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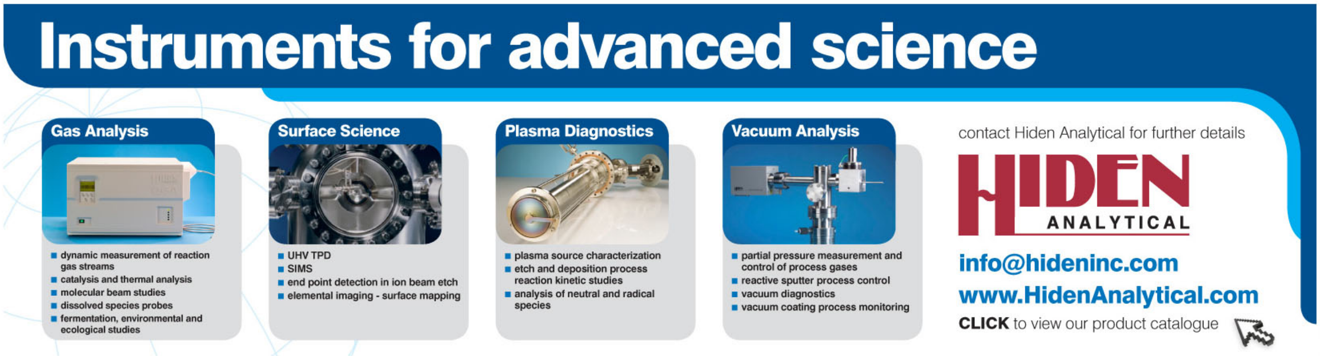

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General orbital invariant MP2-F12 theory

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A general form of orbital invariant explicitly correlated second-order closed-shell Møller-Plesset perturbation theory (MP2-F12) is derived, and compact working equations are presented. Many-electron integrals are avoided by resolution of the identity (RI) approximations using the complementary auxiliary basis set approach. A hierarchy of well defined levels of approximation is introduced, differing from the exact theory by the neglect of terms involving matrix elements over the Fock operator. The most accurate method is denoted as MP2-F12/**3**B. This assumes only that Fock matrix elements between occupied orbitals and orbitals outside the auxiliary basis set are negligible. For the chosen ansatz for the first-order wave function this is exact if the auxiliary basis is complete. In the next lower approximation it is assumed that the occupied orbital space is closed under action of the Fock operator [generalized Brillouin condition (GBC)]; this is equivalent to approximation **2**B of Klopper and Samson [J. Chem. Phys. **116**, 6397 (2002)]. Further approximations can be introduced by assuming the extended Brillouin condition (EBC) or by neglecting certain terms involving the exchange operator. A new approximation MP2-F12/**3**C, which is closely related to the MP2-R12/C method recently proposed by Kedžuch *et al.* [Int. J. Quantum Chem. **105**, 929 (2005)] is described. In the limit of a complete RI basis this method is equivalent to MP2-F12/**3**B. The effect of the various approximations (GBC, EBC, and exchange) is tested by studying the convergence of the correlation energies with respect to the atomic orbital and auxiliary basis sets for 21 molecules. The accuracy of relative energies is demonstrated for 16 chemical reactions. Approximation **3**C is found to perform equally well as the computationally more demanding approximation **3**B. The reaction energies obtained with smaller basis sets are found to be most accurate if the orbital-variant diagonal *Ansatz* combined with localized orbitals is used for the first-order wave function. This unexpected result is attributed to geminal basis set superposition errors present in the formally more rigorous orbital invariant methods. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2712434]

I. INTRODUCTION

One of the most severe limitations in *ab initio* quantum chemistry is the slow convergence of electron correlation energies with respect to the basis set size. For atoms it can be shown that the error in the correlation energy falls off only like $l_{\max}^{-3}$, where $l_{\max}$ is the maximum angular momentum in the basis.[1,2] If the correlation consistent basis sets cc-pV*n*Z of Dunning and co-workers are used,[3–7] where the cardinal number n equals $l_{\max}$, the number of basis functions N_{AO} grows as $l_{\max}^3$; it follows that the error in the correlation energy decays only at the painfully slow rate of $\mathcal{O}(N_{\mathrm{AO}}^{-1})$. For instance, an error of 1 mH remains in the correlation energy of the neon atom even with a cc-pV10Z basis (506 basis functions).[8] The convergence can be improved by basis set extrapolation techniques,[2] but this works well only with large basis sets and is computationally demanding.

The reason for the slow convergence is that the wave function cusp for $r_{12}\rightarrow 0$ and, more importantly, the correlation hole for intermediate values of r_{12} are poorly represented by expansions of the wave function in terms of orbital products (Slater determinants). This situation can be improved by using explicitly correlated wave functions, that is, wave functions that depend explicitly on the interelectronic distances r_{ij}. The introduction of such terms into the wave function greatly accelerates basis set convergence, as shown for helium as early as 1929 by Hylleraas.[9] The penalty for this approach is the introduction of three- and four-electron integrals, even at the level of MP2 theory, and these are so excessively numerous that applications are restricted to tiny systems. The four-electron integrals can be avoided by using the weak orthogonality functional of Szalewicz *et al.*,[10,11] but even then the evaluation of the remaining three-electron integrals is extremely expensive and limits the application of this method to very small molecules.[12]

Currently, the only practical approach for larger systems is to approximate the many-electron integrals using resolutions of the identity (RIs), as first proposed by Kutzelnigg and Klopper.[13] The many-electron integrals are then expressed in terms of sums of products of simpler two-electron

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integrals.[13,14] There have been several recent developments in the field, including the use of separate basis sets for the RI,[14–16] combinations of RI and density fitting (DF) approaches for efficiency[17–19] and accuracy,[20] the use of alternative correlation factors,[18,21–26] the use of quadrature for the many-electron integrals,[27] avoidance of Brillouin approximations,[23] parallel implementation,[28] and local approximations.[25,29] For a recent review of the status of explicitly correlated methods, see Ref. 30.

The relative importance of various approximations has recently been demonstrated.[23] The key finding was that the choice of the correlation factor is much more important than any other approximation. Short-ranged correlation factors such as $\exp(-\beta r_{12})$ were found to give very much improved results as compared to the linear r_{12} factor, which was used by Hylleraas as well as in the original R12 methods of Kutzelnigg and Klopper. The use of a simple Slater function was first proposed by Ten-no[22] and subsequently used by various authors.[18,21–26] Other choices have also been proposed and tested,[24] but the Slater function was found to work at least as well as other functional forms. Methods that are based on such short-ranged correlation factors are now referred to as F12 methods.

Short-ranged correlation factors are particularly important for the treatment of large molecules. Recently, we have developed local explicitly correlated LMP2-R12 (Ref. 29) and LMP2-F12 (Ref. 25) methods which can be applied to rather large molecules (50–100 atoms, up to 4000 basis functions). The numerical accuracy and efficiency of LMP2-F12 were found to be much better than those of LMP2-R12. As will be demonstrated in a forthcoming paper, almost linear scaling of the computational effort with molecular size has now been achieved for the LMP2-F12 method.

Our previous LMP2-F12 (Ref. 25) implementation was based on the simplest possible approximation, denoted as LMP2-F12/$\mathbf{2}^{*}$A(loc). In this approach exchange terms were entirely neglected and an orbital-variant *Ansatz* in combination with localized orbitals was used. Nevertheless, amazingly accurate results were obtained. For a set of 21 molecules, the correlation energies were found to be within 0.5% of the MP2 basis set limit, using augmented triple zeta (aug-cc-pVTZ) basis sets. For the same basis, reaction energies for 16 reactions agreed within 0.2 kcal mol^{-1} with those obtained using very much larger aug-cc-pV5Z basis sets. However, it is known that MP2-F12/$\mathbf{2}^{*}$A somewhat overestimates the correlation energies, and therefore some error compensation is likely.

The current paper is a result of our efforts to develop these local F12 methods further. Rather than using the simplest approximation, we now attempt to remove *all* approximations apart from those inherent in the wave function *Ansatz* and the RI; this should enable us to explore the true limits of the method, independent of any error compensations. In order to reintroduce local approximations at a later stage, it is important to derive the MP2-F12 equations in an orbital invariant form. This means that the optimized energy is invariant to unitary transformations among the occupied orbitals, and therefore either canonical or localized orbitals can be used. Most previous formulations were based on an orbital invariant *Ansatz* for the first-order wave function,[14,31] but then the equations were derived for the special case of a canonical orbital basis, in which the Fock operator is diagonal. Other orbital invariant formulations can be found in Refs. 15, 32, and 33.

TABLE I. Basis sets and orbital spaces used in this work.

Type	Acronym	Indices
Non-orthogonal atomic basis functions		
Atomic orbital basis	AO	$\mu,\nu,\ldots$
Auxiliary basis set	ABS	$\mu',\nu',\ldots$
Orthogonal orbital spaces		
Occupied orbitals	Occ	$i,j,\ldots$
Virtual orbitals	Virt	$a,b,\ldots$
Any molecular orbitals	MO	$r,s,\ldots$
Complementary auxiliary orbitals	CA	$x,y,\ldots$
Complete orthonormal or RI basis	RI	$\alpha,\beta,\ldots$

The theory for MP2-R12 with auxiliary basis sets has been presented before in various papers.[14–16,33] However, due to the numerous approximations and different notations, it is rather difficult for researchers who are not very familiar with these theories to get an overview and understanding of the many approximations. We have therefore attempted to derive the most general equations in the simplest possible form. This allows us to discuss all methods and approximations on an equal footing and to give a clearer insight into some of the approximations used.

In Sec. II, we will present the general formulation of the theory. Some technical aspects will be discussed in Sec. III. Finally, extensive results for all methods will be presented and discussed in Sec. IV.

II. ORBITAL INVARIANT MP2-F12 THEORY

The theory involves a number of different basis sets and orbital spaces. For easy reference these are summarized in Table I. The indices i, j, k, l, m, n, and o run over occupied orbitals, a, b, c, and d over virtual orbitals, and r, s, t, and u over all molecular orbitals (MO basis). The MOs are expanded in an atomic orbital (AO) basis $\{\mu,\nu,\rho,\sigma\}$.

The indices $\alpha,\beta,\ldots$ refer to a complete orthonormal one-electron basis, which is used to represent the RI. In practice, this is approximated by a finite orbital basis (RI approximation). As first suggested by Valeev,[16] it is advantageous to represent the RI by a linearly independent subspace of the union of the AO basis $\{\mu,\nu\}$ and an additional auxiliary basis set (ABS) $\{\mu',\nu'\}$. It is then possible to construct an orthogonal orbital basis which can be decomposed into the MO basis and its orthogonal complement. The functions in the orthogonal complement are denoted as complementary auxiliary (CA) orbitals and carry the indices x and y. As will be discussed in further detail in Sec. III C, the orthogonal CA orbitals are linear combinations of the AO and ABS basis sets. Following Valeev, we will refer to this choice of RI basis as the "CABS approach." We note that Valeev[16] has denoted the union of the MO and CA spaces as CABS+, but for simplicity we will use the acronym RI.

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One advantage of the CABS approach is that the union of the AO and ABS bases is larger than the ABS basis alone (unless the latter contains the AO basis), and therefore a more accurate approximation of the RI can be expected. Even more important is that the CABS approach leads to considerable simplifications of the theory since many terms cancel. As will be discussed in later sections, without CABS these cancellations would be incomplete, and spurious contributions may arise. We will therefore use the CABS approach throughout this paper.

Our theory applies to closed-shell reference functions and is spin free; i.e., all orbital indices refer to spatial functions $|\alpha\rangle \equiv \phi_\alpha(\mathbf{r})$, and the two-electron functions $|\alpha\beta\rangle \equiv \phi_\alpha(\mathbf{r}_1)\phi_\beta(\mathbf{r}_2)$ are spin-free products of orbitals. Summation over repeated dummy indices is assumed throughout this paper.

A. Definition of the first-order wave function

For closed-shell reference functions the complete set of doubly excited spin adapted configurations can be generated using products of excitation operators

$$\hat{E}_{\alpha i} = \eta_\alpha^\dagger \eta_i + \bar{\eta}_\alpha^\dagger \bar{\eta}_i, \tag{1}$$

where η_i and $\eta_\alpha^\dagger$ are the usual spin-orbital annihilation and creation operators, respectively, and the bar indicates beta spin. The first-order interacting space is spanned by the doubly excited configurations

$$|\Phi_{ij}^{\alpha\beta}\rangle = \hat{E}_{\alpha i}\hat{E}_{\beta j}|0\rangle, \tag{2}$$

where $|0\rangle \equiv |\Psi^{(0)}\rangle$ is the Hartree-Fock reference function. Note that in this definition there is no restriction of α and β to the virtual and complementary orbital spaces. The contributions of $\hat{E}_{ii}\hat{E}_{jj}|0\rangle$, which are proportional to the reference function, are projected out in the first-order wave function, as defined below. The singly excited configurations Φ_i^a and semi-internal configurations Φ_{ij}^{ak} and Φ_{ij}^{ka} do not contribute to the first-order wave function for closed-shell reference functions. It should be noted that single excitations Φ_i^α can give a contribution if α is outside the orbital basis. Even though it would be straightforward to include such contributions in the first-order wave function we exclude them in the current work by definition.

In R12 or F12 methods, the complete set of doubly excited configurations is approximated by the conventional configurations Φ_{ij}^{ab} and a small set of explicitly correlated configurations Φ_{ij}^{kl}, which are well suited to describe the correlation hole near the wave function cusp for $r_{12} \rightarrow 0$,

$$|\Phi_{ij}^{ab}\rangle = \hat{E}_{ai}\hat{E}_{bj}|0\rangle, \tag{3}$$

$$|\Phi_{ij}^{kl}\rangle = |\Phi_{ij}^{\alpha\beta}\rangle \mathcal{F}_{\alpha\beta}^{kl}, \tag{4}$$

with

$$\mathcal{F}_{\alpha\beta}^{kl} = \langle kl|\hat{F}_{12}\hat{Q}_{12}|\alpha\beta\rangle. \tag{5}$$

The $\mathcal{F}_{\alpha\beta}^{kl}$ can be viewed as contraction coefficients which project the full space of doubly excited configurations $|\Phi_{ij}^{\alpha\beta}\rangle$ to the small set $|\Phi_{ij}^{kl}\rangle$. The *correlation factor* $\hat{F}_{12} \equiv F(r_{12})$ depends on the interelectronic distance r_{12}. In the linear R12 methods, $\hat{F}_{12} = r_{12}$. In the current work we will use

$$F(r_{12}) = \exp(-\beta r_{12}), \tag{6}$$

but the derivation will be independent of the form of this function.

The projector $\hat{Q}_{12}$ ensures strong orthogonality of the explicitly correlated functions Φ_{ij}^{kl} to the reference function, which is necessary to formulate pair theories.[34] It can be chosen in different ways,[14,16,35–37]

$$\textit{Ansatz } \mathbf{1}: \quad \hat{Q}_{12} = (1-\hat{p}_1)(1-\hat{p}_2), \tag{7}$$

$$\textit{Ansatz } \mathbf{2}: \quad \hat{Q}_{12} = (1-\hat{o}_1)(1-\hat{o}_2), \tag{8}$$

$$\textit{Ansatz } \mathbf{3}: \quad \hat{Q}_{12} = (1-\hat{o}_1)(1-\hat{o}_2)(1-\hat{v}_1\hat{v}_2). \tag{9}$$

Here, $\hat{o} = |i\rangle\langle i|$, $\hat{v} = |a\rangle\langle a|$, and $\hat{p} = |r\rangle\langle r|$ are one-electron projection operators onto the occupied, virtual, and full orbital spaces, respectively, and the subscripts refer to the electron coordinates on which these act. *Ansatz* **1** and *Ansatz* **2** are equivalent and give the same results if the MO and RI orbital spaces are identical.[14] However, if a larger RI basis is used, they are different, and *Ansatz* **2**, which has been used in the MP2-R12 (Refs. 14 and 15) and MP2-F12 (Ref. 24) methods of Klopper and co-workers, gives much better results.

Ansatz **3** (Refs. 16, 18, and 37) is entirely equivalent to *Ansatz* **2** as long as no approximations are introduced. The term $1-\hat{v}_1\hat{v}_2$ has no effect on the results, but projects out the contributions of the conventional configurations $|\Phi_{ij}^{ab}\rangle$ from the explicitly correlated part. This not only minimizes couplings between the conventional and explicitly correlated first-order equations (Sec. II B), but also leads to simpler and more transparent equations. The formalism in the current paper is therefore based on *Ansatz* **3**. Even though *Ansatz* **2** and *Ansatz* **3** are equivalent and both have been denoted as *Ansatz* **2** in some previous papers,[18,23,25,29] in the current work we prefer to distinguish between them for two reasons: first, the working equations are different, and one must be careful when comparing our current formulation with previous papers. Second, some approximations have been proposed on the basis of the equations for *Ansatz* **2**,[14,15] while others will be proposed in Sec. II H using *Ansatz* **3**. Some of these approximations are not the same in *Ansatz* **2** and *Ansatz* **3** and lead to different results in the two cases (see Appendix).

For *Ansatz* **3**, $\hat{Q}_{12}|rs\rangle = 0$ and it follows that $\mathcal{F}_{rs}^{kl} = 0$ [Eq. (5)]. Thus, the explicitly correlated configurations $|\Phi_{ij}^{kl}\rangle = |\Phi_{ij}^{\alpha\beta}\rangle \mathcal{F}_{\alpha\beta}^{kl}$ are orthogonal to the reference function and conventional configurations, i.e., $\langle\Phi_{ij}^{kl}|\Psi^{(0)}\rangle = 0$ and $\langle\Phi_{ij}^{ab}|\Phi_{ij}^{kl}\rangle = 0$. Note that the latter orthogonality relation is not valid for *Ansatz* **2**, and this is one of the reasons for the simplifications mentioned above.

The first-order wave function can now be written in compact form as

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$$\Psi^{(1)} = \tfrac{1}{2}|\Phi_{ij}^{rs}\rangle T_{rs}^{ij} = \tfrac{1}{2}\left(|\Phi_{ij}^{ab}\rangle T_{ab}^{ij} + |\Phi_{ij}^{\alpha\beta}\rangle \mathcal{F}_{\alpha\beta}^{kl} T_{kl}^{ij}\right) \tag{10}$$

with $T_{rs}^{ij}=T_{sr}^{ji}$ and $T_{ak}^{ij}=T_{ka}^{ij}=0$. Here, the sum over rs effectively runs over kl and ab and thus includes the conventional and explicitly correlated contributions.

Since the configurations $|\Phi_{ij}^{rs}\rangle$ and $|\Phi_{ij}^{sr}\rangle$ are pairwise nonorthogonal, it is convenient also to define contravariant configurations

$$|\tilde{\Phi}_{ij}^{rs}\rangle = \tfrac{1}{6}\left(2|\Phi_{ij}^{rs}\rangle + |\Phi_{ij}^{sr}\rangle\right), \tag{11}$$

which have the property

$$\langle\tilde{\Phi}_{ij}^{rs}|\Psi^{(1)}\rangle = T_{rs}^{ij}. \tag{12}$$

Writing the first-order wave function in this basis,

$$|\Psi^{(1)}\rangle = \tfrac{1}{2}|\tilde{\Phi}_{ij}^{rs}\rangle \tilde{T}_{rs}^{ij}, \tag{13}$$

and equating this to Eq. (10) yields for the corresponding amplitudes in the contravariant basis

$$\tilde{T}_{rs}^{ij} = 2T_{rs}^{ij} - T_{sr}^{ij}. \tag{14}$$

Finally, we note that the contravariant explicitly correlated configurations can be expressed in the complete basis of doubly excited contravariant configurations as

$$|\tilde{\Phi}_{ij}^{kl}\rangle = |\tilde{\Phi}_{ij}^{\alpha\beta}\rangle \mathcal{F}_{\alpha\beta}^{kl}. \tag{15}$$

This relation is useful in the derivation of the residual equations in the next section.

B. The Hylleraas functional and the first-order equations

The amplitudes T_{ab}^{ij} and T_{kl}^{ij} are determined by minimizing the Hylleraas functional

$$E_2 = \langle\Psi^{(1)}|\hat{H}^{(0)} - E^{(0)}|\Psi^{(1)}\rangle + 2\langle\Psi^{(1)}|\hat{H}|\Psi^{(0)}\rangle. \tag{16}$$

This yields the linear first-order equations $R_{rs}^{ij}=0$ with the residuals

$$R_{rs}^{ij} = \langle\tilde{\Phi}_{ij}^{rs}|\hat{H}^{(0)} - E^{(0)}|\Psi^{(1)}\rangle + \langle\tilde{\Phi}_{ij}^{rs}|\hat{H}|\Psi^{(0)}\rangle. \tag{17}$$

In Møller-Plesset perturbation theory the zeroth order Hamiltonian is chosen to be

$$\hat{H}^{(0)} = \sum_{i=1}^{N_{\mathrm{el}}} \hat{f}_i = \sum_{\alpha\beta} \hat{E}_{\alpha\beta} f_{\alpha\beta}, \tag{18}$$

where $\hat{f}_i$ is the Fock operator for electron i and

$$f_{\alpha\beta} = \langle\alpha|\hat{f}|\beta\rangle. \tag{19}$$

Using Eq. (15) the residuals can be expressed as

$$R_{ab}^{ij} = r_{ab}^{ij}, \tag{20}$$

$$R_{kl}^{ij} = \mathcal{F}_{\alpha\beta}^{kl} r_{\alpha\beta}^{ij}. \tag{21}$$

The matrix elements $r_{\alpha\beta}^{ij}$ are the residuals in the complete orthonormal orbital basis and have the form

$$r_{\alpha\beta}^{ij} = K_{\alpha\beta}^{ij} + f_{\alpha\gamma} t_{\gamma\beta}^{ij} + t_{\alpha\gamma}^{ij} f_{\gamma\beta} - f_{io} t_{\alpha\beta}^{oj} - t_{\alpha\beta}^{io} f_{oj}. \tag{22}$$

Since excitations are only possible in virtual and complementary space orbitals, the matrix elements $r_{\alpha\beta}^{ij}$ are assumed to be zero if α or β refers to an occupied orbital, i.e., $r_{kl}^{ij}=r_{k\beta}^{ij}=r_{\alpha k}^{ij}=0$. Similarly, $t_{kl}^{ij}=t_{\alpha k}^{ij}=t_{k\beta}^{ij}=0$. Using $t_{\alpha\beta}^{ij}=\delta_{\alpha a}\delta_{\beta b}T_{ab}^{ij}+\mathcal{F}_{\alpha\beta}^{kl}T_{kl}^{ij}$ and Eq. (21), one obtains for the residuals

$$\begin{aligned} R_{ab}^{ij} = {} & K_{ab}^{ij} + f_{ac}T_{cb}^{ij} + T_{ac}^{ij}f_{cb} - f_{io}T_{ab}^{oj} - T_{ab}^{io}f_{oj} + T_{mn}^{ij}C_{ab}^{mn} \\ & - \mathcal{F}_{ab}^{mn}[f_{io}T_{mn}^{oj} + T_{mn}^{io}f_{oj}], \end{aligned} \tag{23}$$

$$\begin{aligned} R_{kl}^{ij} = {} & V_{kl}^{ij} + B_{kl,mn}T_{mn}^{ij} - X_{kl,mn}[f_{io}T_{mn}^{oj} + T_{mn}^{io}f_{oj}] + C_{ab}^{kl}T_{ab}^{ij} \\ & - \mathcal{F}_{ab}^{kl}[f_{io}T_{ab}^{oj} + T_{ab}^{io}f_{oj}], \end{aligned} \tag{24}$$

where the basic matrix elements are defined as

$$K_{\alpha\beta}^{ij} = \langle ij|r_{12}^{-1}|\alpha\beta\rangle, \tag{25}$$

$$V_{kl}^{ij} = K_{\alpha\beta}^{ij}\mathcal{F}_{\alpha\beta}^{kl} = \langle ij|r_{12}^{-1}\hat{Q}_{12}\hat{F}_{12}|kl\rangle, \tag{26}$$

$$\begin{aligned} B_{kl,mn} &= \mathcal{F}_{\alpha\beta}^{kl}f_{\alpha\gamma}\mathcal{F}_{\gamma\beta}^{mn} + \mathcal{F}_{\alpha\beta}^{kl}f_{\beta\gamma}\mathcal{F}_{\alpha\gamma}^{mn} \\ &= \langle kl|\hat{F}_{12}\hat{Q}_{12}(\hat{f}_1 + \hat{f}_2)\hat{Q}_{12}\hat{F}_{12}|mn\rangle, \end{aligned} \tag{27}$$

$$X_{kl,mn} = \mathcal{F}_{\alpha\beta}^{kl}\mathcal{F}_{\alpha\beta}^{mn} = \langle kl|\hat{F}_{12}\hat{Q}_{12}\hat{F}_{12}|mn\rangle, \tag{28}$$

$$C_{ab}^{kl} = f_{a\gamma}\mathcal{F}_{\gamma b}^{kl} + \mathcal{F}_{a\gamma}^{kl}f_{\gamma b} = \langle kl|\hat{F}_{12}\hat{Q}_{12}(\hat{f}_1 + \hat{f}_2)|ab\rangle. \tag{29}$$

In order to derive working equations for the matrix elements $B_{kl,mn}$, it is convenient to use

$$\hat{Q}_{12}\hat{f}_{12}\hat{Q}_{12} = \hat{\mathcal{S}}(\hat{f}_{12}\hat{Q}_{12} - \hat{P}_{12}\hat{f}_{12}\hat{Q}_{12}), \tag{30}$$

where $\hat{f}_{12}=\hat{f}_1+\hat{f}_2$ and the symmetrizing operator $\hat{\mathcal{S}}$ is defined by $\hat{\mathcal{S}}\hat{O}=(\hat{O}+\hat{O}^{\dagger})/2$. Inserting this into Eq. (27) yields

$$B_{kl,mn} = \hat{\mathcal{S}}[A_{kl,mn} - Z_{kl,mn} - F_{ab}^{kl}C_{ab}^{mn}], \tag{31}$$

where

$$A_{kl,mn} = \langle kl|\hat{F}_{12}\hat{f}_{12}\hat{Q}_{12}\hat{F}_{12}|mn\rangle, \tag{32}$$

$$Z_{kl,mn} = \langle kl|\hat{F}_{12}(\hat{o}_1\hat{f}_1 + \hat{o}_2\hat{f}_2)\hat{Q}_{12}\hat{F}_{12}|mn\rangle. \tag{33}$$

The matrix elements $A_{kl,mn}$ arise from $\hat{f}_{12}\hat{Q}_{12}$ [Eq. (30)], while the remaining terms are obtained by expanding $\hat{P}_{12}\hat{f}_{12}\hat{Q}_{12}$. The derivation of these expressions uses the identity $(\hat{o}_1\hat{f}_2+\hat{o}_2\hat{f}_1)\hat{Q}_{12}=0$ and does not require any approximations for $\hat{P}_{12}$. RI approximations will be needed, however, to resolve the remaining projectors $\hat{Q}_{12}$ [Sec. II C].

In terms of these quantities the Hylleraas energy is obtained as

$$E_2 = \tilde{T}_{ab}^{ij}(K_{ab}^{ij} + R_{ab}^{ij}) + \tilde{T}_{kl}^{ij}(V_{kl}^{ij} + R_{kl}^{ij}). \tag{34}$$

For the optimized amplitudes the residuals vanish and

$$(E_2)_{\min} = E^{(2)} = \tilde{T}_{ab}^{ij}K_{ab}^{ij} + \tilde{T}_{kl}^{ij}V_{kl}^{ij}. \tag{35}$$

The equations given above are independent of the *Ansatz*.

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However, the explicit form of the basic matrix elements V^{ij}_{kl}, $X_{kl,mn}$, C^{kl}_{ab}, $B_{kl,mn}$, and $\mathcal{F}^{kl}_{ab}$ differs for *Ansatz* **2** and *Ansatz* **3**. As mentioned earlier, for *Ansatz* **3** we have $\mathcal{F}^{kl}_{ab}=0$, and therefore the last terms in Eqs. (23) and (24) vanish. Couplings of the two sets of equations are then introduced solely by the matrices C^{kl}_{ab}. In *Ansatz* **2**, however, the $\mathcal{F}^{kl}_{ab}$ are nonzero, which leads to additional terms and couplings (see the Appendix).

A partial decoupling of the first-order equations [Eq.(24)] can be achieved by defining singlet ($p=1$) and triplet ($p=-1$) pairs,

$$R^{ij,p}_{kl} = \tfrac{1}{2}(R^{ij}_{kl} + pR^{ij}_{lk}), \tag{36}$$

$$T^{ij,p}_{kl} = \tfrac{1}{2}(T^{ij}_{kl} + pT^{ij}_{lk})(2-\delta_{kl}), \tag{37}$$

for $i \geqslant j$, $k \geqslant l$ and $p=\pm 1$ (for $p=-1$ the diagonal terms $i=j$ and $k=l$ are not included). Using $B_{kl,mn}=B_{lk,nm}$, the equations for $p=1$ and $p=-1$ can then be solved independently for $i \geqslant j$, $k \geqslant l$ (*Ansatz* **3**),

$$\begin{aligned} R^{ij,p}_{kl} &= V^{ij,p}_{kl} + \sum_{m \geqslant n} B^{(p)}_{kl,mn} T^{ij,p}_{mn} + C^{kl,p}_{ab} T^{ij,p}_{ab} \\ &\quad - \sum_{m \geqslant n} X^{(p)}_{kl,mn} [f_{io} T^{oj,p}_{mn} + T^{io,p}_{mn} f_{oj}], \end{aligned} \tag{38}$$

where

$$B^{(p)}_{kl,mn} = \tfrac{1}{2}(B_{kl,mn} + pB_{lk,mn}). \tag{39}$$

Other quantities such as $V^{ij,p}_{kl}$, $C^{kl,p}_{ab}$, and $X^{(p)}_{kl,mn}$ are defined analogously. Note that there is no need to normalize the spin-coupled configurations. In the spin-coupled representation, the energy contribution of the explicitly correlated part is given by

$$\Delta E_2 = \sum_{i \geqslant j} (2-\delta_{ij}) \sum_{p} (2-p) \sum_{k \geqslant l} T^{ij,p}_{kl} (V^{ij,p}_{kl} + R^{ij,p}_{kl}). \tag{40}$$

The following sections deal with approximations for the four types of basic matrix elements V^{ij}_{kl}, $B_{kl,mn}$, C^{kl}_{ab}, and $X_{kl,mn}$ using *Ansatz* **3**.

C. RI approximations

So far, no approximations have been introduced, and within the MP2-F12 ansatz the expressions given in the previous section are exact. However, the evaluation of the matrix elements which contain the projector $\hat{Q}_{12}$ requires three- and four-electron integrals. For example,

$$\langle ij | r_{12}^{-1} \hat{o}_1 \hat{F}_{12} | kl \rangle = \langle ijm | r_{12}^{-1} \hat{F}_{32} | mlk \rangle. \tag{41}$$

In matrix elements involving the Fock operator also four-electron integrals arise.

Note that the Dirac bracket notation $|m\rangle\langle m|$ implies that the integrations arising from the bra $\langle m|$ and ket $|m\rangle$ are independent. In order to obtain the right hand side of Eq. (41), one of the integration variables must be renamed. More formally, this can be achieved by expressing $\hat{o}_1$ and $\hat{o}_2$ as

$$\hat{o}_1 = |\phi_m(\mathbf{r}_1)\rangle \hat{\tau}_{13} \langle \phi_m(\mathbf{r}_1)|, \tag{42}$$

$$\hat{o}_2 = |\phi_m(\mathbf{r}_2)\rangle \hat{\tau}_{24} \langle \phi_m(\mathbf{r}_2)|, \tag{43}$$

where the operator $\hat{\tau}_{ij}$ renames the electron coordinates $\mathbf{r}_i$ to $\mathbf{r}_j$, which occur in the integration with the bra functions $\langle \phi_m(\mathbf{r}_i)|$.

Currently, the only practical method to avoid the many-electron integrals is through the use of RI approximations, as first proposed by Kutzelnigg and Klopper[13] and Klopper and Samson.[14] In this approximation one makes the replacement

$$\hat{o}_1 \rightarrow \hat{o}_1 \hat{p}'_2, \tag{44}$$

where $\hat{p}'_2 = |\alpha(\mathbf{r}_2)\rangle\langle\alpha(\mathbf{r}_2)|$ is the resolution of the identity for electron 2. The three-electron integrals then factorize into sums of products of two-electron integrals, e.g.,

$$\begin{aligned} \langle ij | r_{12}^{-1} \hat{o}_1 \hat{F}_{12} | kl \rangle &= \langle ij | r_{12}^{-1} \hat{o}_1 \hat{p}'_2 \hat{F}_{12} | kl \rangle \\ &= \langle ij | r_{12}^{-1} | m\alpha \rangle \langle m\alpha | \hat{F}_{12} | kl \rangle. \end{aligned} \tag{45}$$

As long as the RI basis is complete, this is exact. Of course, in practice, a finite RI basis is used and the convergence behavior has to be checked.

The projector $\hat{Q}_{12}$ (*Ansatz* **3**) can now be expanded as

$$\hat{Q}_{12} = 1 - \hat{P}_{12}, \tag{46}$$

$$\begin{aligned} \hat{P}_{12} &= \hat{o}_1 + \hat{o}_2 - \hat{o}_1\hat{o}_2 + \hat{v}_1\hat{v}_2 \\ &= |m\alpha\rangle\langle m\alpha| + |\alpha m\rangle\langle \alpha m| - |mn\rangle\langle mn| + |ab\rangle\langle ab|. \end{aligned} \tag{47}$$

Using $\hat{v}_i = \hat{p}_i - \hat{o}_i$, the projector $\hat{P}_{12}$ can be rewritten as

$$\begin{aligned} \hat{P}_{12} &= |m\alpha\rangle\langle m\alpha| + |\alpha m\rangle\langle \alpha m| - |rm\rangle\langle rm| - |mr\rangle\langle mr| \\ &\quad + |rs\rangle\langle rs|. \end{aligned} \tag{48}$$

Furthermore, in the CABS approach $|\alpha\rangle\langle\alpha|$ can be replaced by $|r\rangle\langle r| + |x\rangle\langle x|$. The latter expression then simplifies to

$$\hat{P}_{12} = |xm\rangle\langle xm| + |mx\rangle\langle mx| + |rs\rangle\langle rs|. \tag{49}$$

If the AO and RI bases are the same, the terms involving the CA orbitals x vanish. The remainder $\hat{Q}_{12} = 1 - |rs\rangle\langle rs|$ is just the projector for *Ansatz* **1**; i.e., in this case there is no difference between the *Ansätze* **1** and **3**. The projector for *Ansatz* **2** differs by an additional term $\hat{v}_1\hat{v}_2$, but in the absence of further approximations this has no effect on the results (see the Appendix).

For simplicity in later expressions, we introduce the notation

$$\hat{P}_{12} = |\alpha\beta\rangle P_{\alpha\beta} \langle \alpha\beta|, \tag{50}$$

where it is assumed that the basis $\{\alpha, \beta\}$ contains all orbital spaces $(i, j, a, b, x, \text{and } y)$. The matrix elements V^{ij}_{kl} and $X_{kl,mn}$ can then be written as

$$V^{ij}_{kl} = K^{F}_{ij,kl} - K^{ij}_{\alpha\beta} P_{\alpha\beta} F^{kl}_{\alpha\beta}, \tag{51}$$

$$X_{kl,mn} = F^{2}_{kl,mn} - F^{kl}_{\alpha\beta} P_{\alpha\beta} F^{mn}_{\alpha\beta}, \tag{52}$$

where $K^{ij}_{\alpha\beta}$ has been defined in Eq. (25) and where

$$F^{kl}_{\alpha\beta} = \langle kl | \hat{F}_{12} | \alpha\beta \rangle, \tag{53}$$

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$$F^2_{kl,mn} = \langle kl|\hat{F}^2_{12}|mn\rangle, \tag{54}$$

$$K^F_{ij,kl} = \langle ij|r^{-1}_{12}\hat{F}_{12}|kl\rangle. \tag{55}$$

The short-hand notation $K^{ij}_{\alpha\beta}P_{\alpha\beta}F^{kl}_{\alpha\beta}$ takes the explicit form

$$K^{ij}_{\alpha\beta}P_{\alpha\beta}F^{kl}_{\alpha\beta} = K^{ij}_{rs}F^{kl}_{rs} + K^{ij}_{xm}F^{kl}_{xm} + K^{ij}_{mx}F^{kl}_{mx}. \tag{56}$$

It should be noted that the CA functions x are linear combinations of the AO and ABS functions (Sec. III C). Thus, despite the formal simplification by using CABS, the computational effort is not reduced, unless the ABS contains the AO basis set.

Most terms arising from the unity operator $1=\hat{P}_{12}+\hat{Q}_{12}$, for instance, $K^F_{ij,kl}$ and $F^2_{kl,mn}$ defined above, can be evaluated analytically. However, as will be discussed in Sec. II F, there are some exchange terms for which this is not possible, and then the unity must be approximated by a double RI $|\alpha\beta\rangle\langle\alpha\beta|$:

$$\begin{aligned}\hat{Q}_{12} = {} & |\alpha\beta\rangle\langle\alpha\beta| - |rs\rangle\langle rs| - |\alpha m\rangle\langle\alpha m| - |m\alpha\rangle\langle m\alpha| \\ & + |rm\rangle\langle rm| + |mr\rangle\langle mr|.\end{aligned} \tag{57}$$

Separating again the MO and CA spaces leads to a cancellation of the terms $-|rs\rangle\langle rs|$. This cancellation is essential for the applicability of some approximations we will discuss in Sec. II H. The projector then takes the much simpler form

$$\hat{Q}_{12} = |ax\rangle\langle ax| + |xa\rangle\langle xa| + |xy\rangle\langle xy|. \tag{58}$$

Obviously, if the AO basis is used to represent the RI, i.e., when the CA space is empty, all matrix elements that are evaluated using this form of the projector will vanish.

D. GBC and EBC approximations

The RI approximation [Eqs. (47)–(49)] is sufficient to evaluate the matrix elements V^{ij}_{kl} and $X_{kl,mn}$, which do not contain Fock operators. However, the matrix elements $B_{kl,mn}$ and C^{kl}_{ab} involve products of the correlation factor $\hat{F}_{12}$ and the Fock operators, and matrix elements over such products cannot be evaluated analytically. In order to factorize these products, additional RI approximations are needed, which introduce the assumption that the action of the Fock operator on any orbital can be represented in the RI basis,

$$\hat{f}|i\rangle = |k\rangle f_{ki} + |x'\rangle f_{x'i} \overset{\text{GBC}}{\approx} |k\rangle f_{ki}, \tag{59}$$

$$\hat{f}|a\rangle = |c\rangle f_{ca} + |x'\rangle f_{x'a} \overset{\text{EBC}}{\approx} |c\rangle f_{ca}, \tag{60}$$

$$\hat{f}|y\rangle = |r\rangle f_{ry} + |x'\rangle f_{x'y}. \tag{61}$$

In our program the ABS used to construct the CA orbitals $|x'\rangle$ in these expansions can be different from the one used to approximate the projector $\hat{Q}_{12}$. However, for the sake of simplicity we will not distinguish between different RI bases in the following and set $x'=x$.

In Eqs. (59) and (60) we have used the standard Brillouin conditions $f_{ai}=0$, which are fulfilled for optimized Hartree-Fock orbitals. For the exact Hartree-Fock orbitals the matrix elements f_{xi} are zero, and the occupied orbital space is closed under application of the Fock operator. For finite AO basis sets the contributions $|x\rangle f_{xi}$ can still be expected to be small; in fact, they are minimal if the AO basis set has been optimized by minimization of the Hartree-Fock energy. Assuming the generalized Brillouin condition (GBC) is equivalent to neglecting these contributions. Previous work has shown that this is an excellent approximation,[23] but the underlying theory of the calculations in that work has not yet been published.[38] Further support for this conclusion will be given in the present paper.

A less well justified assumption is that the virtual orbital space is also closed under the application of the Fock operator, which is implied by the extended Brillouin condition (EBC), used in Eq. (60). Neglecting the matrix elements f_{xa} therefore leads to larger errors. Again, this error should diminish if the AO basis gets larger and more complete. However, there is no reason to assume that the matrix elements f_{xy} are small, and therefore expansions as in Eq. (61) should be used only with great care.

If the EBC approximation is made, the coupling terms C^{kl}_{ab} vanish and the first-order equations for the conventional and explicitly correlated amplitudes, Eqs. (23) and (24), respectively, decouple.

E. Commutator approximations

The matrix elements $B_{kl,mn}$ and C^{kl}_{ab} involve matrix elements such as $G^{kl}_{\alpha\beta}=\langle kl|\hat{F}_{12}\hat{f}_{12}|\alpha\beta\rangle$. In order to factorize these, double RI expansions involving Eqs. (59)–(61) would be necessary. This is very slowly converging with the size of the RI basis, and is therefore useless in practice.

Kutzelnigg and Klopper have suggested the following alternative approach which avoids the use of Eqs. (60) and (61) entirely. The closed-shell Fock operator has the form

$$\hat{f} = \hat{t} + \hat{v} + 2\hat{j} - \hat{k}, \tag{62}$$

where $\hat{t}$, $\hat{v}$, $\hat{j}$, and $\hat{k}$ are the kinetic energy, external potential, Coulomb, and exchange operators, respectively. Of these operators, only $\hat{t}$ and $\hat{k}$ are nonlocal and do not commute with $\hat{F}_{12}$. One can therefore write

$$\hat{F}_{12}\hat{f}_{12} = [\hat{F}_{12},\hat{t}_{12}] - [\hat{F}_{12},\hat{k}_{12}] + \hat{f}_{12}\hat{F}_{12}, \tag{63}$$

with $\hat{t}_{12}=\hat{t}_1+\hat{t}_2$ and $\hat{k}_{12}=\hat{k}_1+\hat{k}_2$. Defining intermediate orbitals

$$|\tilde{\alpha}\rangle = \hat{k}|\alpha\rangle = |\beta\rangle k_{\beta\alpha}, \tag{64}$$

$$|\bar{k}\rangle = (\hat{f}+\hat{k})|k\rangle = |\beta\rangle(f_{\beta k} + k_{\beta k}) \tag{65}$$

$$\overset{\text{GBC}}{\approx} |j\rangle f_{jk} + |\beta\rangle k_{\beta k}, \tag{66}$$

the matrix elements $G^{kl}_{\alpha\beta}$ can be expanded as

$$G^{kl}_{\alpha\beta} = U^{kl}_{\alpha\beta} + F^{\bar{k}l}_{\alpha\beta} + F^{k\bar{l}}_{\alpha\beta} - F^{kl}_{\tilde{\alpha}\beta} - F^{kl}_{\alpha\tilde{\beta}}, \tag{67}$$

where the commutator integrals

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$$U^{kl}_{\alpha\beta} = \langle kl|[\hat{F}_{12},\hat{t}_{12}]|\alpha\beta\rangle \tag{68}$$

can be evaluated analytically.[18,39]

In Eq. (67) the Fock operators only act on the occupied orbitals k,l, and therefore Eq. (59) is sufficient to approximate the last term. The contributions of f_{jk} can be readily evaluated, and those of f_{xk} are very small. Neglecting f_{xk}, as done in the "standard approximations" of Kutzelnigg and Klopper, corresponds to the assumption that the GBC is valid. However, it is not necessary to make this approximation since if $(\hat{f}+\hat{k})$ is expanded as a whole, no other extra effort than computing the full Fock operator in the RI basis is required. Note that $\hat{f}+\hat{k}$ is the Fock operator *without* exchange (Hartree operator).

The exchange operators in the last two terms still act on any orbitals α,β, but using partial wave expansions[13,40] it has been shown for atoms that RI expansions of the product $\hat{F}_{12}\hat{k}_{12}$ should converge much faster than for $\hat{F}_{12}\hat{f}_{12}$.

In the following sections we will introduce the approximations **3**A, **3**B, and **3**C, which differ solely in the way $A_{kl,mn}$ and C^{kl}_{ab} are evaluated. In approximation **3**B the commutator approach is used for all terms, while in approximation **3**C direct RIs are used for expanding the Fock operator in the terms arising from $\hat{F}_{12}\hat{f}_{12}\hat{P}_{12}\hat{F}_{12}$ as well as for computing C^{kl}_{ab}. Approximation **3**A differs from **3**B by neglecting all contributions of the exchange commutator in $A_{kl,mn}$ (but the exchange terms are kept in C^{kl}_{ab}).

F. Approximation 3B

Approximation **3**B as presented here is a generalization of approximation **2**B introduced by Klopper and Samson[14] and Klopper.[15] It reduces to approximation **2**B if the GBC is assumed. In these methods the commutator approach [Eq. (63)] is used to evaluate the matrix elements $A_{kl,mn}$ and C^{kl}_{ab},

$$A_{kl,mn} \overset{\mathbf{3}\mathrm{B}}{=} U^F_{kl,mn} - U^{kl}_{\alpha\beta}P_{\alpha\beta}F^{mn}_{\alpha\beta} + \bar{X}_{kl,mn} - \tilde{Y}_{kl,mn}, \tag{69}$$

$$C^{kl}_{ab} \overset{\mathbf{3}\mathrm{B}}{=} U^{kl}_{ab} - f_{ac}F^{kl}_{cb} - F^{kl}_{ac}f_{cb} + F^{\bar{k}l}_{ab} + F^{k\bar{l}}_{ab} - F^{kl}_{\tilde{a}b} - F^{kl}_{a\tilde{b}}, \tag{70}$$

where we define the integrals

$$U^F_{kl,mn} = \langle kl|[\hat{F}_{12},\hat{t}_{12}]\hat{F}_{12}|mn\rangle, \tag{71}$$

$$\bar{X}_{kl,mn} = \langle kl|(\hat{f}_{12}+\hat{k}_{12})\hat{F}_{12}\hat{Q}_{12}\hat{F}_{12}|mn\rangle, \tag{72}$$

$$\tilde{Y}_{kl,mn} = \langle kl|\hat{F}_{12}\hat{k}_{12}\hat{Q}_{12}\hat{F}_{12}|mn\rangle. \tag{73}$$

The commutator integrals $U^F_{kl,mn}$ can again be evaluated analytically.[18,39] The matrix elements $\bar{X}_{kl,mn}$ are defined exactly as in Eq. (52), but computed using the intermediate orbitals $|\bar{k}\rangle$ as defined in Eq. (65),

$$\bar{X}_{kl,mn} = X_{\bar{k}l,mn} + X_{k\bar{l},mn}. \tag{74}$$

The only way to approximate the exchange contributions $\tilde{Y}_{kl,mn}$ is by a double RI, but the rate of convergence for the leading term $\hat{F}_{12}\hat{k}_{12}\hat{F}_{12}$ with the highest angular momentum in the ABS is $\mathcal{O}(l_{\max}^{-7})$ for atoms,[13,40] i.e., very fast. Using the CABS form of the projector given in Eq. (58), we obtain

$$\tilde{Y}_{kl,mn} = \tilde{F}^{kl}_{xa}F^{mn}_{xa} + \tilde{F}^{kl}_{ax}F^{mn}_{ax} + \tilde{F}^{kl}_{xy}F^{mn}_{xy}, \tag{75}$$

where

$$\tilde{F}^{kl}_{\alpha\beta} = F^{kl}_{\tilde{\alpha}\beta} + F^{kl}_{\alpha\tilde{\beta}}, \tag{76}$$

with intermediate orbitals $|\tilde{\alpha}\rangle = \hat{k}|\alpha\rangle$ [Eq. (64)].

It has sometimes been argued that the commutator $[\hat{F}_{12},\hat{k}_{12}]$ is small and can therefore be neglected in a good approximation. Even though it is true that the matrix elements over the commutator are much smaller than those over the individual operator products $\hat{F}_{12}\hat{k}_{12}$ and $\hat{k}_{12}\hat{F}_{12}$, they are still sizeable. Neglecting the exchange terms in C^{kl}_{ab} leads to large and unacceptable errors. In fact, it is a much better approximation to neglect the matrices C^{kl}_{ab} entirely (EBC approximation) than to neglect just the exchange terms.

Using Eq. (58), the matrix $Z_{kl,mn}$ [Eq. (33)] can be expressed as

$$Z_{kl,mn} = F^{kl}_{\check{o}x}F^{mn}_{ox} + F^{kl}_{x\check{o}}F^{mn}_{xo} + F^{kl}_{\check{o}a}F^{mn}_{oa} + F^{kl}_{a\check{o}}F^{mn}_{ao}, \tag{77}$$

where

$$|\check{o}\rangle = |y\rangle f_{yo}. \tag{78}$$

Obviously, the matrix elements $Z_{kl,mn}$ vanish if the GBC is assumed. As will be demonstrated in Sec. IV, the contributions of $Z_{kl,mn}$ are very small and can normally be neglected.

In approximation **2**B of Klopper and Samson the GBC is assumed; i.e., the matrix elements $Z_{kl,mn}$ are neglected and the intermediate orbitals used to compute $\bar{X}_{kl,mn}$ are approximated as in Eq. (66). The matrices C^{kl}_{ab} are evaluated according to Eq. (70), again using the intermediate orbitals in Eq. (66).

G. Approximation 3C

A disadvantage of the commutator approach is that the integrals $U^{kl}_{\alpha\beta}$ are difficult and expensive to compute. Furthermore, various integrals in approximation **3**B involve two RI or CA indices, and the computational effort therefore scales quadratically with the size of the ABS. The latter problem can be avoided using the GBC and hybrid approximations as proposed by Klopper[15] (Sec. II H).

An alternative way to avoid both problems was proposed by Kedžuch *et al.*[33] These authors derived equations for $B_{kl,mn}$ using the CABS approach, but numerical results were only presented for the case that the RI basis equals the AO basis, i.e., using *Ansatz* **1**. Furthermore, in their formalism the coupling between explicit and conventional amplitude equations was assumed to be zero, which is not correct if an auxiliary basis set is used. Even though their derivation is rather complicated and their final equations look quite different from ours, it is straightforward to show that the expressions for $B_{kl,mn}$ are equivalent, provided no approximations are made (i.e., the GBC is not assumed and $Z_{kl,mn}$ is not neglected).

In approximation **3**C only the term which arises from the unit operator in $\hat{Q}_{12}$ is treated with the commutator approach,

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while the remainder is evaluated directly using the RI expansion of $\hat{P}_{12}$. Thus, the expensive integrals $U^{kl}_{\alpha\beta}$ are not needed (the integrals $U^{F}_{kl,mn}$ are much simpler). The matrix elements $A_{kl,mn}$ and C^{kl}_{ab} then take the form

$$A_{kl,mn} \overset{\mathbf{3}\text{C}}{=} U^{F}_{kl,mn} + F^{2}_{\bar{k}l,mn} + F^{2}_{k\bar{l},mn} - \tilde{Y}_{kl,mn} - \bar{F}^{kl}_{\alpha\beta} P_{\alpha\beta} F^{mn}_{\alpha\beta}, \tag{79}$$

$$C^{kl}_{ab} \overset{\mathbf{3}\text{C}}{=} f_{a\alpha} F^{kl}_{\alpha b} + F^{kl}_{a\alpha} f_{\alpha b} - f_{ca} F^{kl}_{cb} - F^{kl}_{ac} f_{cb} = f_{ax} F^{kl}_{xb} + F^{kl}_{ax} f_{xb}, \tag{80}$$

where, in analogy to Eq. (76),

$$\bar{F}^{kl}_{\alpha\beta} = F^{kl}_{\bar{\alpha}\beta} + F^{kl}_{\alpha\bar{\beta}}, \tag{81}$$

with $|\bar{\alpha}\rangle = (\hat{f} + \hat{k})|\alpha\rangle$ (Eq. (65)).

From Eq. (80) it is obvious that the matrix elements C^{kl}_{ab} vanish if the EBC is assumed ($f_{xa}=0$). As already mentioned, in this case the residual equations [Eqs. (23) and (24)] for the conventional and explicit amplitudes decouple. It is important to note that the terms $-f_{ac}F^{kl}_{cb} - F^{kl}_{ac}f_{cb}$, which arise from the term $-\hat{v}_1\hat{v}_2$ in the projector of *Ansatz* **3**, cancel with the contributions of $|c\rangle f_{ca}$ in Eq. (60), provided the orbital basis is contained in the RI basis. This is guaranteed in the CABS approach, which is therefore strongly recommended in order to avoid spurious contributions caused by incomplete cancellation of individually large terms.

Two remarks are important regarding the expansions in Eq. (79), which require integrals of the types

$$F^{kl}_{\bar{x}i} = (f_{xr} + k_{xr}) F^{kl}_{ri} + (f_{xy} + k_{xy}) F^{kl}_{yi}, \tag{82}$$

$$F^{kl}_{x\bar{i}} = F^{kl}_{xr}(f_{ri} + k_{ri}) + F^{kl}_{xy}(f_{yi} + k_{yi}). \tag{83}$$

First, Eq. (82) involves the undesirable expansion of Eq. (61). Whether or not this will lead to slow convergence with the size of the RI basis and to significant errors will be investigated in Sec. IV. Second, the evaluation of the integrals F^{kl}_{xy} in Eq. (83) formally requires AO integrals with two ABS indices. Nevertheless, a quadratic dependence of the CPU time is avoided if robust density fitting is used to evaluate the integrals,[17,18]

$$F^{kl}_{x\bar{i}} = F^{A}_{kx} D^{A}_{l\bar{i}} + D^{A}_{kx} F^{A}_{l\bar{i}} - F^{A}_{kx} F_{AB} F^{B}_{l\bar{i}}, \tag{84}$$

where

$$F_{AB} = (A|\hat{F}_{12}|B), \tag{85}$$

$$J_{AB} = (A|r_{12}^{-1}|B), \tag{86}$$

$$F^{A}_{kx} = (A|\hat{F}_{12}|kx), \tag{87}$$

$$D^{A}_{kx} = (\mathbf{J}^{-1})_{AB}(A|r_{12}^{-1}|kx). \tag{88}$$

The indices A,B denote the fitting basis set. Since the transformation is performed at the level of the three-index integrals, the computational effort for the assembly according to Eq. (84) depends only linearly on the size of the RI basis. Furthermore, each of the required three-index integrals depends only on one RI index. Note that this is not the case for approximation **3**B. In this case integrals such as $F^{\tilde{kl}}_{\alpha i}$ are needed, which require three-index integrals $(A|r_{12}^{-1}|\mu'\nu')$.

The double RI needed to compute the exchange terms $\tilde{Y}_{kl,mn}$ still scales quadratically with the size of the RI basis. This term is the same in approximations **3**B and **3**C. In the next section we will discuss further approximations which avoid this problem.

H. Approximations of the exchange terms

In order to avoid quadratic scaling with the RI basis, Klopper suggested to approximate all exchange contributions in $A_{kl,mn}$ by using the AO basis for the RIs involving $\hat{k}$ [Eq. (66)] and to neglect the matrix $\tilde{\mathbf{Y}}$ entirely (in Ref. 15 this is called **P**). Klopper argued that "the contributions originating from **P** have been extremely small…, and when we replace some of the indices which refer to auxiliary orbitals by standard orbitals… the matrix **P** vanishes completely." Using *Ansatz* **3** and CABS leads to an equivalent but perhaps clearer justification: from Eq. (75) it is immediately obvious that $\tilde{\mathbf{Y}}$ vanishes exactly if the CA space is empty. This approximation will be denoted as HY1,

$$\tilde{Y}_{kl,mn} \overset{\text{HY1}}{\approx} 0. \tag{89}$$

The neglect of $\tilde{\mathbf{Y}}$ is also possible in approximation **3**C and will be denoted as **3**C(HY1).

A better approximation would be to neglect only $|xy\rangle\langle xy|$ in Eqs. (58) and (75). This corresponds to using the approximate projector

$$\hat{Q}_{12} \approx |ax\rangle\langle ax| + |xa\rangle\langle xa| \tag{90}$$

and leads to the new approximation

$$\tilde{Y}_{kl,mn} \overset{\text{HY2}}{\approx} \tilde{F}^{kl}_{xa} F^{mn}_{xa} + \tilde{F}^{kl}_{ax} F^{mn}_{ax} \tag{91}$$

denoted as HY2.

The approximations **3**C(HY1) and **3**C(HY2) are both sufficient to avoid most of the quadratic dependencies of the computational resources (CPU and storage) on the ABS (except for the overlap, Fock and exchange matrices, which are needed in the ABS, and one-index transformations $\mu' \rightarrow x$ of the integrals which are unavoidable). However, approximation **3**B(HY2) still scales quadratically. This can be avoided by approximating the intermediate orbitals $|\bar{k}\rangle$ used to compute $\bar{X}_{kl,mn}$ only in the AO basis. This leads to the HX approximation

$$|\bar{k}\rangle \overset{\text{HX}}{\approx} |j\rangle f_{jk} + |r\rangle k_{rk}. \tag{92}$$

Combining HY1 and HX is analogous to Klopper's "hybrid approximation."[15] In the current paper, this will be denoted as **3**B(HXY1). However, it should be noted that this method leads to slightly different results than Klopper's hybrid approximation, which was based on *Ansatz* **2** (see the Appendix). If HX is combined with HY2, one arrives at approximation **3**B(HXY2). Note that in all cases the matrices C^{kl}_{ab} are

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computed using the more accurate intermediate orbitals as defined in Eq. (65) or (66) (depending on whether the GBC is used or not).

Finally, HY1 combined with complete neglect of the exchange contributions in $\bar{X}_{kl,mn}$ leads to approximation **3**A,

$$|\bar{k}\rangle \overset{\mathbf{3}\mathrm{A}}{\approx} |j\rangle f_{jk}, \tag{93}$$

$$\bar{X}_{kl,mn} \overset{\mathbf{3}\mathrm{A}}{\approx} f_{kj}X_{jl,mn} + f_{lj}X_{kj,mn}, \tag{94}$$

$$\tilde{Y}_{kl,mn} \overset{\mathbf{3}\mathrm{A}}{\approx} 0. \tag{95}$$

We note that approximation **3**A is not identical to Klopper's approximation **2**A′ since in **3**A some exchange contributions are kept in the **B** matrix via the contributions of the matrices C_{ab}^{mn} [Eq. (31)]. In approximation **3***A the EBC is assumed and the matrices C_{ab}^{kl} are neglected in Eqs. (23), (24), and (31). It can then be shown that the energy corrections for the explicitly correlated parts of approximations **3***A and **2***A′ as defined by Klopper and Samson[14] are equivalent, but there appears to be an inconsistency with the general definition of *Ansatz* **2*** as given in Ref. 15 (see the Appendix).

I. Diagonal approximations

In the early R12 methods of Kutzelnigg and Klopper a non orbital-invariant *Ansatz* has been used, in which only the "diagonal" explicitly correlated configurations

$$\Phi_{ij}^{ij,p} = \tfrac{1}{2}(\Phi_{ij}^{ij} + p\Phi_{ji}^{ij}) \tag{96}$$

for $p=\pm 1$ were included in the first-order wave function (alternatively, if the spin-coupled formulation is not used, the configurations Φ_{ij}^{ij} and Φ_{ji}^{ij} would have to be included, but pairwise couplings between these would remain). Then, only the diagonal elements $B_{ij,ij}^{(p)}$ need to be computed and, as shown in our previous work,[25] this makes it possible to devise local approximations for which the computational effort scales only linearly with molecular size. However, this *Ansatz* is not invariant with respect to unitary transformations among the occupied orbitals, and not size consistent if canonical orbitals are used. It is therefore recommended only in combination with localized orbitals. Recently, Tew and Klopper[41] have shown that the diagonal *Ansatz* is particularly useful for the calculation of weak intermolecular forces since artifical geminal basis set superposition errors (BSSEs) introduced via the coupling **B** matrix elements are avoided. Furthermore, in Sec. IV it will be demonstrated that—unexpectedly—the diagonal approximation leads to much better results than the invariant methods when energy differences such as reaction energies are computed. Possibly, this is also due to a reduction of BSSE effects.

TABLE II. Summary of approximations. (Numbers in parentheses refer to equation numbers.)

Method	$A_{kl,mn}$	$\tilde{Y}_{kl,mn}$	$\lvert\bar{k}\rangle$[a]	C_{ab}^{kl}	$Z_{kl,mn}$
3A	(69)	0	(93)	(70)	0
3*A	(69)	0	(93)	0	0
3B(+Z)	(69)	(75)	(65)	(70)	(77)
3B	(69)	(75)	(65)	(70)	0
3B (GBC)	(69)	(75)	(66)	(70)	0
3*B	(69)	(75)	(65)	0	0
3B(HXY1)	(69)	0	(92)	(70)	0
3B(HXY2)	(69)	(91)	(92)	(70)	0
3C(+Z)	(79)	(75)	(65)	(80)	(77)
3C	(79)	(75)	(65)	(80)	0
3*C	(79)	(75)	(65)	0	0
3C(HY1)	(79)	0	(65)	(80)	0
3C(HY2)	(79)	(91)	(65)	(80)	0

[a] $|\bar{k}\rangle$ refers to the intermediate orbitals used to compute $\bar{X}_{kl,mn}$ and $\bar{F}_{kl,mn}^{2}$ for approximations **3**B and **3**C, respectively.

In our previous work we have used the diagonal *Ansatz* **3***A [in Ref. 25 this was denoted as **2***A(loc)], and the contributions of the **X** matrix were entirely neglected. The justification for the latter approximation is that for canonical orbitals the overall contribution of $X_{kl,mn}^{(p)}$ to the residuals $R_{ij}^{ij,p}$ is (within the GBC approximation)[14]

$$\tfrac{1}{2}X_{kl,mn}^{(p)}[\epsilon_k + \epsilon_l + \epsilon_m + \epsilon_n - 2(\epsilon_i + \epsilon_j)]T_{mn}^{ij,p}. \tag{97}$$

If the diagonal approximation is used, these terms cancel identically. If, furthermore, the EBC approximation is made, i.e., the coupling terms C_{ab}^{kl} are neglected, the first-order equations [Eq. (38)] decouple completely and their solution becomes trivial. With localized orbitals the Fock matrix is not diagonal and the contributions of $X_{kl,mn}^{(p)}$ do not cancel exactly, but their neglect is still a very good approximation for *Ansatz* **3***A.

In the current work, we will also test the diagonal approximation for the methods **3**B and **3**C, for which the neglect of $X_{kl,mn}^{(p)}$ is not possible. With the diagonal *Ansatz* the residuals [Eq. (38)] for the explicitly correlated configurations simplify to

$$\begin{aligned} R_{ij}^{ij,p} = {} & V_{ij}^{ij,p} + B_{ij,ij}^{(p)}T_{ij}^{ij,p} + C_{ab}^{ij,p}T_{ab}^{ij,p} - X_{ij,kj}^{(p)}f_{ik}T_{kj}^{kj,p} \\ & - X_{ij,ik}^{(p)}T_{ik}^{ik,p}f_{kj}; \end{aligned} \tag{98}$$

i.e., the equations for different pairs are still coupled. A complete decoupling can be achieved by neglecting the off-diagonal elements of $\mathbf{X}^{(p)}$, i.e., approximating the last two terms by $-X_{ij,ij}^{(p)}(f_{ii}+f_{jj})T_{ij}^{ij,p}$. These approximations will be denoted, e.g., as **3**C(DX), while the use of the fully coupled equation [Eq. (98)] will be denoted as **3**C(D). If also the EBC approximation is used, i.e., the matrices $C_{ab}^{ij,p}$ are neglected, the corresponding methods are denoted as **3***C(DX) and **3***C(D), respectively.

J. Summary of the hierarchy of approximations

The various approximations and the corresponding equations are summarized in Table II. Theoretically, the most accurate approximation is **3**B(+Z), while the least accurate is **3***A. For the given *Ansatz*, **3**B(+Z) does not involve any approximations other than the RIs. The commutator approach is used to minimize the errors caused by the RI. Neglect of the very small matrix elements $Z_{kl,mn}$ leads to the standard approximation **3**B. If the GBC is used in all terms that involve $\hat{f}$, the method becomes equivalent to approxima-

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tion **2**B of Klopper and Samson.[14] The somewhat less accurate EBC approximation leads to $C^{kl}_{ab}=0$ and therefore to a decoupling of the amplitude equations [Eqs. (23) and (24)]. For simplicity, methods in which $C^{kl}_{ab}=0$ will be denoted by a star, i.e., **3***A, **3***B, and **3***C. Note that for consistency with the corresponding methods of Klopper and Samson, the approximation $C^{kl}_{ab}=0$ is only assumed in Eqs. (23), (24), and (31). The matrix $A_{kl,mn}$, defined in Eq. (32), implicitly contains a further contribution which can be expressed as $C^{kl}_{ab}F^{mn}_{ab}$, but this is not neglected. Furthermore, in approximation **3***C the EBC is not used in any other terms involving the Fock operators.

The approximations **3**A and **3***A neglect the exchange commutator $[\hat{F}_{12},\hat{k}_{12}]$ in $A_{kl,mn}$ entirely and the GBC approximation is always used. Intermediate approximations of the exchange terms are introduced in approximations HY1, HY2, and HX. The combination of HY1 and HX (HXY1) is similar to Klopper's hybrid approximation.[15] However, since different matrix elements are neglected in *Ansätze* **2** and **3**, the results are not identical (see the Appendix). More accurate than HY1 is the new approximation HY2, which in combination with HX gives HXY2. For simplicity, we will denote the recommended hybrid methods **3**B(HXY2) and **3**C(HY2) simply as **3**B(HY) and **3**C(HY), respectively.

In approximation **3**C the computation of the difficult commutator integrals $U^{kl}_{\alpha\beta}$ is avoided. In addition, fewer transformed integral classes are needed. Therefore, **3**C is computationally significantly cheaper than **3**B. However, it involves expansions such as the one in Eq. (61), and the convergence with the RI basis is therefore expected to be slower than for approximation **3**B. In the limit of an infinite RI basis the methods **3**B and **3**C should give the same results. As will be demonstrated in Sec. IV, very small differences are found in practice, and therefore **3**C is usually preferable.

The computational resources for methods **3**A, **3***A, **3**B(HXY1), **3**B(HXY2), **3**C(HY1), and **3**C(HY2) scale linearly with the size of the RI basis. All other methods scale quadratically. In summary, **3**C(HY2) should therefore yield the best compromise of accuracy and cost.

III. IMPLEMENTATION

A. Integral evaluation and transformation

The Slater function was fitted by a linear combination of Gaussians

$$e^{-\beta r_{12}} \approx \sum_{i=1}^{n} c_i e^{-\alpha_i r_{12}^2}, \tag{99}$$

and the coefficients c_i as well as the exponents α_i were determined by least squares fitting

$$\Delta = \int_0^\infty W(r_{12})\left[e^{-\beta r_{12}} - \sum_{i=1}^{n} c_i e^{-\alpha_i r_{12}^2}\right]^2 r_{12}^2 dr_{12}, \tag{100}$$

with weighting function

$$W(r_{12}) = e^{-(\pi\beta^2)^{1/3} r_{12}}. \tag{101}$$

All two-electron integrals are computed using robust density fitting approximations.[17,18] Due to the various sets of intermediate orbitals involved, this leads to very many different intermediates. In order to handle this efficiently and to minimize sources of error, we have developed a program which allows us to define any number of different transformation sets. A recursive object oriented algorithm is used, and previously computed intermediates are automatically reused whenever possible. The design is similar to an earlier recursive integral generator developed by May.[42]

The three-index integrals over kinetic energy commutators involve integrals with the operator $r_{12}^2\hat{F}_{12}$; in previous work these were computed from $\hat{F}_{12}$ integrals with higher angular momentum.[18] Recently, we have found that three-index versions of the recurrence relations of Weber and Daul[43] offer greatly improved numerical stability and have been used in all of the calculations presented here. Some numerical problems remain for third-row atoms in large basis sets (pentuple zeta), but these have no effect on the results presented here. Recently, numerical errors have also been discussed by Valeev.[26] In agreement with his work we found that the numerical errors are much reduced if the diagonal approximation is used and if the coupling between explicit and conventional amplitudes is neglected (EBC approximation).

B. Solution of the first-order equations

The equations for the conventional and explicitly correlated amplitudes are only weakly coupled. The linear equations [Eqs. (23) and (24)] can therefore be solved iteratively. Updates for the conventional amplitudes are obtained as

$$\Delta T^{ij,p}_{ab} = -R^{ij,p}_{ab}(\epsilon_a + \epsilon_b - f_{ii} - f_{jj})^{-1}, \tag{102}$$

where we assume that canonical virtual orbitals are used, and ϵ_a and ϵ_b are the corresponding orbital energies (if noncanonical virtual orbitals are used, one can transform the residuals to a canonical basis and backtransform the amplitude updates to the original basis, as done, e.g., in local correlation methods[44]). Updates for the amplitudes $T^{ij,p}_{kl}$ are obtained as

$$\Delta T^{ij,p}_{kl} = -[(\mathbf{B}^{(p)})^{-1}]_{kl,mn} R^{ij,p}_{mn}. \tag{103}$$

Here and in the remainder of this section, we assume $i \geqslant j$, $k \geqslant l$, and $m \geqslant n$.

In the canonical case the first-order equations can be written as

$$0 = K^{ij,p}_{ab} + E^{ij}_{ab}T^{ij,p}_{ab} + T^{ij,p}_{kl}C^{kl,p}_{ab}, \tag{104}$$

$$0 = V^{ij,p}_{kl} + B^{ij,p}_{kl,mn}T^{ij,p}_{mn} + C^{kl,p}_{ab}T^{ij,p}_{ab}, \tag{105}$$

with

$$E^{ij}_{ab} = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j, \tag{106}$$

$$B^{ij,p}_{kl,mn} = B^{(p)}_{kl,mn} - X^{(p)}_{kl,mn}(\epsilon_i + \epsilon_j). \tag{107}$$

These equations can be solved noniteratively using a partitioning technique. First, one solves for T^{ij}_{kl},

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$$T^{ij,p}_{kl} = -[(\tilde{\mathbf{B}}^{ij,p})^{-1}]_{kl,mn}\tilde{V}^{ij,p}_{mn}, \tag{108}$$

with

$$\tilde{V}^{ij,p}_{mn} = V^{ij,p}_{mn} - C^{mn,p}_{ab}K^{ij,p}_{ab}/E^{ij}_{ab}, \tag{109}$$

$$\tilde{B}^{ij,p}_{kl,mn} = B^{ij,p}_{kl,mn} - C^{kl,p}_{ab}C^{mn,p}_{ab}/E^{ij}_{ab}. \tag{110}$$

The correlation energy can then be written as the sum of the conventional MP2 energy $E^{(2)}_{\mathrm{MP2}}$ and the F12 correction $\Delta E^{(2)}_{\mathrm{F12}}$,

$$E^{(2)} = E^{(2)}_{\mathrm{MP2}} + \Delta E^{(2)}_{\mathrm{F12}}, \tag{111}$$

$$\Delta E^{(2)}_{\mathrm{F12}} = \sum_{i\geqslant j}(2-\delta_{ij})\sum_{p}(2-p)\sum_{k\geqslant l}\tilde{V}^{ij,p}_{kl}T^{ij,p}_{kl}. \tag{112}$$

The disadvantage of this method, which has also been used by Klopper and Samson[14] as well as Valeev[26] is that $B^{ij,p}_{kl,mn}$ must be constructed and inverted for each pair (ij,p), leading to a very steep scaling of $\mathcal{O}(N^6_{\mathrm{occ}}N^2_{\mathrm{virt}})$. Valeev[26] stated a scaling of $\mathcal{O}(N^8_{\mathrm{occ}})$, but this refers only to the inversion but not the construction of $B^{ij,p}_{kl,mn}$.[51]

In the iterative method the matrix $\mathbf{B}$ is independent of the pair indices ij and therefore needs to be inverted only once for each p (alternatively, the *LU* decomposition can be computed once). Thus, if one assumes that the number of iterations is independent of the molecular size, the scaling is only $\mathcal{O}(N^4_{\mathrm{occ}}N^2_{\mathrm{virt}})$. Depending on the method, the construction of the $\mathbf{B}$ matrix scales as $\mathcal{O}(N^4_{\mathrm{occ}}N^2_{\mathrm{RI}})$ or $\mathcal{O}(N^4_{\mathrm{occ}}N_{\mathrm{RI}}N_{\mathrm{AO}})$. Therefore, the overall scaling is $\mathcal{O}(\mathcal{N}^6)$, where $\mathcal{N}$ is a measure for the molecular size.

It should be noted that in the iterative method the coupling of the explicit and conventional residual equations leads to a change of the conventional amplitudes T^{ij}_{ab}, and ΔE_2 as defined in Eq. (40) is not equal to the total energy correction $\Delta E^{(2)}_{\mathrm{F12}}$. We therefore first solve the conventional MP2 (or LMP2) equations [i.e., Eq. (23) with $C^{kl}_{ab}=0$] to obtain the conventional correlation energy. The conventional amplitudes T^{ij}_{ab} are then used as a starting guess when solving the full set of equations, and $\Delta E^{(2)}_{\mathrm{F12}}$ is then obtained as the difference of the final total energy and the conventional MP2 energy.

C. CABS treatment

In the CABS approach the RI is approximated in the union of the AO and ABS basis sets. In practice, orthogonal RI or CA orbitals are never constructed explictly. The orthogonal complement of the AO basis can be obtained by projecting the AO basis out of the ABS

$$|\tilde{\mu}'\rangle = \left(1 - |\rho\rangle[\mathbf{S}^{-1}_{\mathrm{AO}}]_{\rho\sigma}\langle\sigma|\right)|\mu'\rangle. \tag{113}$$

The overlap matrix of this space is

$$[\mathbf{S}_{\mathrm{CA}}]_{\mu'\nu'} = [\mathbf{S}_{\mathrm{ABS}}]_{\mu'\nu'} - \langle\mu'|\rho\rangle[\mathbf{S}^{-1}_{\mathrm{AO}}]_{\rho\sigma}\langle\sigma|\nu'\rangle. \tag{114}$$

The CA basis may be (almost) linearly dependent, and then singularities are removed by singular value decomposition (SVD), yielding a positive definite $\mathbf{S}_{\mathrm{CA}}$. In the SVD the eigenvectors of $\mathbf{S}_{\mathrm{CA}}$ which correspond to eigenvalues smaller than a certain threshold are removed from the basis. By default, we choose this threshold to be $\max(10^{-6}, s_{\max}\times 10^{-8})$, where $s_{\max}$ is the largest eigenvalue of $\mathbf{S}_{\mathrm{CA}}$. We note that the CABS approach for the double RI, which involves quite a large number of matrix multiplications, is more sensitive to numerical errors than the remaining RI expansions. Therefore, a larger threshold of $s_{\max}\times 10^{-6}$ was used in this case. This threshold has very little effect on the correlation energies.

The projection $|x\rangle\langle x|$ onto the CA space can be written as

$$\begin{aligned}|x\rangle\langle x| &= |\tilde{\mu}'\rangle[\mathbf{S}^{-1}_{\mathrm{CA}}]_{\mu'\nu'}\langle\tilde{\nu}'|\\ &= |\mu'\rangle\bar{S}_{\mu'\nu'}\langle\nu'| + |\rho\rangle\bar{S}_{\rho\sigma}\langle\sigma| - \bar{S}_{\nu'\rho}\left(|\nu'\rangle\langle\rho| + |\rho\rangle\langle\nu'|\right),\end{aligned} \tag{115}$$

where

$$\bar{S}_{\mu'\sigma} = [\mathbf{S}^{-1}_{\mathrm{CA}}]_{\mu'\nu'}\langle\nu'|\rho\rangle[\mathbf{S}^{-1}_{\mathrm{AO}}]_{\rho\sigma}, \tag{116}$$

$$\bar{S}_{\mu'\nu'} = [\mathbf{S}^{-1}_{\mathrm{CA}}]_{\mu'\nu'}, \tag{117}$$

$$\bar{S}_{\rho\sigma} = [\mathbf{S}^{-1}_{\mathrm{AO}}]_{\rho\tau}\langle\tau|\mu'\rangle\bar{S}_{\mu'\sigma}. \tag{118}$$

If the full AO+CA (RI) space is required, $[\mathbf{S}^{-1}_{\mathrm{AO}}]_{\rho\sigma}$ is added to $\bar{S}_{\rho\sigma}$, and then a similar expansion holds for $|\alpha\rangle\langle\alpha|$. If the ABS contains the AO basis as a subset, exactly the same results are obtained with and without the CABS approach. In this case the above procedure allows the elimination of the AO basis functions from the ABS basis, which can lead to significant savings. Otherwise, the same integrals are needed with and without CABS, and therefore the computational effort is not much affected.

As pointed out in various places of this paper, the CABS approach is important to guarantee the exact cancellations of various terms. These cancellations would be incomplete without CABS (unless the ABS contains the AO basis). Furthermore, use of the SVD ensures numerical stability of the RI expansions.

IV. RESULTS

In order to test the performance of the various methods, we used the same test molecules as in our previous work.[25] The geometries were optimized at the MP2 level using the aug-cc-pVTZ basis set. Results for a subset of these molecules have also been presented in the recent review of Klopper *et al.*[30] using the same geometries. In all calculations we employed the augmented correlation consistent aug-cc-pV*n*Z basis sets of Kendall *et al.*[45] In the Hartree-Fock calculations as well as for the computation of the exchange and Fock operators, density fitting with the V5Z/JKFIT auxiliary basis of Weigend[46] has been used. For the density fitting of the remaining two-electron integrals in the MP2-F12 calculations, the aug-cc-pV*n*Z/MP2FIT sets of Weigend *et al.*[47] were employed. Unless otherwise noted, the cc-pV*n*Z/JKFIT basis sets were also used as RI auxiliary basis sets since we found in our previous work[25] that these converge well and yield very stable results for reaction energies. The CABS approach was used throughout, with the default thresholds given in Sec. III C. The exponent of the Slater function in the

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TABLE III. Exponents and fitting coefficients for the Slater function.

i	α_i	c_i
1	274.649 57	0.050 14
2	49.652 31	0.080 45
3	13.286 54	0.127 74
4	4.065 03	0.203 16
5	1.220 90	0.300 57
6	0.323 35	0.213 45

correlation factor was chosen to be $1.4a_0^{-1}$. This value was found to be close to optimum for the augmented correlation consistent basis sets. The Slater function was approximated by an expansion of six Gaussians, and the expansion coefficients were fitted as described in Sec. III A. The resulting exponents and coefficients are shown in Table III. For the noninvariant diagonal approximations the orbitals have been localized using the Pipek-Mezey[48] method.

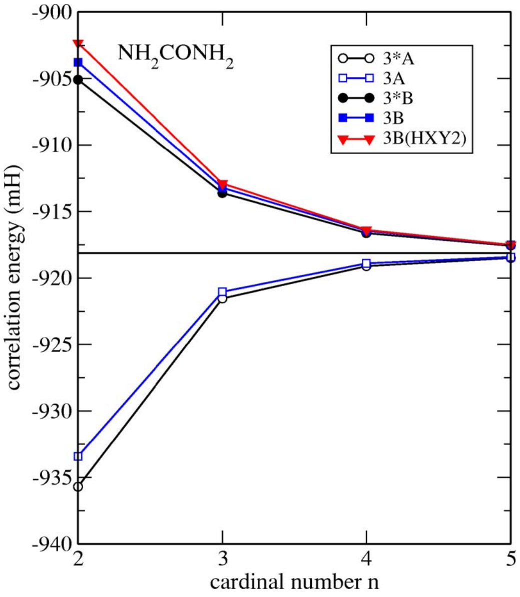

FIG. 1. Convergence of the correlation energy with aug-cc-pVnZ basis sets for NH_2CONH_2. The horizontal line indicates the CBS limit, estimated according to the procedure described in the text.

First, we will demonstrate the accuracy of the various approximations as a function of the basis set. In order to minimize errors due to density fitting and the RI approximations, these calculations have been performed with large auxiliary basis sets (see headers of the tables). The results for methods $\mathbf{3}^*$A, **3**A, $\mathbf{3}^*$B, **3**B(GBC), **3**B, **3**C, **3**B(+Z), and **3**C(+Z) are presented in Table IV. As expected, the errors of all approximations diminish quickly with increasing basis set. The effect of the GBC approximation is very small, even for the double zeta basis. The error introduced by neglect of the Z terms is even an order of magnitude smaller, and these terms will therefore be neglected in all further calculations. However, since the remaining GBC terms require practically no additional effort and are needed for the equivalence of the **3**B and **3**C approximations in the limit of a complete RI basis, they are included by default in these two methods.

Figure 1 shows the convergence of the correlation energies with increasing basis set for urea, NH_2CONH_2. The convergence behavior seen in this figure is very typical for all other molecules studied in this work. The MP2-F12/**3**B and MP2-F12/**3**C energies differ only by a few μH and cannot be distinguished on the scale of the figure. Therefore,

TABLE IV. Comparison of valence correlation energies ($-E_{\mathrm{corr}}/\mathrm{mH}$) for various MP2-F12 approximations for different basis sets. [Using density fitting with aug-cc-pV5Z/MP2FIT basis. The cc-pV5Z/JKFIT basis and the CABS approach were used for the RI. AVnZ refers to the aug-cc-pVnZ basis sets of Kendall *et al.* (Ref. 45). See text for other details.]

Molecule	AO basis	$\mathbf{3}^*$A	**3**A	$\mathbf{3}^*$B	**3**B(GBC)	**3**B	**3**C	**3**B(+Z)	**3**C(+Z)
H_2O	AVDZ	306.931	304.588	297.125	294.929	295.044	295.054	295.017	295.027
	AVTZ	301.468	301.168	298.946	298.649	298.634	298.631	298.631	298.629
	AVQZ	300.939	300.840	300.144	300.054	300.043	300.045	300.045	300.047
	AV5Z	300.822	300.806	300.529	300.513	300.510	300.515	300.510	300.516
H_2O_2	AVDZ	582.747	579.357	563.720	560.466	560.380	560.381	560.299	560.301
	AVTZ	571.792	571.367	566.833	566.408	566.391	566.390	566.393	566.392
	AVQZ	570.683	570.534	569.083	568.947	568.925	568.936	568.928	568.938
	AV5Z	570.459	570.419	569.861	569.820	569.815	569.829	569.815	569.829
HNCO	AVDZ	667.087	666.462	646.386	645.613	645.477	645.465	645.362	645.350
	AVTZ	658.577	658.183	652.939	652.523	652.456	652.447	652.451	652.442
	AVQZ	657.134	656.910	655.313	655.096	655.065	655.073	655.067	655.076
	AV5Z	656.769	656.676	656.082	655.985	655.978	655.984	655.978	655.984
$HCOOCH_3$	AVDZ	926.039	923.788	896.330	894.044	894.038	894.049	893.864	893.874
	AVTZ	911.460	911.030	903.685	903.228	903.212	903.204	903.212	903.204
	AVQZ	909.161	909.021	906.694	906.557	906.523	906.531	906.526	906.534
	AV5Z	908.610	908.582	907.683	907.648	907.640	907.648	907.640	907.649
NH_2CONH_2	AVDZ	934.749	933.411	905.101	903.617	903.792	903.792	903.654	903.654
	AVTZ	921.373	921.036	913.615	913.243	913.213	913.199	913.207	913.193
	AVQZ	919.049	918.907	916.618	916.481	916.442	916.450	916.445	916.453
	AV5Z	918.471	918.431	917.566	917.522	917.513	917.519	917.513	917.519

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TABLE V. Comparison of valence correlation energies ($-E_{\mathrm{corr}}$/mH) for various hybrid approximations. [Using density fitting with aug-cc-pV5Z/MP2FIT basis. The cc-pV5Z/JKFIT basis and the CABS approach were used for the RI. AV*n*Z refers to the aug-cc-pV*n*Z basis sets of Kendall *et al.* (Ref. 45). See text for other details.]

Molecule	AO basis	**3**B	**3**B(HX)	**3**B(HXY1)	**3**B(HXY2)	**3**C	**3**C(HY1)	**3**C(HY2)
H_2O	AVDZ	295.044	295.274	292.542	294.590	295.054	292.343	294.374
	AVTZ	298.634	298.568	298.214	298.507	298.631	298.275	298.570
	AVQZ	300.043	300.020	299.982	300.014	300.045	300.007	300.040
	AV5Z	300.510	300.502	300.497	300.501	300.515	300.510	300.515
H_2O_2	AVDZ	560.380	560.820	555.462	559.514	560.381	555.069	559.086
	AVTZ	566.391	566.262	565.560	566.147	566.390	565.684	566.274
	AVQZ	568.925	568.876	568.796	568.866	568.936	568.855	568.926
	AV5Z	569.815	569.800	569.789	569.799	569.829	569.818	569.827
HNCO	AVDZ	645.477	645.807	640.280	644.400	645.465	639.974	644.064
	AVTZ	652.456	652.361	651.595	652.228	652.447	651.677	652.313
	AVQZ	655.065	655.022	654.929	655.010	655.073	654.980	655.061
	AV5Z	655.978	655.964	655.950	655.963	655.984	655.969	655.983
$HCOOCH_3$	AVDZ	894.038	894.499	886.986	892.634	894.049	886.589	892.193
	AVTZ	903.212	903.063	902.043	902.888	903.204	902.180	903.028
	AVQZ	906.523	906.467	906.339	906.450	906.531	906.402	906.514
	AV5Z	907.640	907.622	907.602	907.620	907.648	907.629	907.646
NH_2CONH_2	AVDZ	903.792	904.186	896.769	902.323	903.792	896.423	901.937
	AVTZ	913.213	913.075	912.070	912.902	913.199	912.189	913.025
	AVQZ	916.442	916.391	916.268	916.375	916.450	916.327	916.434
	AV5Z	917.513	917.497	917.477	917.495	917.519	917.500	917.517

only the MP2-F12/**3**B ones are shown. As known from previous work, the **3**B energies converge from above towards the basis set limit, while the **3**A energies converge from below. Surprisingly, the **3**A ones converge better, and in many cases already the aug-cc-pVTZ value is very close to the basis set limit. Clearly, this is due to some error compensation. The better convergence of **3**A energies is more pronounced for molecules containing oxygen atoms than for pure hydrocarbons.

The convergence behavior discussed above suggests that estimates of the complete basis set (CBS) limits can be obtained by averaging the **3**A and **3**B correlation energies with certain weight factors. Following Samson and Klopper,[32] we determined weight factors f_{3A} and f_{3B} ($f_{3A}+f_{3B}=1$) such that for a given molecule the averaged value is the same for the aug-cc-pVQZ and aug-cc-pV5Z basis sets. This leads to

$$f_{3A} = (B_5 - B_4)/(A_4 - A_5 + B_5 - B_4), \qquad (119)$$

where A_n and B_n are the MP2-F12/**3**A and MP2-F12/**3**B correlation energies for the aug-cc-pV*n*Z orbital basis. Using this procedure, we find for most molecules values of f_{3A} between 0.7 and 0.8; only for hydrocarbons such as C_2H_4 and C_2H_6 the weights are somewhat smaller. For comparison, similar estimates have been computed from the MP2-F12/**3**A(D) and MP2-F12/**3**C(D) energies. The average absolute difference of the two estimates is 0.042 mH; the maximum deviation amounts to 0.078 mH.

The various hybrid approximations are compared in Table V. The effect of the HX approximation is very small. The HY1 and HY2 approximations reduce the absolute values of the correlation energies. As expected, the HY2 approximation is much more accurate than the HY1 approximation. The HXY2 energies are also shown in Fig. 1, and this demonstrates clearly that the error due to this approximation is negligible as compared to the basis set error.

The convergence of the correlation energies with the size of the RI basis is shown for some molecules in Table VI. In our previous work we have found that for the $\mathbf{2}^{*}$A(loc) method the cc-pV*n*Z/JKFIT basis sets of Weigend[46] work very well. The same is confirmed here for the **3**B and **3**C methods. As can be seen in Table VI, the convergence is faster than with the uncontracted aug-cc-pV*n*Z basis sets. It should be noted that the s,p sets are the same in all cc-pV*n*Z/JKFIT bases. We found, however, that larger s,p sets have virtually no effect on the results. The convergence is best for the **3**A method; there is no significant difference for methods **3**B and **3**C. This is very satisfying since **3**C is computationally much cheaper (typically a factor of 2) than **3**B.

The correlation energies for all 21 molecules obtained with the aug-cc-pVTZ basis set and the corresponding DF and RI basis sets (RI: cc-pVTZ/JKFIT and DF: aug-cc-pVTZ/MP2FIT) are listed in Table VII. More extensive data for the aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z basis sets can be found in the supplementary material.[49] The estimated basis set limits are given in the last column. For all molecules the **3**A method yields with the cc-pVTZ basis correlation energies which are too large by about 0.3%–0.4%, while the **3**B and **3**C methods underestimate the correlation energies by 0.6%–0.7%. Even with the aug-cc-pVDZ basis the correlation energies are within 2% of the basis set limits. The convergence will even be better with

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TABLE VI. Convergence behavior of valence correlation energies ($-E_{\mathrm{corr}}$/mH) with RI basis for different methods. (Using density fitting with aug-cc-pV5Z/MP2FIT basis and the aug-cc-pVTZ AO basis.)

Molecule	RI basis[a]	**3**A	**3**B	**3**C	RI basis[b]	**3**A	**3**B	**3**C
H_2O	VTZ/JKFIT	301.214	298.688	298.682	AVQZ(u)	301.277	298.730	298.714
	VQZ/JKFIT	301.166	298.670	298.685	AV5Z(u)	301.175	298.674	298.665
	V5Z/JKFIT	301.168	298.634	298.631	AV6Z(u)	301.161	298.669	298.659
H_2O_2	VTZ/JKFIT	571.508	566.530	566.543	AVQZ(u)	571.597	566.586	566.567
	VQZ/JKFIT	571.369	566.464	566.476	AV5Z(u)	571.382	566.471	566.456
	V5Z/JKFIT	571.367	566.391	566.390	AV6Z(u)	571.363	566.441	566.432
HNCO	VTZ/JKFIT	658.319	652.554	652.540	AVQZ(u)	658.414	652.623	652.573
	VQZ/JKFIT	658.176	652.500	652.507	AV5Z(u)	658.191	652.506	652.494
	V5Z/JKFIT	658.183	652.456	652.447	AV6Z(u)	658.172	652.479	652.465
$HCOOCH_3$	VTZ/JKFIT	911.207	903.345	903.355	AVQZ(u)	911.357	903.454	903.407
	VQZ/JKFIT	911.026	903.275	903.286	AV5Z(u)	911.048	903.295	903.273
	V5Z/JKFIT	911.030	903.212	903.204	AV6Z(u)	911.016	903.258	903.238
NH_2CONH_2	VTZ/JKFIT	921.210	913.340	913.331	AVQZ(u)	921.342	913.428	913.365
	VQZ/JKFIT	921.036	913.280	913.287	AV5Z(u)	921.052	913.282	913.266
	V5Z/JKFIT	921.036	913.213	913.199	AV6Z(u)	921.025	913.245	913.231

[a] JK-density fitting basis sets of Weigend (Ref. 46).

[b] Uncontracted aug-cc-pVnZ basis sets (Ref. 45).

new correlation consistent basis sets, optimized by Peterson for the MP2-F12/**3**C method.[50] With these new basis sets, which will be published elsewhere, the double zeta results will be almost as good as the current triple zeta ones. In addition, the accuracy of the Hartree-Fock values will be significantly improved since the total energy and not just the correlation energy was optimized.

Despite the remarkably fast convergence of the correlation energies with basis set size, the absolute errors of the aug-cc-pVTZ values still amount to several mH. For example, the error of the **3**C energy for urea is about 3 kcal/mol. It is therefore important to investigate how large and systematic errors of energy differences are. For this purpose we have computed reaction energies for the same 16 reactions as in Ref. 29. The reactions are listed in Table VIII. In order to separate effects arising from the Hartree-Fock contributions, only the errors of the correlation energy contributions are considered here. Since the absolute values of the reaction energies can be easily computed from the data in Table VII, we will discuss only the errors relative to the

TABLE VII. Valence correlation energies ($-E_{\mathrm{corr}}$/mH) for different methods using AO-basis aug-cc-pVTZ. (DF and RI basis sets are used. They correspond to the AO basis.)

Molecule	**3***A	**3**A	**3**B	**3**C	**3**B(HY)	**3**C(HY)	CBS[a]
H_2	34.297	34.244	34.095	34.095	34.093	34.092	34.242
CH_4	219.894	219.655	218.133	218.122	218.101	218.100	219.017
NH_3	265.381	265.106	263.125	263.106	263.061	263.073	264.505
H_2O	301.521	301.221	298.689	298.683	298.577	298.634	300.786
C_2H_2	347.551	347.094	344.200	344.190	344.115	344.148	346.081
C_2H_4	374.103	373.797	370.879	370.865	370.814	370.825	372.617
C_2H_6	411.347	411.062	408.066	408.055	408.008	408.015	409.591
CO	406.670	406.354	402.630	402.620	402.468	402.552	405.393
H_2CO	450.465	450.129	446.268	446.270	446.122	446.204	449.065
CH_3OH	487.004	486.633	482.613	482.606	482.476	482.539	485.304
H_2O_2	571.959	571.533	566.543	566.556	566.327	566.463	570.350
H_2CCO	611.552	611.176	605.907	605.937	605.746	605.853	609.396
C_2H_4O	651.328	651.018	645.581	645.579	645.413	645.495	648.909
CH_3CHO	642.916	642.576	637.181	637.189	637.011	637.105	640.532
C_2H_5OH	680.418	680.031	674.527	674.525	674.366	674.441	677.779
HNCO	658.762	658.363	652.585	652.570	652.395	652.476	656.534
$HCONH_2$	687.658	687.322	681.424	681.409	681.218	681.313	685.262
CO_2	690.691	690.328	684.002	683.994	683.777	683.885	688.557
HCOOH	721.898	721.513	715.086	715.091	714.834	714.980	719.527
$HCOOCH_3$	911.696	911.259	903.375	903.384	903.101	903.257	908.316
NH_2CONH_2	921.603	921.261	913.368	913.358	913.106	913.236	918.148

[a] Estimates of the basis set limit as explained in the text.

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TABLE VIII. Test reactions.

No.	Reaction		
1	$C_2H_2+H_2$	→	C_2H_4
2	$C_2H_4+H_2$	→	C_2H_6
3	$C_2H_6+H_2$	→	$2CH_4$
4	$CO+H_2$	→	H_2CO
5	H_2CO+H_2	→	CH_3OH
6	$H_2O_2+H_2$	→	$2H_2O$
7	$C_2H_2+H_2O$	→	CH_3CHO
8	$C_2H_4+H_2O$	→	C_2H_5OH
9	CH_3CHO+H_2	→	C_2H_5OH
10	$CO+NH_3$	→	$HCONH_2$
11	$CO+H_2O$	→	CO_2+H_2
12	$HNCO+NH_3$	→	NH_2CONH_2
13	CH_3OH+CO	→	$HCOOCH_3$
14	$HCOOH+NH_3$	→	$HCONH_2+H_2O$
15	$CO+H_2O_2$	→	CO_2+H_2O
16	H_2CCO+H_2CO	→	C_2H_4O+CO

values obtained from the estimated CBS energies. The accuracy of these reference values is estimated to be better than 0.05 kcal/mol. This is consistent with the fact that the reaction energies for the two different estimates discussed above differ only by 0.01–0.02 kcal/mol.

Figure 2 shows the errors of the **3**A and **3**C correlation contributions to the reaction energies. The results for approximation **3**B are virtually identical to those of **3**C and therefore not shown. Unexpectedly, it is found that the formally most rigorous methods **3**B and **3**C yield the largest absolute errors (up to about 0.4 kcal/mol). If the coupling between the equations for the explicit and conventional amplitudes is neglected ($\mathbf{3}^*$A and $\mathbf{3}^*$C), the maximum errors decrease to about 0.25 kcal/mol. And if also the diagonal approximation is used, the maximum error decreases to about 0.1 kcal/mol. This is significantly smaller than the basis set error of the Hartree-Fock reaction energies[25] for the same basis set. Qualitatively, this behavior is similar for the **3**A, **3**B, and **3**C families of methods, and it therefore seems not to be related to approximations in the treatment of the exchange terms. The result is also independent of the choice of the RI basis. The errors are largest for the reactions (7), (8), (12), and (13), which are addition reactions involving H_2O, NH_3, or CO. The errors are negative, which means that the correlation energies of the larger product molecules are overestimated relative to those of the smaller reactants. This points to a similar explanation as given in a recent paper of Tew and Klopper,[41] in which they found that binding energies of rare gas dimers were significantly overestimated with MP2-F12/A but accurately predicted with MP2-F12/$\mathbf{2}^*$A(D). They attributed this effect to geminal basis set superposition errors, caused by couplings via the off-diagonal elements of the **B** matrix.

The results for the aug-cc-pVDZ and aug-cc-pVQZ basis sets are qualitatively similar. Table IX shows the error statistics for different basis sets and methods. For comparison, also the errors of the standard MP2 reaction energies, as well as those of extrapolated MP2 energies are shown. The MP2-F12/$\mathbf{3}^*$C(D) results for basis aug-cc-pV*n*Z are seen to be more accurate than the extrapolated values obtained from the aug-cc-pV*n*Z and aug-cc-pV($n+1$)Z energies. The MP2-F12/$\mathbf{3}^*$C(D)/aug-cc-pVTZ are even more accurate than the MP2[45] extrapolated values. Clearly, the accuracy obtained with $\mathbf{3}^*$C(D)/aug-cc-pVTZ is sufficient for all practical purposes. Even with the aug-cc-pVDZ basis, chemical accuracy (1 kcal/mol) is achieved for the correlation contributions, but in this case the errors of the Hartree-Fock reaction energies are unacceptably large. This situation will be improved with the new basis sets[50] mentioned earlier.

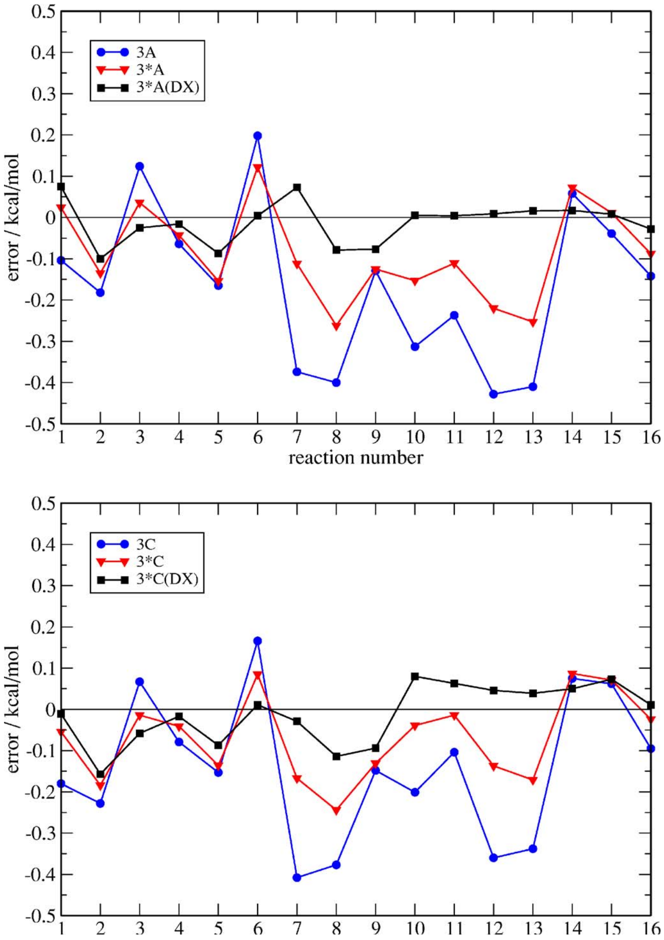

FIG. 2. Errors of the MP2-F12/**3**A (upper panel) and MP2-F12/**3**C (lower panel) correlation contributions of the reaction energies relative to the CBS estimates. AO basis: aug-cc-pVTZ; DF basis: aug-cc-pVTZ/MP2FIT; RI basis: cc-pVTZ/JKFIT.

Finally, we note that the hybrid approximations have only a negligible effect on the reaction energies. The differences between approximations **3**C and **3**C(HY2) can hardly be distinguished on the scale of Fig. 2, and the average errors deviate from the ones in Table IX by at most 0.02 kcal/mol. Due to the additional HX approximation necessary to avoid quadratic scaling of the CPU time with the size of the RI basis, the differences between **3**B and **3**B(HXY2) are slightly larger but still entirely negligible as compared to other errors.

V. SUMMARY AND CONCLUSIONS

A general form of orbital invariant explicitly correlated second-order closed-shell Møller-Plesset perturbation theory (MP2-F12) has been derived, and compact and transparent

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TABLE IX. Root mean square and maximum absolute errors (in parentheses) of the reaction energies for different methods and basis sets. All values are in kcal mol^{-1}.

Method	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ
MP2	1.71 (3.47)	0.57 (1.18)	0.26 (0.50)
MP2(CBS)[a]	0.45 (0.81)	0.22 (0.35)	0.08 (0.17)
3A	0.79 (1.42)	0.25 (0.43)	0.10 (0.18)
3*A	0.48 (1.02)	0.14 (0.26)	0.04 (0.08)
3*A(DX)	0.35 (0.77)	0.05 (0.10)	0.03 (0.06)
3B	0.52 (1.10)	0.22 (0.39)	0.09 (0.15)
3*B	0.33 (0.71)	0.12 (0.23)	0.04 (0.07)
3*B(DX)	0.36 (0.73)	0.07 (0.15)	0.03 (0.05)
3C	0.54 (1.13)	0.22 (0.41)	0.09 (0.15)
3C(D)	0.34 (0.80)	0.13 (0.28)	0.06 (0.09)
3*C	0.35 (0.75)	0.12 (0.24)	0.04 (0.07)
3*C(D)	0.35 (0.76)	0.07 (0.16)	0.03 (0.05)
3*C(DX)	0.36 (0.74)	0.07 (0.16)	0.03 (0.05)

[a] Extrapolated using the aug-cc-pVnZ and aug-cc-pV$(n+1)$Z basis sets, assuming $E_n = E_{\mathrm{CBS}} + A/n^3$.

working equations have been presented. A hierarchy of well defined levels of approximation has been introduced. They differ from the exact theory by the neglect of terms involving matrix elements over the Fock operator. The effect of the various approximations (GBC, EBC, and exchange) has been tested for 21 molecules, and the accuracy of relative energies has been demonstrated for 16 chemical reactions. Even with the aug-cc-pVDZ basis set, chemical accuracy (<1kcal mol^{-1}) is achieved.

The new approximation **3**C, which is based on the recent work of Kedžuch *et al.*,[33] has been tested for the first time with auxiliary RI basis sets. The convergence of the correlation energies with the size of the RI basis is found to be similar as for the computationally more demanding **3**B method. In the limit of a complete RI basis, both methods become equivalent. In practice, differences of the absolute errors are found to be very small, and energy differences computed with the **3**B and **3**C methods are virtually identical. The **3**C method is not only easier to implement but also numerically more stable and more efficient than **3**B since the difficult single commutator integrals involving the kinetic energy operators are avoided. Using our implementation with density fitting for the integrals, the **3**C method is typically a factor of 2 faster than the **3**B method.

Based on the CABS approach, new well defined hybrid approximations have been proposed for the **3**B and **3**C methods. In these methods a quadratic dependence of the CPU time on the size of the RI basis is avoided. The absolute errors of the correlation energies due to these approximations are significantly smaller than those of the hybrid approximations proposed earlier by Klopper,[15] and errors of relative energies are entirely negligible.

Surprisingly, it has been found that the theoretically most rigorous methods, namely, **3**B and **3**C, yield the least accurate reaction energies when smaller basis sets are used. Much more accurate results are obtained if coupling terms in the first-order equations are neglected. In particular, the non-orbital invariant diagonal approximations in combination with localized orbitals give highly accurate results.

The finding that the simplest methods, namely, **3***A(D) and **3***C(D), yield the most accurate energy differences is of practical importance since the diagonal approximations are most suitable for the introduction of local approximations.[25,29] The local approximations make it possible to treat quite large molecules (≈ 100 atoms). However, the 16 simple reactions investigated here are certainly still insufficient to draw general conclusions. A more extensive study for more than 50 reactions is currently under way. Conformational energy differences and activation energies will be studied as well. All calculations reported in this work have been performed with MOLPRO.[52]

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APPENDIX: EQUIVALENCE OF ANSATZ 2 AND ANSATZ 3

The relation of the matrix elements for *Ansatz* **2** and *Ansatz* **3** can be obtained using

$$\hat{Q}_{12}^{(\mathbf{2})} = \hat{Q}_{12}^{(\mathbf{3})} + \hat{v}_1\hat{v}_2, \tag{A1}$$

where $\hat{Q}_{12}^{(\mathbf{3})} \equiv \hat{Q}_{12}$ is the projector for *Ansatz* **3**. Using the general definitions in Eqs. (5) and (26)–(29) yields

$$V_{kl}^{ij,(\mathbf{2})} = V_{kl}^{ij,(\mathbf{3})} + K_{ab}^{ij}F_{ab}^{kl}, \tag{A2}$$

$$B_{kl,mn}^{(\mathbf{2})} = B_{kl,mn}^{(\mathbf{3})} + D_{ab}^{kl}F_{ab}^{mn} + C_{ab}^{kl,(\mathbf{3})}F_{ab}^{mn} + F_{ab}^{kl}C_{ab}^{mn,(\mathbf{3})}, \tag{A3}$$

$$X_{kl,mn}^{(\mathbf{2})} = X_{kl,mn}^{(\mathbf{3})} + F_{ab}^{kl}F_{ab}^{mn}, \tag{A4}$$

$$C_{ab}^{kl,(\mathbf{2})} = C_{ab}^{kl,(\mathbf{3})} + D_{ab}^{kl}, \tag{A5}$$

$$\mathcal{F}_{ab}^{kl,(\mathbf{2})} = F_{ab}^{kl}, \tag{A6}$$

where

$$D_{ab}^{kl} = f_{ac}F_{cb}^{kl} + F_{ac}^{kl}f_{cb}. \tag{A7}$$

Note that $D_{ab}^{kl}F_{ab}^{mn} = D_{ab}^{mn}F_{ab}^{kl}$. For the sake of simplicity we also define

$$\check{T}_{ab}^{ij} = f_{ac}T_{cb}^{ij} + T_{ac}^{ij}f_{cb}, \tag{A8}$$

$$\bar{T}_{rs}^{ij} = f_{io}T_{rs}^{oj} + T_{rs}^{io}f_{oj}. \tag{A9}$$

Inserting these expressions into Eqs. (23) and (24) and using $D_{ab}^{mn}T_{ab}^{ij} = F_{ab}^{mn}\check{T}_{ab}^{ij}$ yields, after some rearrangements,

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$$R^{ij,(2)}_{ab} = K^{ij}_{ab} + \check{T}^{ij,(2)}_{ab} - \bar{T}^{ij,(2)}_{ab} + C^{mn,(3)}_{ab} T^{ij,(2)}_{mn} + D^{mn}_{ab} T^{ij,(2)}_{mn} - F^{mn}_{ab} \bar{T}^{ij,(2)}_{mn} \quad (A10)$$

$$R^{ij,(2)}_{kl} = V^{ij,(3)}_{kl} + B^{(3)}_{kl,mn} T^{ij,(2)}_{mn} - X^{(3)}_{kl,mn} \bar{T}^{ij,(2)}_{mn} + C^{kl,(3)}_{ab} (T^{ij,(2)}_{ab} + F^{mn}_{ab} T^{ij,(2)}_{mn}) + F^{kl}_{ab} R^{ij,(2)}_{ab}. \quad (A11)$$

The last term is a multiple of the first equation and vanishes for the solution, i.e., $R^{ij,(2)}_{ab}=0$. Using

$$T^{ij,(3)}_{kl} = T^{ij,(2)}_{kl} \equiv T^{ij}_{kl}, \quad (A12)$$

$$T^{ij,(3)}_{ab} = T^{ij,(2)}_{ab} + F^{mn}_{ab} T^{ij,(2)}_{mn}, \quad (A13)$$

it follows

$$\check{T}^{ij,(2)}_{ab} - \bar{T}^{ij,(2)}_{ab} + D^{mn}_{ab} T^{ij}_{mn} - F^{mn}_{ab} \bar{T}^{ij}_{mn} = \check{T}^{ij,(3)}_{ab} - \bar{T}^{ij,(3)}_{ab}, \quad (A14)$$

and we obtain the result

$$R^{ij,(2)}_{ab} = R^{ij,(3)}_{ab}, \quad (A15)$$

$$R^{ij,(2)}_{kl} = R^{ij,(3)}_{kl} + F^{kl}_{ab} R^{ij,(3)}_{ab}. \quad (A16)$$

Thus, provided the residual equations for *Ansatz* **2** are solved with amplitudes $T^{ij,(2)}_{ab}$, it follows that the equations for *Ansatz* **3** are solved with $T^{ij,(3)}_{ab}$. The solutions T^{ij}_{kl} are the same in both cases. The equivalence of the energies follows from

$$E^{(2)} = \tilde{T}^{ij,(2)}_{ab} K^{ij}_{ab} + \tilde{T}^{ij}_{kl} V^{ij,(2)}_{kl} = \tilde{T}^{ij,(3)}_{ab} K^{ij}_{ab} + \tilde{T}^{ij}_{kl} V^{ij,(3)}_{kl}. \quad (A17)$$

[Eqs. (14) and (35)]. This derivation is independent of the actual approximations used for the matrix elements and is therefore valid for *Ansatz* **3**B and *Ansatz* **3**C as long as no further approximations are introduced.

However, if the hybrid approximations are used, the results of the two *Ansätze* are no longer identical. In *Ansatz* **3**B(HY1) we neglect $\tilde{Y}^{(3)}_{kl,mn}$ [Eq. (75)], while in Klopper's hybrid approximation the corresponding quantity

$$\tilde{Y}^{(2)}_{kl,mn} = \tilde{Y}^{(3)}_{kl,mn} + \tilde{F}^{kl}_{ab} F^{mn}_{ab} \quad (A18)$$

is neglected. The difference $\tilde{F}^{kl}_{ab} F^{mn}_{ab}$ does not cancel when expressing the **2**B equations in terms of the **3**B quantities since this approximation is *not* made in the matrices $C^{kl,(3)}_{ab}$. Therefore, the equations are no longer equivalent.

Finally, we consider approximation **3***, for which the matrices $C^{kl,(3)}_{ab}$ and $Z^{(3)}_{kl,mn}$ are neglected. The **B** matrix then takes the form

$$B^{(3*)}_{kl,mn} = \hat{S} A^{(3)}_{kl,mn}. \quad (A19)$$

Neglecting $C^{kl,(3)}_{ab}$ in Eqs. (A3) and (A5) leads for *Ansatz* **2*** to the definitions

$$B^{(2*)}_{kl,mn} = B^{(3*)}_{kl,mn} + F^{kl}_{ab} D^{mn}_{ab}, \quad (A20)$$

$$C^{(2*)}_{kl,ab} = D^{kl}_{ab}. \quad (A21)$$

The first-order equations for *Ansatz* **2*** then become

$$0 = K^{ij}_{ab} + \check{T}^{ij,(2*)}_{ab} - \bar{T}^{ij,(2*)}_{ab} + D^{mn}_{ab} T^{ij,(2*)}_{mn} - F^{mn}_{ab} \bar{T}^{ij,(2*)}_{mn}, \quad (A22)$$

$$0 = V^{ij,(3)}_{kl} + B^{(3*)}_{kl,mn} T^{ij,(2*)}_{mn} - X^{(3)}_{kl,mn} \bar{T}^{ij,(2*)}_{mn} + F^{kl}_{ab} [K^{ij}_{ab} + \check{T}^{ij,(2*)}_{ab} - \bar{T}^{ij,(2*)}_{ab} + D^{mn}_{ab} T^{ij,(2*)}_{mn} - F^{mn}_{ab} \bar{T}^{ij,(2*)}_{mn}]. \quad (A23)$$

Again, the term in square brackets in the second equation equals the first equation, and if this is removed the equation becomes identical to the one for *Ansatz* **3***. Obviously, similar relations to those in Eqs. (A12) and (A13) are then valid for *Ansatz* **2***, and in this case the $T^{ij,(3*)}_{ab}$ are equal to the conventional MP2 amplitudes. It is then easy to show that the energies for *Ansatz* **2*** and **3*** are the same.

For the special case of canonical orbitals we can define

$$B^{ij,(2)}_{kl,mn} = B^{(2)}_{kl,mn} - (\epsilon_i + \epsilon_j) X^{(2)}_{kl,mn}, \quad (A24)$$

$$C^{ij,(2)}_{kl,ab} = C^{kl,(2)}_{ab} - (\epsilon_i + \epsilon_j) F^{kl}_{ab}, \quad (A25)$$

$$B^{ij,(3*)}_{kl,mn} = B^{(3*)}_{kl,mn} - (\epsilon_i + \epsilon_j) X^{(3)}_{kl,mn} = B^{ij,(2)}_{kl,mn} - \tfrac{1}{2} (F^{kl}_{ab} C^{ij,(2)}_{mn,ab} + F^{mn}_{ab} C^{ij,(2)}_{kl,ab}). \quad (A26)$$

The first-order equations for *Ansätze* **2*** and **3*** can then both be written in the simple forms

$$0 = K^{ij}_{ab} + E^{ij}_{ab} T^{ij}_{ab}, \quad (A27)$$

$$0 = V^{ij,(3)}_{kl} + B^{ij,(3*)}_{kl,mn} T^{ij}_{mn}. \quad (A28)$$

The definitions of $V^{ij,(3)}_{kl}$ [Eq. (A2)] and $B^{ij,(3*)}_{kl,mn}$ [Eq. (A26)] in terms of the quantities for *Ansatz* **2** are exactly the same as in Eqs. (45) and (46), respectively, of Klopper and Samson,[14] and therefore the energy corrections for the explicitly correlated parts are equivalent. Note that no artifical symmetrization of $B^{ij,(3*)}_{kl,mn}$ was necessary in our derivation.

However, Klopper and Samson arrived at the definition of their quantity $\tilde{B}^{(ij)}_{kl,mn}$ (our $B^{ij,(3*)}_{kl,mn}$) in a different way. They argued that their Eq. (46) is obtained by modifying solely one of the coupling matrices $C^{ij,(2)}_{kl,ab}$ in their Eq. (12) [which corresponds to our Eq. (110)]. This means that the coupling matrix in just one of the two first-order equations is modified. If this is done in the equation for the explicitly correlated amplitudes, one arrives at

$$0 = K^{ij}_{ab} + E^{ij}_{ab} T^{ij,(2*)}_{ab} + C^{ij,(2)}_{mn,ab} T^{ij,(2*)}_{mn}, \quad (A29)$$

$$0 = V^{ij,(3)}_{kl} + (B^{ij,(2)}_{kl,mn} - F^{kl}_{ab} C^{ij,(2)}_{mn,ab}) T^{ij,(2*)}_{mn}, \quad (A30)$$

where the solution $T^{ij,(2*)}_{ab}$ of Eq. (A29) has been used to derive Eq. (A30). After (artificial) symmetrization of $B^{ij,(2)}_{kl,mn} - F^{kl}_{ab} C^{ij,(2)}_{mn,ab}$ the second equation becomes identical to Eq. (A28), and yields the correct explicitly correlated amplitudes $T^{ij,(2*)}_{mn}$. These can be used to compute the correct energy correction $\Delta E^{(2)}_{\mathrm{F12}}$, as defined in Eq. (112), and the total correlation energy can be obtained by adding the conventional MP2 energy $E^{(2)}_{\mathrm{MP2}}$. However, if one would instead also solve the first equation for the amplitudes $T^{ij,(2*)}_{ab}$ and compute the correlation energy straightforwardly as

$$E^{(2)} = \tilde{T}^{ij,(2*)}_{ab} K^{ij}_{ab} + \tilde{T}^{ij,(2*)}_{kl} V^{ij,(2)}_{kl} \quad (A31)$$

a different result would be obtained. Therefore, modifying the matrices $C^{kl,(2)}_{ab}$ in just one of the two equations is inher-

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ently inconsistent. In Ref. 15 Klopper noted that the modified matrices $C_{ab}^{kl,(\mathbf{2})}$ are only used in the equation for the conventional amplitudes. But this does not even lead to an equivalent equation for the explicitly correlated amplitudes, and therefore the definitions of *Ansatz* **2*** in Refs. 14 and 15 are inconsistent.

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