2/AV5Z and DF-RMP2-F12/A(2)VTZ electron affinities, ionization potentials, and atomization energies from RMP2/CBS[56]. VTZ/JKFIT (AE,IP) or AVTZ-JK (EA) and AVTZ/MPFIT (all) auxiliary basis sets are used as described in Sec. III A. The entries are ordered by increasing RMP2/CBS[56] values.

CBS[56] values were obtained by two-point fits of the AV5Z and AV6Z correlation energies for the corresponding species to the extrapolation formula⁵⁹ $E_n = E_{\text{CBS}} + An^{-3}$. Hartree–Fock energy contributions were not extrapolated but taken directly from AV6Z calculations.

All molecular geometries were fully optimized at the RMP2/AVTZ level. The full list of benchmark systems is displayed in Table I.

Table II shows the rms deviations of the conventional RMP2/AV n Z results relative to the extrapolated RMP2/

TABLE III. Dependence of the RMP2-F12 basis set errors on the wave function *Ansatz* and the EBC approximation. The values are rms errors of the total values relative to the RMP2/CBS[56] reference values, including the RHF and singles contributions. In all cases $\beta=0.9a_0^{-1}$ and the AVTZ/A(2)VTZ basis sets as described in Sec. III A were used.

Method	Full	Diagonal	Fixed
		<i>EAs</i> (meV)	
3C	4.653	6.328	5.645
3*C	3.376	4.778	4.816
		<i>IPs</i> (meV)	
3C	6.030	7.228	7.757
3*C	3.788	4.756	5.809
		<i>AEs</i> (kJ/mol)	
3C	1.885	1.068	0.670
3*C	1.687	1.122	0.779

CBS[56] results (including the RHF contribution). The errors are still very large for the AVTZ basis set and decrease only rather slowly with increasing cardinal number of the basis set. As will be shown in the subsequent sections, the basis set convergence is dramatically improved by the explicitly correlated RMP2-F12 methods.

B. Impact of *Ansatz* restrictions

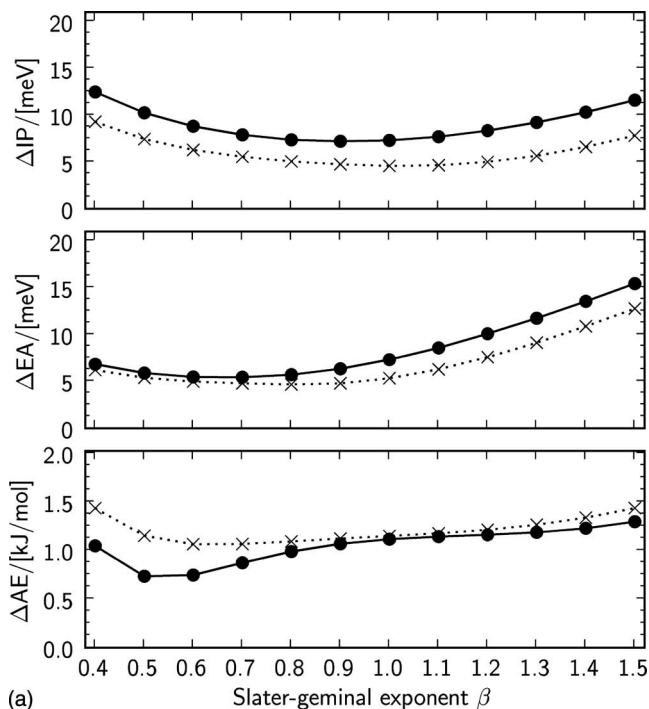
The first aspect we want to note is that the RMP2-F12 method works for all systems and dramatically improves the basis set convergence. There are no obvious outliers and the performance is similar for all individual tested species (see Fig. 1).

Table III lists the rms deviations of the individual benchmark components for the full T_{kl}^j (FULL), diagonal (D), and fixed (FIX) *Ansätze*, as described in Sec. II H. For each case, the coupled and uncoupled (EBC, “*”) results are given.

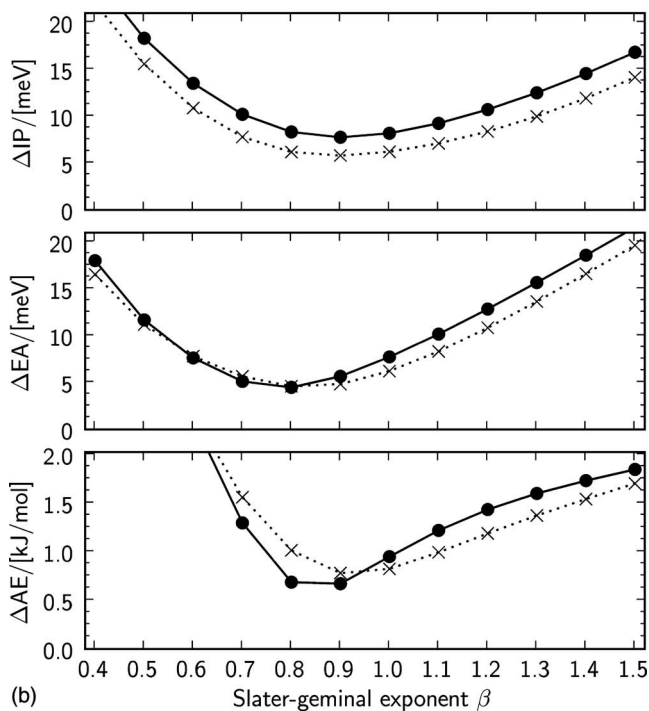
For the atomization energies, the full *Ansatz* leads to worse results than the diagonal and fixed *Ansätze*. This effect can be attributed to the geminal BSSE,^{17,49} as already mentioned. However, in the cases of EAs and IPs, the accuracy of the results increases with increased wave function flexibility. In contrast to atomization or reaction energies the geminal BSSE does not play a significant role for EAs and IPs, because the occupied orbitals of the neutral and ionized species are very similar, and therefore the BSSE effect cancels out.

For the calculations summarized in Table III, the effect of the EBC approximation is significant but rather small for diagonal and fixed methods. For AEs, the results of the coupled methods are slightly better on the average, but for IPs and EAs they are slightly worse (see also Fig. 2). When using inadequate orbital or auxiliary basis sets or geminal exponents, we often found the uncoupled methods to have less basis set limit deviation than the coupled ones.

The reason for this is not really clear, but likely to be related to the externally contracted nature of the F12 configurations. The fixed form of the short-range hole admitted by the F12 configurations is not equally suited for all regions of the molecule. The mean fields generated due to some of



(a)



(b)

FIG. 2. Dependence of F12 basis set errors on β with AVTZ/A2VTZ orbital basis sets with respect to CBS[56] (see text). Shown is the total rms basis set error of the DF-RMP2-F12 methods. Upper panel: 3C(D) (full lines) and 3*C(D) (dotted lines). Lower panel: 3C(FIX) (full lines) and 3*C(FIX) (dotted lines). All 25 EAs, 39 IPs, and 49 AEs are included in the statistics. The scales in the subplots are equal (1 kJ/mol \approx 10.36 meV).

these less-suited regions may provoke a nonoptimal reaction of the conventional amplitudes which try to adjust to their presence.

C. Impact of hybrid approximations

Table IV demonstrates the impact of the hybrid approximations HY1 and HY2 to the $\tilde{Y}_{kl,mn}$ term, which can lead to

TABLE IV. Impact of hybrid approximations on the F12 basis set error. Total rms basis set errors for RMP2-F12/3C(D) are shown. In all cases $\beta = 0.9\alpha_0^{-1}$ and the AVTZ/A(2)VTZ basis sets as described in Sec. III A were used.

Method	Full	HY2	HY1
<i>EAs</i> (meV)			
3C(D)	6.328	6.516	6.884
3*C(D)	4.778	4.868	5.050
<i>IPs</i> (meV)			
3C(D)	7.228	7.457	8.378
3*C(D)	4.756	4.795	5.207
<i>AEs</i> (kJ/mol)			
3C(D)	1.068	1.076	1.011
3*C(D)	1.122	1.128	1.159

significant time and disk space savings. Obviously both approximations produce accurate results. The impact of the HY2 approximation is negligible. The HY1 approximation worsens the basis set convergence noticeably, but not much. This finding is consistent with results for closed-shell molecules.¹⁷

D. Dependence on the geminal exponent

The upper panel of Fig. 2 shows the dependence of the rms deviations of the 3C(D) and 3*C(D) methods on the geminal exponent β . The main finding here is that the dependence is different for different properties. Apparently the parts of the valence region which need to be described accurately are different depending on what is being calculated. For example, in the case of EAs it is very important that the interactions of the highly diffuse outer electrons in the anion are described precisely (which are modeled better by wider correlation holes and thus smaller exponents). The energetics of the other electrons are less important because they are similar for the anion and the neutral species, and thus deficiencies in their description cancel out in the difference.

Unexpectedly, for the 3C(D) method a similar exponent behavior as for the EAs is also found for atomization energies. Although for the AVTZ orbital basis sets the basis error of the actual compounds (i.e., molecules and atoms) typically has a minimum around a geminal exponent of 0.9–1.5 (depending on the involved atoms), the basis set convergence of the AE can be accelerated by using smaller exponents.

Similar calculations for the 3C(FIX) and 3*C(FIX) methods are summarized in the lower panel of Fig. 2. For EAs and IPs a similar but more pronounced behavior as for the 3C(D) method is found. The dependence of the average basis set error on the choice of β is much larger than for the more flexible diagonal method. Unlike for the 3C(D) method, very low β values deteriorate atomization energies instead of improving them.

E. Perturbative Hartree–Fock corrections

We explicitly tested the improvement of the Hartree–Fock treatment achieved by the methods described in Sec. III. In detail, we tested the following perturbative RHF corrections to the DF-RHF/A(2)VTZ energies:

TABLE V. rms error of DF-RHF+(perturbative singles correction) at the A(2)VTZ level relative to RHF/AV6Z. See text for details.

RI and JKFIT:	VTZ/JKFIT		AVTZ-JK	
	Yes	No	Yes	No
Core-Singles:				
ΔEA (meV), (none)				12.593
ΔEA (meV), Singl.			1.652	2.175
ΔEA (meV), Relax.			1.584	2.189
ΔIP (meV), (none)		11.444		11.440
ΔIP (meV), Singl.	3.356	3.126	1.936	1.896
ΔIP (meV), Relax.	2.814	2.860	1.576	1.792
ΔAE (kJ/mol), (none)		3.736		3.706
ΔAE (kJ/mol), Singl.	0.551	0.460	0.659	0.610
ΔAE (kJ/mol), Relax.	0.430	0.402	0.467	0.497

- CABS-singles: The energy difference of “RMP2-singles into the combined MO and CABS basis” minus the “RMP2-singles into the MO basis alone” is added to the DF-RHF energy.
- CABS-RHF-relax: The energy correction from the spin-adapted singles perturbation theory is added to the DF-RHF energy.

As described in Sec. III, the first correction contains a part of the RMP2 singles correlation energy, while the second does not. Both approaches are equivalent in the closed-shell case. The cost of calculating these corrections on their own is similar to that of a single RHF iteration in the complete MO+CA basis set. However, since the occurring Fock matrices are required for the RMP2-F12 anyway, only the additional cost for block diagonalizing the Fock matrix and/or performing a cheap iterative solution remains.

The performance of the different treatments compared with conventional RHF/AV6Z is summarized in Table V. Obviously both approaches greatly improve the DF-RHF energies obtained at the AVTZ or A2VTZ (for EAs) level. Although conventional RHF/AV5Z accuracy is not obtained reliably, in any case the basis set error of the DF-RHF treatment becomes smaller again than that of the F12 correlation treatment (see Table III), which is the main goal.

Both RHF correction treatments have been tested with and without allowing excitations from core electrons. The rationale for allowing these excitations is that the core electrons would also relax if an actual RHF treatment in a larger basis would be performed. They lead to total energies which are much closer to the reference values than when not allowing them, but the effect on energy differences is almost negligible. As they can be calculated for free anyway, we chose to include them by default.

Also, the potential for correcting RHF energies of the CABS-singles and CABS-relax *Ansätze* is very similar. The results of the CABS-RHF-relax approach look slightly better on average. Therefore, and since these results do not include the spurious RMP2 singles correlation contributions, this approach should be used for RHF corrections except if RMP2-F12 *on itself* is actually used as correlation method [i.e., not as some augmentation to, say, RHF-UCCSD(T)].

As the right columns of Table V show, the error can be further decreased by using the augmented JK-fitting basis set described in Sec. III A also for DF of the Fock matrices and for the RI in the IP case. It is not obvious why this basis enhancement does not also improve the results for atomization energies.

V. CONCLUSIONS AND OUTLOOK

The presented DF-RMP2-F12 method shows a basis set convergence of correlation energies which is just as fast as that of its closed-shell counterpart.¹⁷ Furthermore, using already available Fock matrices, the basis set error of the Hartree-Fock treatment could be reduced significantly, and thus rapid convergence of *total* energies was obtained. Already with the medium sized AVTZ basis set, total rms basis set deviations of less than 2 kJ/mol \approx 20 meV were obtained consistently for atomization energies, electron affinities and ionization potentials. Especially AEs and EA pose difficult problems to conventional basis set expansions, which require very large basis sets in order to obtain accurate results for these properties. For the F12 method this is not the case. At AVTZ level, all computed values were closer to the basis set limit than for conventional AV5Z calculations, usually *much* closer.

While the RMP2-F12 methods allows us to calculate RMP2 complete basis set (CBS) limit energies very efficiently, these energies are of course still MP2 energies, and as such of limited accuracy when compared to experimental values. The next important step is therefore to develop an open-shell explicitly correlated coupled-cluster method. We already implemented similar RHF-UCCSD(T)-F12 approximations as recently proposed for closed-shell cases.²² The RMP2-F12 method presented here is the first step in this method. Our preliminary RHF-UCCSD(T)-F12 results are very promising, and will be published elsewhere.

ACKNOWLEDGMENTS

This work was funded in the priority program 1145 by the Deutsche Forschungsgemeinschaft. One of the authors (H.J.W.) is also grateful for generous support by the Fonds der Chemischen Industrie. We thank Fred Manby for providing the integral routines used in the DF-RMP2-F12 program.

APPENDIX: SINGULARITIES OF THE B MATRIX

Singularities and negative eigenvalues in the *B* matrix in Eq. (17) have been reported by several groups. They start to appear when larger systems are being investigated.

The main reason for these singularities is that for extended systems the explicitly correlated configurations (10) become linearly dependent. This is easily seen when considering the configurations in a localized orbital basis. Assume that in

$$\mathcal{F}_{\alpha\beta}^{mn} = \langle \alpha\beta | \hat{Q}_{12} F_{12} | mn \rangle,$$

$$\hat{Q}_{12} = (1 - \hat{o}_1)(1 - \hat{o}_2)(1 - \hat{v}_1\hat{v}_2),$$

the orbitals *m* and *n* are well localized and far apart. Then inevitably in $\mathcal{F}_{\alpha\beta}^{mn}$ only such F_{12} can have nonvanishing impact, for which r_{12} is large, since in

$$\begin{aligned} \langle \alpha\beta | F_{12} | mn \rangle = & \int \int \varphi_{\alpha}^*(\mathbf{r}_1) \varphi_{\beta}^*(\mathbf{r}_2) F_{12}(\|\mathbf{r}_1 - \mathbf{r}_2\|) \\ & \times \varphi_m(\mathbf{r}_1) \varphi_n(\mathbf{r}_2) d^3r_1 d^3r_2. \end{aligned}$$

\mathbf{r}_1 is essentially restricted to the domain of the orbital *m* and \mathbf{r}_2 to that of *n*. Since F_{12} falls off sharply with r_{12} [for real Slater functions with $\exp(-\beta r_{12})$ and for linear combinations of Gaussians as $\exp(-\alpha r_{12}^2)$], the resulting explicitly correlated configurations become almost zero in norm.

This problem could be approached by orthonormalization of the explicitly correlated configurations with respect to $\langle kl | F_{12} F_{12} | mn \rangle$ (note that *X* is their overlap matrix). But ultimately, this would have limited value since the configurations with large r_{12} (i) do not help in the treatment of the correlation problem anyway, (ii) numerical problems are still to be expected in cases with near linear dependencies, and (iii) the explicitly correlated configurations are *legitimately* diminished by \hat{Q}_{12} , since their effect can be achieved with the conventional wave function.

Our current opinion is that they should simply be projected out by projecting R_{kl}^{ij} and T_{kl}^{ij} onto the eigenspace belonging to the non-negative eigenvalues of *B* or *X*, which is already the common practice.

Although this discussion was based on the premise of localized occupied orbitals, the same conclusions hold, of course, for canonical orbitals. After all, these can be obtained from the localized orbitals by a unitary rotation which cannot make the explicit configurations less linearly dependent.

¹E. A. Hylleraas, *Z. Phys.* **54**, 347 (1929).

²W. Kutzelnigg, *Theor. Chim. Acta* **68**, 445 (1985).

³W. Kutzelnigg and W. Klopper, *J. Chem. Phys.* **94**, 1985 (1991).

⁴W. Kutzelnigg and W. Klopper, *J. Chem. Phys.* **94**, 2002 (1991).

⁵J. Noga, W. Kutzelnigg, and W. Klopper, *Chem. Phys. Lett.* **199**, 497 (1992).

⁶R. J. Gdanitz, *J. Chem. Phys.* **109**, 9795 (1998).

⁷J. Noga and W. Kutzelnigg, *J. Chem. Phys.* **101**, 7738 (1994).

⁸W. Klopper and C. C. M. Samson, *J. Chem. Phys.* **116**, 6397 (2002).

⁹E. F. Valeev, *Chem. Phys. Lett.* **395**, 190 (2004).

¹⁰S. Ten-no and F. R. Manby, *J. Chem. Phys.* **119**, 5358 (2003).

¹¹F. R. Manby, *J. Chem. Phys.* **119**, 4607 (2003).

¹²S. Ten-no, *Chem. Phys. Lett.* **398**, 56 (2004).

¹³A. J. May, E. Valeev, R. Polly, and F. R. Manby, *Phys. Chem. Chem. Phys.* **7**, 2710 (2005).

¹⁴D. P. Tew and W. Klopper, *J. Chem. Phys.* **123**, 074101 (2005).

¹⁵H.-J. Werner and F. R. Manby, *J. Chem. Phys.* **124**, 054114 (2006).

¹⁶F. R. Manby, H.-J. Werner, T. B. Adler, and A. J. May, *J. Chem. Phys.* **124**, 094103 (2006).

¹⁷H.-J. Werner, T. B. Adler, and F. R. Manby, *J. Chem. Phys.* **126**, 164102 (2007).

¹⁸J. Noga, S. Kedžuch, and J. Šimunek, *J. Chem. Phys.* **127**, 034106 (2007).

¹⁹H. Fliegl, W. Klopper, and C. Hättig, *J. Chem. Phys.* **122**, 084107 (2005).

²⁰H. Fliegl, C. Hättig, and W. Klopper, *Int. J. Quantum Chem.* **106**, 2306 (2006).

²¹D. P. Tew, W. Klopper, C. Neiss, and C. Hättig, *Phys. Chem. Chem. Phys.* **9**, 1921 (2007).

²²T. B. Adler, G. Knizia, and H.-J. Werner, *J. Chem. Phys.* **127**, 221106

- (2007).
- ²³ R. Polly, H.-J. Werner, P. Dahle, and P. R. Taylor, *J. Chem. Phys.* **124**, 234107 (2006).
- ²⁴ E. F. Valeev, *J. Chem. Phys.* **125**, 244106 (2006).
- ²⁵ D. P. Tew, W. Klopper, and F. R. Manby, *Chem. Phys. Lett.* **127**, 174105 (2007).
- ²⁶ R. J. Gdanitz, *J. Chem. Phys.* **109**, 9795 (1998).
- ²⁷ R. J. Gdanitz, *J. Chem. Phys.* **110**, 706 (1999).
- ²⁸ J. R. Flores and R. J. Gdanitz, *J. Chem. Phys.* **123**, 144316 (2005).
- ²⁹ W. Cardoen, R. J. Gdanitz, and J. Simons, *J. Phys. Chem. A* **110**, 564 (2006).
- ³⁰ S. Ten-no, *Chem. Phys. Lett.* **447**, 175 (2007).
- ³¹ J. Noga, P. Valiron, and W. Klopper, *J. Chem. Phys.* **115**, 2022 (2001).
- ³² J. Noga and P. Valiron, *Chem. Phys. Lett.* **324**, 166 (2000).
- ³³ W. Klopper and J. Noga, *ChemPhysChem* **4**, 32 (2003).
- ³⁴ D. P. Tew, W. Klopper, M. Heckert, and J. Gauss, *J. Phys. Chem. A* **111**, 11242 (2007).
- ³⁵ R. A. Bachorz, W. Klopper, and M. Gutowski, *J. Chem. Phys.* **126**, 085101 (2007).
- ³⁶ M. W. Wong and L. Radom, *J. Phys. Chem.* **99**, 8582 (1995).
- ³⁷ C. J. Parkinson, P. M. Mayer, and L. Radom, *Theor. Chem. Acc.* **102**, 92 (1999).
- ³⁸ C. W. Murray and N. C. Handy, *J. Chem. Phys.* **97**, 6509 (1992).
- ³⁹ P. J. Knowles, J. S. Andrews, R. D. Amos, N. C. Handy, and J. Pople, *Chem. Phys. Lett.* **186**, 130 (1991).
- ⁴⁰ H. B. Schlegel, *J. Phys. Chem.* **92**, 3075 (1988).
- ⁴¹ W. J. Lauderdale, J. F. Stanton, J. Gauss, J. D. Watts, and R. J. Bartlett, *J. Chem. Phys.* **97**, 6606 (1992).
- ⁴² W. J. Lauderdale, J. F. Stanton, J. Gauss, J. D. Watts, and R. J. Bartlett, *Chem. Phys. Lett.* **187**, 21 (1991).
- ⁴³ H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, and M. Schütz, MOLPRO, *Development Version 2006.3, a package of ab initio programs*, 2007 (see <http://www.molpro.net>).
- ⁴⁴ J. F. S. J. Gauss and R. J. Bartlett, *J. Chem. Phys.* **97**, 7825 (1992).
- ⁴⁵ T. D. Crawford, H. F. Schaefer III, and T. J. Lee, *J. Chem. Phys.* **105**, 1060 (1996).
- ⁴⁶ P. J. Knowles, C. Hampel, and H.-J. Werner, *J. Chem. Phys.* **99**, 5219 (1993).
- ⁴⁷ W. Klopper, *J. Chem. Phys.* **120**, 10890 (2004).
- ⁴⁸ W. Klopper, *Chem. Phys. Lett.* **186**, 583 (1991).
- ⁴⁹ D. P. Tew and W. Klopper, *J. Chem. Phys.* **125**, 094302 (2006).
- ⁵⁰ C. Neiss, C. Hättig, and W. Klopper, *J. Chem. Phys.* **125**, 064111 (2006).
- ⁵¹ T. Kato, *Commun. Pure Appl. Math.* **10**, 151 (1957).
- ⁵² R. T. Pack and W. Byers Brown, *J. Chem. Phys.* **45**, 556 (1966).
- ⁵³ R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, *J. Chem. Phys.* **96**, 6796 (1992).
- ⁵⁴ J. T. H. Dunning, K. A. Peterson, and A. Wilson, *J. Chem. Phys.* **114**, 9244 (2001).
- ⁵⁵ F. Weigend, *Phys. Chem. Chem. Phys.* **4**, 4285 (2002).
- ⁵⁶ F. Weigend, A. Köhn, and C. Hättig, *J. Chem. Phys.* **116**, 3175 (2002).
- ⁵⁷ J. Pipek and P. G. Mezey, *J. Chem. Phys.* **90**, 4916 (1989).
- ⁵⁸ L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, *J. Chem. Phys.* **94**, 7221 (1991).
- ⁵⁹ K. L. Bak, P. Jørgensen, J. Olsen, T. Helgaker, and W. Klopper, *J. Chem. Phys.* **112**, 9229 (2000).