

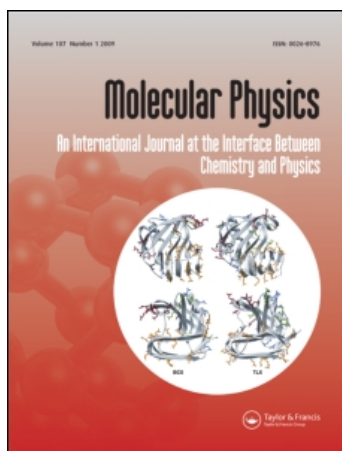
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### Open-shell explicitly correlated F12 methods

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## INVITED ARTICLE

### Open-shell explicitly correlated F12 methods

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In calculations on open-shell systems, spin-flipped geminals must be used in explicitly correlated F12 methods with spin-unrestricted or restricted open-shell Hartree–Fock reference wave functions. We suggest the use of the sp ansatz of Bokhan *et al.* [J. Chem. Phys. **131**, 084105 (2009)] for calculations with fixed F12 amplitudes, but to use a novel contracted geminal approach if the F12 amplitudes are to be optimised. This new approach is denoted MP2-F12-*o* (CCSD(F12)-*o*). The performance of the new approach is assessed by calculating the atomisation energies of a test set comprising 106 molecules containing the atoms H, C, N, O and F, and by calculating the ionisation energies and electron affinities of the atoms C, N, O and F.

**Keywords:** open-shell systems; electron correlation; geminals; correlation cusp

#### 1. Introduction

R12 explicitly correlated electronic structure methods overcome the slow convergence of orbital expansions by employing geminal basis functions that closely resemble the correlation holes in electronic wave functions [1,2]. These methods have developed rapidly over the last seven years and are emerging as robust tools for computational chemistry, where small basis sets may be used to obtain near basis set limit accuracy [3]. The principal differences between the early and modern R12 methods are the use of a complementary auxiliary basis set (CABS) for the resolution of the identity approximation, employed to evaluate the many-electron integrals [4,5], and the use of a Slater-type correlation factor for the geminal basis functions [6]. Methods that use nonlinear correlation factors instead of the original linear factor are commonly referred to as F12 methods. So far, the F12 approach has been combined with MP2 [6], CASPT2 [7] and coupled-cluster wave function methods up to CCSDTQ [8–11]. In addition, many researchers have improved the efficiency of F12 methods through density fitting [12,13], improved methods for evaluating Fock matrix elements for geminal functions [14,15], localisation techniques [16–19] and by constructing specially optimised basis sets [20–22].

One further development is the rational generator approach of Ten-no [23]. In this approach the *s*- and *p*-wave coalescence conditions [24,25] for the

first-order wave function are used to predetermine the F12 amplitudes instead of optimising them. The fixed-amplitude method is computationally less demanding because only the diagonal elements of the spin-adapted F12 matrix elements need to be computed and no equations for the F12 amplitudes need to be solved. Moreover, the fixed-amplitude method is free from geminal basis set superposition error, which arises if the amplitudes are optimised [26], and is free from the numerical problems associated with inverting the geminal Fock matrix, which becomes non-positive definite in some limits [27]. The loss of accuracy due to the reduced variational degrees of freedom is slight and the fixed-amplitude method is used increasingly in F12 calculations, particularly for explicitly correlated coupled-cluster singles and doubles methods (CCSD-F12) [28–34].

The extension of the fixed-amplitude approach to open-shell systems has been attempted only recently [27,30,32,35] and has led to a re-evaluation of the geminal basis used for open-shell calculations [32]. Bokhan *et al.* demonstrated that, contrary to the closed-shell case, it is not possible to satisfy both the *s*- and *p*-wave UMP2 coalescence conditions using the functions  $f(r_{12})|ij\rangle$  alone.  $|ij\rangle$  is the usual two-electron determinant of occupied spin-orbitals *i* and *j* and  $f(r_{12})$  is the correlation factor. To satisfy the *s*- and *p*-wave coalescence conditions for open-shell MP2-F12 calculations, Bokhan *et al.* introduced a spin-flipped geminal basis and have subsequently performed

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calculations at the UMP2-F12 level [35]. They demonstrated that the basis set convergence without the spin-flipped basis is limited by the  $X^{-5}$  behavior for the pair energies where one orbital is singly occupied in the HF reference, arising from the unsatisfied  $p$ -wave derivative discontinuity. By including the spin-flipped basis, the  $X^{-7}$  convergence behavior of F12 methods for closed-shell species is achieved for open-shell species. For high-spin ROHF references, Knizia *et al.* have also included spin-flipped geminal basis functions in their RMP2-F12 and CCSD-F12x methods [30], noting improved performance for atomisation energies, electron affinities and ionisation potentials compared with their earlier open-shell fixed-amplitude approach [27].

Nevertheless, a number of questions remain unanswered for open-shell F12 calculations. For UHF references, the combined basis of normal and spin-flipped geminals contains many near linear dependencies and including both sets with full variational flexibility leads to severe numerical problems. Indeed, Bokhan *et al.* only considered the diagonal orbital-variant method and, even here, a singular value decomposition was necessary. We consider the optimisation of coefficients for both normal and spin-flipped geminals as undesirable since it results in an unbalanced treatment of open- and closed-shell systems, favoring the open-shell species. It is also numerically problematic and can lead to steps in potential energy surfaces. In this work we suggest that a contracted geminal basis should be used, that is, fixed linear combinations of normal and spin-flipped geminals with contraction coefficients determined by the  $s$ - and  $p$ -wave coalescence conditions. Our approach can be unproblematically combined with the original orbital-invariant ansatz, and can be extended to the UCCSD(F12) level of theory, using ROHF or UHF references, with minimal changes to the existing UCCSD(F12) program.

To properly assess the impact of spin-flipped geminals on the accuracy of a calculation, it is necessary to make a comparison with analogous methods without the spin-flipped geminals. When optimising the amplitudes, the comparison is between the original orbital invariant formulation of Ref. [36] and the new methods presented here. However, no open-shell fixed-amplitude method exists in the literature where the coalescence conditions are fulfilled as far as possible within the normal geminal basis, that is, without spin-flipped functions. In this work we derive such a fixed-amplitude method for MP2-F12 with UHF and ROHF references that is both orbital invariant and size extensive and reduces to Ten-no's

rational generator method when the  $\alpha$  and  $\beta$  orbitals are identical.

## 2. The geminal basis for open-shell F12 calculations

Stemming from the original ideas of Kutzelnigg [1], the geminal basis in F12 methods is chosen such that the  $s$ - and  $p$ -wave coalescence conditions can be satisfied for every spin-adapted first-order pair function  $u_{ij}^s$ . The  $s$ -wave condition applies to the singlet pair functions,  $u_{ij}^0$ , and the  $p$ -wave condition to the triplet pair functions  $u_{ij}^1$ ,

$$u_{ij}^0 = u_{ij}^0(r_{12}=0) + \frac{1}{2}r_{12}(|ij\rangle + |ji\rangle)(2 + 2\delta_{ij})^{-1/2} + \mathcal{O}(r_{12}^2), \quad (1)$$

$$u_{ij}^1 = \mathbf{r}_{12} \cdot \left. \frac{\partial u_{ij}^1}{\partial \mathbf{r}_{12}} \right|_{r_{12}=0} + \frac{1}{4}r_{12}|ij\rangle + \mathcal{O}(r_{12}^3), \quad \alpha\alpha, \quad \beta\beta, \quad (2)$$

$$u_{ij}^1 = \mathbf{r}_{12} \cdot \left. \frac{\partial u_{ij}^1}{\partial \mathbf{r}_{12}} \right|_{r_{12}=0} + \frac{1}{4}r_{12}(|ij\rangle - |ji\rangle)2^{-1/2} + \mathcal{O}(r_{12}^3), \quad \alpha\beta. \quad (3)$$

$|ij\rangle$  is a two-electron determinant of spin-orbitals  $i$  and  $j$ , where it is understood that the first orbital has  $\alpha$  spin and the second has  $\beta$  spin, for the opposite-spin case. We use this convention consistently throughout this article. Introducing variational flexibility into an orbital-invariant manner [36], the first-order pair functions are expanded as

$$u_{ij} = \sum_{a < b} t_{ab}^{ij} |ab\rangle + \sum_{k < l} c_{kl}^{ij} \hat{Q}_{12} f(r_{12}) |kl\rangle, \quad (4)$$

where  $k, l$  run over occupied and  $a, b$  over virtual Hartree–Fock spin-orbitals.  $\hat{Q}_{12}$  is the strong orthogonality operator and  $\partial f(r_{12})/\partial r_{12}|_{r_{12}=0} = 1$ . For restricted closed-shell systems, Equations (1) and (3) can be used to select fixed F12 amplitudes,

$$c_{kl}^{ij} = \frac{1}{4} \delta_k^i \delta_l^j, \quad \alpha\alpha, \quad \beta\beta, \quad (5)$$

$$c_{kl}^{ij} = \frac{3}{8} \delta_k^i \delta_l^j + \frac{1}{8} \delta_l^i \delta_k^j, \quad \alpha\beta. \quad (6)$$

Indeed, in the limit of a large orbital basis, variationally optimised F12 amplitudes tend to these values. The derivation of Equations (1)–(3) assumes that singlet and triplet pair functions can be constructed and thus is only rigorous for closed-shell restricted first-order pair functions. For UMP2 using ROHF or

UHF references, the coalescence conditions must be re-examined in terms of spin-orbitals. Our derivation of the coalescence conditions for open-shell MP2 is reported in the appendix and we consider both UHF and ROHF references. In complete agreement with the work of Bokhan *et al.*, we find that Equation (2) holds for the same-spin pairs and for the  $\alpha\beta$  pairs

$$u_{ij} = u_{ij}(r_{12} = 0) + \frac{1}{2}r_{12}(|ij\rangle + |\bar{j}\bar{i}\rangle)2^{-1/2} + r_{12} \cdot \left. \frac{\partial u_{ij}}{\partial \mathbf{r}_{12}} \right|_{r_{12}=0} + \frac{1}{4}r_{12}(|ij\rangle - |\bar{j}\bar{i}\rangle)2^{-1/2} + \mathcal{O}(r_{12}^2). \quad (7)$$

The spin-orbital  $\bar{i}$  has the same spatial component as  $i$ , but the spin component is flipped such that  $\bar{i} = (\hat{s}_+ + \hat{s}_-)i$ . Notably, both  $s$ - and  $p$ -wave coalescence conditions apply to the opposite-spin pair functions, even though it is not possible to construct singlet and triplet functions from the corresponding pairs of occupied spin-orbitals. As concluded by Bokhan *et al.*, it is only possible to satisfy both  $s$ - and  $p$ -type derivative discontinuities if spin-flipped functions are included in the geminal basis. Equation (4) thus becomes

$$u_{ij} = \sum_{a<b} t_{ab}^{ij} |ab\rangle + \sum_{k<l} c_{kl}^{ij} \hat{Q}_{12} f(r_{12}) |kl\rangle + \sum_{k<\bar{l}} c_{k\bar{l}}^{ij} \hat{Q}_{12} f(r_{12}) |k\bar{l}\rangle. \quad (8)$$

Equation (7) is naturally also valid for closed-shell HF references and, in this case, the spin-flipped functions are obviously always present in the normal geminal basis and the functions  $f(r_{12})|k\bar{l}\rangle$  are redundant. For ROHF references, the only spin-flipped functions missing from the normal geminal basis are those where either  $k$  or  $l$  belongs to a singly occupied restricted HF orbital and thus has no spin-flipped counterpart among the HF occupied orbitals.

### 2.1. Fixed F12 amplitudes in ROMP2-F12 and UMP2-F12

The coefficients in Equation (8) may be selected using the coalescence conditions, which gives

$$c_{kl}^{ij} = \frac{1}{4} \delta_k^i \delta_l^j, \quad c_{k\bar{l}}^{ij} = 0, \quad \alpha\alpha, \quad \beta\beta, \quad (9)$$

$$c_{kl}^{ij} = \frac{3}{8} \delta_k^i \delta_l^j, \quad c_{k\bar{l}}^{ij} = \frac{1}{8} \delta_l^i \delta_k^j, \quad \alpha\beta. \quad (10)$$

This method is orbital invariant and size extensive and is also size consistent when combined with a

UHF reference. It yields  $X^{-7}$  convergence behaviour for both restricted and unrestricted MP2-F12 calculations and thus gives a balanced treatment of open- and closed-shell species. This spin-flipped SP ansatz has previously been implemented for ROHF-based MP2-F12 and CCSD-F12x by Knizia *et al.* [30] and also for UHF-based MP2-F12 by Bokhan *et al.* [35]. We will refer to MP2-F12 methods that use spin-flipped geminals with this choice of fixed amplitudes as MP2-F12-*sp*.

To assess the effect of including the spin-flipped geminals, we must define a fixed-amplitude method where the geminal basis is restricted to that of Equation (4). The best choice of fixed amplitudes is to satisfy the derivative discontinuities as far as possible within the basis available. For ROHF references and restricted orbitals, this corresponds to

$$c_{kl}^{ij} = \frac{1}{4} \delta_k^i \delta_l^j, \quad \alpha\alpha, \quad \beta\beta, \quad (11)$$

$$c_{kl}^{ij} = \frac{3}{8} \delta_k^i \delta_l^j + \frac{1}{8} \delta_l^i \delta_k^j, \quad \alpha\beta, \quad 'd', \quad (12)$$

$$c_{kl}^{ij} = \frac{1}{2} \delta_k^i \delta_l^j, \quad \alpha\beta, \quad 's', \quad (13)$$

where 'd' denotes pairs  $ij$  where both  $i$  and  $j$  refer to orbitals that are doubly occupied and 's' pairs where either  $i$  or  $j$  is singly occupied in the ROHF reference. For 'd' pairs, both the  $s$ - and  $p$ -wave discontinuities can be satisfied, but for 's' pairs, only the  $s$ -wave cusp can be satisfied. This choice differs from that of Ref. [27], where  $c_{kl}^{ij} = \frac{3}{8} \delta_k^i \delta_l^j$  was used for the 's' pairs. However, it is easily verified that, in the limit of a large orbital basis, the optimised amplitudes tend to our values. Upon rotating the orbitals, for example for semi-canonicalisation or localisation, the  $\alpha\beta$  amplitudes become

$$c_{kl}^{ij} = \frac{1}{2} \delta_k^i \delta_l^j - \frac{1}{8} \sum_{mn} s_{in} s_{kn} s_{mj} s_{ml} + \frac{1}{8} s_{il} s_{kj}, \quad (14)$$

where  $s_{il}$  is the spatial overlap between the  $\alpha$  spin-orbital  $\phi_i$  and the  $\beta$  spin-orbital  $\phi_l$ . For calculations based on UHF references, we suggest that Equation (14) is the best choice within the constraints of the normal geminal basis, even though neither the  $s$ - nor the  $p$ -wave conditions are rigorously met (the coefficients are based on the overlap and not on how closely  $\phi_i \phi_k$  matches  $\phi_i \phi_j$  at  $r_{12} = 0$ ). Such a choice is both orbital invariant, size extensive and, importantly, size consistent, by virtue of the dependence on the overlap  $s_{il}$ . We will refer to this method as MP2-F12- $\tilde{sp}$ .

As an aside, we note that the Quantum Monte Carlo community makes a different choice for open-shell calculations [37] which, when applied to MP2-F12 theory, corresponds to

$$c_{kl}^{ij} = \frac{1}{4} \delta_k^i \delta_l^j, \quad \alpha\alpha, \quad \beta\beta, \quad (15)$$

$$c_{kl}^{ij} = \frac{1}{2} \delta_k^i \delta_l^j, \quad \alpha\beta. \quad (16)$$

Here, only the  $s$ -wave cusp is satisfied for the  $\alpha\beta$  pairs. For restricted closed-shell systems, this reduces to  $c_{ij}^{ij} = \frac{1}{2}$  for the spin-adapted singlet pairs, and  $c_{ij}^{ij} = \frac{1}{4}, \frac{1}{4}$  and  $\frac{1}{4}$  for the  $m_s = 1, 0, -1$  components of the triplet excitations, respectively. Although this is both orbital invariant and size consistent, it clearly introduces spin-contamination [23] and we do not consider it further.

Concerning the relative computational costs of the above choices, we make the following observations, which apply to density fitted MP2-F12. For closed-shell calculations, we remind the reader that the integral transformation steps scale as  $N^4$ , that the contractions of three-index integrals to build four-index quantities scale as  $N^5$  and that the contractions of the four-index quantities to build the  $\mathbf{B}$  and  $\mathbf{V}$  matrices scale as  $N^4$ , because only the diagonals of the spin-adapted matrices are required for the fixed-amplitude ansatz. For open-shell calculations:

- (1) The  $N^4$  steps increase by a factor of 2 since integrals for  $\alpha$  and  $\beta$  orbitals are required. This is true for the Coulomb, exchange and Fock transformed integrals even if restricted orbitals are used. For the spin-flipped method, the prefactor is increased by a further factor of 2, since spin-flipped integrals are required. This further factor of 2 is avoided if restricted orbitals are used (RMP2-F12).
- (2) The  $N^5$  contractions are twice as expensive as in the closed-shell case (again, this also applies to the most expensive contractions in RMP2-F12). For the spin-flipped method, a further factor of 2 arises due to the spin-flipped geminals, but this is avoided for RMP2-F12.
- (3) For both the normal and spin-flipped fixed-amplitude methods,  $N^4$  scaling can be recovered for the final construction of the  $\alpha\beta$   $\mathbf{B}$  and  $\mathbf{V}$  matrices by appropriately contracting four-index quantities with the fixed amplitudes. For spin-flip this is trivial and, for the overlap-based approach, due to the factorisability of the terms in Equation (14) into separate

transformations for  $\alpha$  and  $\beta$  orbitals, this can be achieved by four  $N^5$  contractions with a low prefactor (they scale at most as  $O^3 V^2$ , where  $O$  is the number of active occupied orbitals and  $V$  is the maximum number of virtual or CABS orbitals). We note that an analogous contraction has been utilised by Köhn to simplify the equations for restricted closed-shell F12 methods [33].

To summarise, using spin-flipped geminals is approximately twice as expensive as using the normal geminal basis with Equations (11)–(14), unless restricted orbitals are used, in which case the two methods have comparable cost. Numerical tests comparing the performance of the two approaches are reported in Section 3.

## 2.2. Optimised F12 amplitudes in ROMP2-F12 and UMP2-F12

Equation (4) presents no special difficulties upon variational optimisation of the F12 amplitudes  $c_{kl}^{ij}$ , beyond those sometimes encountered for closed-shell calculations. Indeed, this method has been employed for open-shell R12 calculations for the past 15 years. Equation (8), on the other hand, contains large redundancies between the normal and spin-flipped geminals for restricted open- or closed-shell HF references, which become severe near linear dependencies when an unrestricted HF reference is used. Bokhan *et al.* have proposed deleting geminals based on singular value decomposition to remove the linear dependence. For ROHF-based MP2-F12, this is not necessary since the redundancies can be removed exactly by constructing the geminal basis from the restricted orbitals. However, we consider that a balanced treatment of open- and closed-shell species will only be obtained if the size of the geminal basis is proportional to the number of correlated electron pairs. We therefore propose that Equation (8) should be replaced by

$$u_{ij} = \sum_{a < b} t_{ab}^{ij} |ab\rangle + \sum_{k < l} c_{kl}^{ij} \hat{Q}_{12} f(r_{12}) (c|kl\rangle + \bar{c}|\bar{l}\bar{k}\rangle), \quad (17)$$

where the contraction coefficients  $c$  and  $\bar{c}$  are determined using the coalescence conditions

$$c = \frac{1}{4}, \quad \bar{c} = 0, \quad \alpha\alpha, \quad \beta\beta, \quad (18)$$

$$c = \frac{3}{8}, \quad \bar{c} = \frac{1}{8}, \quad \alpha\beta. \quad (19)$$

It should be noted that, for same-spin pairs, the spin-flipped geminals always have exactly zero contribution. Variational optimisation of the  $c_{kl}^{ij}$  is no more complicated than if Equation (4) is used. Restricting  $c_{kl}^{ij}$  to the diagonal amplitudes  $c_{ij}^{ij}$  results in a non-orbital invariant method and we do not consider it here, although it may be useful in combination with localisation techniques. In Section 3 we present results of calculations where the F12 amplitudes are optimised with and without the flipped contributions. We will refer to the standard orbital invariant method, without spin-flipped geminals, as MP2-F12- $\delta$  and to the new method including the flipped functions as MP2-F12- $o$ . For comparison, we also report ROHF-based calculations where the non-redundant set of normal and flipped variational parameters are optimised separately, which will be denoted MP2-F12- $o^+$ .

The relative computational cost of including or excluding spin-flipped geminals has been discussed in the previous section for the fixed-amplitude MP2-F12 methods. If the coefficients in Equation (4) or (17) are variationally optimised, then  $N^6$  contractions are required for the construction of the  $\mathbf{B}$  and  $\mathbf{V}$  matrices, and also for the inclusion of coupling terms between  $t_{ab}^{ij}$  and  $c_{kl}^{ij}$  when solving the amplitude equations. Extending the approach of Bokhan *et al.* to the invariant ansatz for UHF-based MP2-F12 would lead to a fourfold increase in the  $N^6$  contractions for the  $\alpha\beta$   $\mathbf{B}$  matrix compared with neglecting spin-flipped geminals and a twofold increase for the  $\alpha\beta$   $\mathbf{V}$  matrix. If an ROHF reference is used, this corresponds to the MP2-F12- $o^+$  method and only the spin-flipped geminals for the ‘ $s$ ’ pairs need be computed in addition to the normal geminals, leading to a slight increase in the prefactor for the  $N^6$  contractions compared with MP2-F12- $\delta$ . However, if the geminal basis is contracted as we suggest, there is no additional computational cost for including the spin-flipped functions for the  $N^6$  steps.

### 2.3. The geminal basis in open-shell CCSD-F12 calculations

At the CCSD level of theory it has been standard practice [38] to use the geminal basis appropriate for MP2 and also to use the MP2 coalescence conditions to define fixed F12 amplitudes [28,29,32], even though the MP2 and coupled-cluster coalescence conditions differ [39]. Köhn has recently included additional geminals that amend this deficiency, demonstrating that they are important for response properties [33]. For ground-state energies, however, selecting the geminal basis and amplitudes based on MP2 appears

to be sufficient and we pursue this approach here. Switching to second quantisation, the doubles cluster operator becomes

$$\hat{T}_2 = \frac{1}{4} \sum_{abj} t_{ab}^{ij} \hat{\tau}_{ij}^{ab} + \frac{1}{8} \sum_{kij} c_{kl}^{ij} \sum_{\mu\nu} w_{\mu\nu}^{kl} \hat{\tau}_{ij}^{\mu\nu}, \quad (20)$$

where  $\mu$  and  $\nu$  are orbitals in the complete basis and

$$w_{\mu\nu}^{kl} = c \langle \mu\nu | \hat{Q}_{12} f(r_{12}) | kl \rangle + \bar{c} \langle \mu\nu | \hat{Q}_{12} f(r_{12}) | \bar{l}\bar{k} \rangle. \quad (21)$$

The contraction coefficients are  $c = \frac{1}{4}$ ,  $\bar{c} = 0$  for like-spin pairs and  $c = \frac{3}{8}$ ,  $\bar{c} = \frac{1}{8}$  for  $\alpha\beta$  pairs, or simply  $c = 1$  and  $\bar{c} = 0$  if spin-flipped geminals are not to be included. For the fixed-amplitude method, Equations (11) and (14) are recommended in the absence of spin-flipped geminals and if spin-flipped geminals are included, then  $c_{kl}^{ij} = \delta_k^i \delta_l^j$ . If a UCCSD-F12 program is available that uses the normal geminal basis, all that is required to extend it to employ the spin-flipped geminal basis is to replace the F12 integrals with the above linear combination of normal and flipped integrals. In Section 4 we present results of spin-flipped calculations at the ROHF-based UCCSD(F12) level of theory.

## 3. MP2-F12

Our focus is on the effect of the spin-flipped geminals on the correlation treatment. For ROHF-based MP2, contributions from both single and double excitations occur, but they are uncoupled and the singles energy depends only on the Fock matrix elements. Since the basis set convergence for the singles and doubles are thus very different, we partition the MP2 energy into  $\text{HF}_+ = E_{\text{HF}} + f_i^a t_a^i$  and the doubles correlation contribution.

### 3.1. Atomisation energies

We have recently computed a set of basis set limit frozen-core (fc) MP2 energies for a set of 106 molecules of H, C, N, O and F to an accuracy of 99.95%, which are intended as a test set for F12 methods [40]. Here we use these benchmarks to assess the relative performance of the MP2-F12- $\tilde{sp}$ , MP2-F12- $sp$ , MP2-F12- $\delta$ , MP2-F12- $o$  and MP2-F12- $o^+$  methods for atomisation energies using the cc-pVXZ-F12 orbital basis sets [20] with X = D, T and Q. All UMP2-F12 calculations are based on RHF or ROHF references and were performed with the TURBOMOLE program package using the default options, namely Ansatz 2, approximation B, the specially optimised complementary auxiliary basis sets of Peterson and co-workers [21]

Table 1. Basis set limit HF and valence MP2 and CCSD correlation energies for the atoms C, N, O and F in  $E_h$ .

Atom		$E_{HF}$	MP2 correlation	CCSD correlation
C	Carbon	-37.6886122	-0.0818650	-0.0980777
N	Nitrogen	-54.4009236	-0.1138167	-0.1258611
O	Oxygen	-74.8093817	-0.1792901	-0.1910343
F	Fluorine	-99.4093241	-0.2477734	-0.2534840

Table 2. Basis set error statistics for the  $HF_+$  and doubles correlation contributions to fc-MP2-F12 atomisation energies ( $\text{kJ mol}^{-1}$  per valence electron).  $HF_+$  refers to  $E_{HF} + f_i^a t_a^i + f_i^p t_p^i$ .

MP2-F12	cc-pVDZ-F12		cc-pVTZ-F12		cc-pVQZ-F12	
	$\bar{\Delta}$	$\sigma$	$\bar{\Delta}$	$\sigma$	$\bar{\Delta}$	$\sigma$
$HF_+$	-0.13	0.05	-0.02	0.01	0.00	0.00
$\tilde{sp}$	0.16	0.23	0.08	0.06	0.03	0.02
$sp$	-0.34	0.11	-0.07	0.03	-0.02	0.01
$\delta$	0.09	0.12	0.07	0.04	0.03	0.02
$o$	-0.14	0.08	-0.02	0.02	-0.01	0.01
$o^+$	-0.18	0.09	-0.05	0.03	-0.01	0.01

and the aug-cc-pwCV(X+1)Z MP2-fitting [41] and aug-cc-pV(X+1)Z RI-*JK* basis sets [42] for density fitting. The Slater-type correlation factor was expanded in six Gaussians [43] and the exponents for the Slater function were 0.9, 1.0 and  $1.1 a_0^{-1}$  for the cc-pVXZ-F12 basis sets, X = D, T and Q, and  $1.4 a_0^{-1}$  for the aug-cc-pVXZ basis sets. The integrals involving the single commutator of  $f(r_{12})$  with the kinetic energy were computed from the matrix representation of the Fock and exchange matrices. Furthermore, a singles perturbative correction was added to the HF energy using Equation (48) of Ref. [27] for ROHF (see Ref. [30] or [44] for the closed-shell case). In our previous work, the basis set limits for the atoms were computed using the MP2-F12- $\delta$  method. The corresponding MP2-F12- $o$  energies are slightly closer to the basis set limit and we use these improved benchmarks (Table 1) in this work.

In Table 2 we report the mean  $\bar{\Delta}$  and standard deviation  $\sigma(s_N)$  for basis set errors of atomisation energies using MP2-F12 methods with and without the spin-flipped geminal basis. Results for both the fixed-amplitude (MP2-F12- $\tilde{sp}$ , MP2-F12- $sp$ ) and optimised (MP2-F12- $\delta$ , MP2-F12- $o$ , MP2-F12- $o^+$ ) approaches are presented. In all cases, the inclusion of spin-flipped geminals decreases both the mean and standard deviation of the basis set errors for the correlation energy contributions, which indicates that a more balanced treatment of atoms and molecules has

been achieved. For the triple- and quadruple-zeta quality basis sets, the improvement is at least a factor of 2.

Comparing the MP2-F12- $\tilde{sp}$  and MP2-F12- $sp$  results, we note that if the spin-flipped geminals are excluded, the correlating basis set for the atoms is poorer than that for the molecules, contrary to all experience with conventional MP2 calculations. As a result, the basis set errors for the HF and correlation contributions have on average opposite signs, which leads to a cancellation of errors for the total MP2 atomisation energies. By including the spin-flipped geminals, the correlating basis set for the atoms is better than that of the molecules, as usually expected, which reverses the sign of the errors and results in a deterioration in the mean basis set errors for the total MP2 atomisation energies (not reported in Table 1). The improvement in the standard deviation, however, is retained.

For the methods where the  $c_{kl}^{ij}$  are variationally optimised, the mean basis set errors are smaller in magnitude than for the fixed-amplitude methods, while the standard deviations are similar. Since the errors for the spin-flipped and normal geminal calculations decrease from opposite directions, this represents an improvement in the correlation description rather than a cancellation of errors due to basis set superposition error, which would favor the molecules over the atoms. The effect of fully optimising both the normal and spin-flipped geminal amplitudes may be seen by comparing the results for MP2-F12- $o$  and MP2-F12- $o^+$ . We find that the basis set errors are fairly similar and conclude that the contraction coefficients  $c$  and  $\bar{c}$  used in the MP2-F12- $o$  method are close to optimal. The mean error for MP2-F12- $o^+$  is more negative than that of MP2-F12- $o$ , which indicates that the geminal basis is less balanced, favoring the atoms over the molecules. We therefore recommend the MP2-F12- $o$  approach.

### 3.2. Ionisation potentials and electron affinities

The statistics for the atomisation energies in the previous section give an indication of how balanced the method is for treating open- and closed-shell systems. Here we investigate the effect of spin-flip on the relative accuracy of atoms and ions. In Table 3 we report basis set errors of ionisation potentials and electron affinities of C, N, O and F, computed using fc-MP2-F12/cc-pVXZ-F12, X = D, T and Q, with and without spin-flipped functions. The effect of spin-flip on the basis set error of the total correlation energy is largest for the  $s^2p^4$  configuration, and the importance

Table 3. Basis set errors in the fc-MP2-F12 HF<sub>+</sub> and doubles correlation contributions to ionisation potentials and electron affinities (meV). HF<sub>+</sub> refers to  $E_{\text{HF}} + f_i^a t_a^i + f_i^p t_p^i$ .

Basis	MP2-F12	IP				EA			MAD
		C	N	O	F	C	O	F	
cc-pVDZ-F12	HF <sub>+</sub>	5.9	6.4	3.5	4.2	1.7	1.4	1.1	3.5
	$\tilde{sp}$	10.6	10.8	59.0	2.3	40.1	24.1	-22.5	24.2
	<i>sp</i>	8.4	8.3	40.1	39.4	40.8	52.1	45.7	33.5
	$\tilde{o}$	11.1	12.5	32.3	12.9	39.8	43.0	26.9	25.5
cc-pVTZ-F12	<i>o</i>	8.1	9.2	28.8	24.5	38.5	52.8	46.4	29.8
	HF <sub>+</sub>	1.6	2.0	2.3	2.9	0.7	1.4	1.7	1.8
	$\tilde{sp}$	4.1	3.8	15.1	-1.8	28.9	21.6	4.8	11.4
	<i>sp</i>	3.0	2.7	10.6	7.7	28.8	29.9	21.1	14.8
cc-pVQZ-F12	$\tilde{o}$	4.3	4.3	11.1	2.0	29.1	26.4	13.9	13.0
	<i>o</i>	3.2	3.1	8.9	6.2	28.5	30.5	22.4	14.7
	HF <sub>+</sub>	0.2	0.2	0.5	0.4	0.0	0.0	-0.4	0.2
	$\tilde{sp}$	1.1	1.3	4.8	-0.4	12.9	22.5	9.4	7.5
	<i>sp</i>	0.7	1.0	3.3	2.2	12.9	24.7	14.1	8.4
	$\tilde{o}$	1.2	1.4	4.1	0.3	12.9	23.4	11.0	7.8
	<i>o</i>	0.7	1.1	3.2	2.0	12.7	24.8	14.3	8.4

of spin-flip decreases monotonically when progressing to either the  $s^2p^0$  or the  $s^2p^6$  configuration. Thus the IPs for C, N and O are improved with spin-flip, while F deteriorates. Similarly, the EAs of O and F deteriorate. The mean absolute basis set error over the seven energy differences does not improve upon incorporating spin-flipped geminals into the wave function, but the errors do become more uniform.

Clearly, when computing electron affinities, the capability of the basis to represent the diffuse electron cloud is an issue. The cc-pVXZ-F12 basis sets do not appear to contain sufficiently diffuse functions for the correlation treatment of the anions. Moreover, our investigations show that the aug-cc-pVXZ basis sets do not perform better than the cc-pVXZ-F12 basis sets for the EAs computed here. It should be noted that the HF error has been greatly reduced by the CABS singles correction. The necessity for more diffuse functions is particularly important in F12 methods, which may be seen from the dependence of the basis set errors on the exponent  $\gamma$  of the correlation factor. Figures 1–3 show the  $\gamma$  dependence of the MP2-F12-*sp* and MP2-F12-*o* basis set errors of C, O and F, respectively, together with their cations and anions, using the cc-pVTZ-F12 basis. The MP2-F12-*o* curves for the anions differ strongly from those of the atoms and cations and lie far below the corresponding MP2-F12-*sp* curves (for O and F) at low values of  $\gamma$ . The exaggerated importance of off-diagonal (and diagonal for C) excitations into long-range geminals for the MP2-F12-*o* method is due to the lack of sufficiently diffuse functions in the orbital basis and leads to the undesirable  $\gamma$  dependence. Figures 1–3 also demonstrate that, choosing  $\gamma$

based on the neutral atom, necessarily biases the geminal basis in favor of the atom. The exponent  $\gamma$  is related to the extent of the correlation hole, which is naturally smaller for the cation (larger  $\gamma$ ) with a contracted electron density and larger for the anion (smaller  $\gamma$ ). In the case of the cations, however, this bias does not appear to be severe.

## 4. UCCSD(F12)

### 4.1. Atomisation energies

Benchmark fc-CCSD correlation energies for a subset of 30 of the 106 molecules of our test set have recently been computed using the CCSD(F12) method with the same orbital and auxiliary basis sets as for the fc-MP2 benchmarks [45]. The corresponding benchmark valence CCSD correlation energies for the atoms are reported in Table 1, computed using the UCCSD(F12)-*o* method with semi-canonical ROHF orbitals. We expect that, just as for the MP2 correlation energies, these benchmarks are accurate to 99.95% and we used them to assess the effect of including spin-flipped functions in CCSD(F12) calculations. In Table 4 we present basis set errors for the CCSD(F12)- $\tilde{sp}$ , CCSD(F12)-*sp*, CCSD(F12)- $\tilde{o}$  and CCSD(F12)-*o* methods for atomisation energies using the cc-pVXZ-F12 orbital basis sets. The same auxiliary basis sets and F12 ansatz and approximations were used as for the MP2-F12 calculations discussed in Section 3.1.

We find that the improvements obtained for MP2-F12 by including spin-flipped geminals are



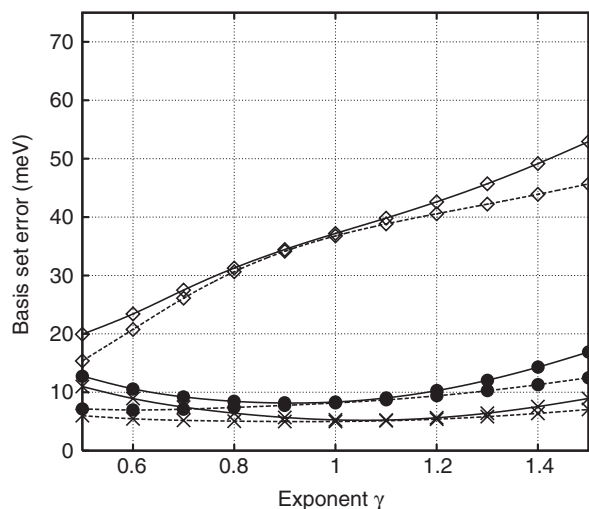


Figure 1. The  $\gamma$  dependence of MP2-F12-*o* (dashed line) and MP2-F12-*sp* (solid line) basis set errors (meV) in the doubles correlation energies for  $C^+$  ( $\times$ ),  $C$  ( $\bullet$ ) and  $C^-$  ( $\diamond$ ), using the cc-pVTZ-F12 orbital basis.

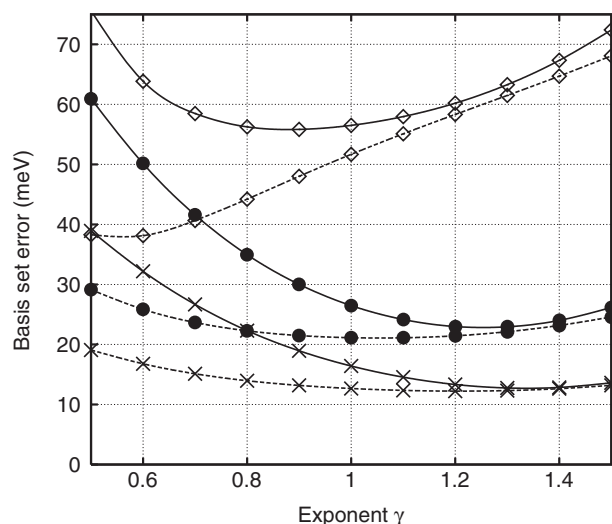


Figure 2. The  $\gamma$  dependence of MP2-F12-*o* (dashed line) and MP2-F12-*sp* (solid line) basis set errors (meV) in the doubles correlation energies for  $O^+$  ( $\times$ ),  $O$  ( $\bullet$ ) and  $O^-$  ( $\diamond$ ), using the cc-pVTZ-F12 orbital basis.

mirrored in the CCSD(F12) results and the discussion for MP2-F12 applies equally well to CCSD(F12). We note, however, that the standard deviation of the basis set error is somewhat larger on average for CCSD than for MP2. One possible source for this additional uncertainty is the incomplete basis for the singles contribution to the correlation energies, which is more important for open-shell systems than closed-shell systems. Unfortunately, the decomposition of the basis set limit fc-CCSD energies into doubles and

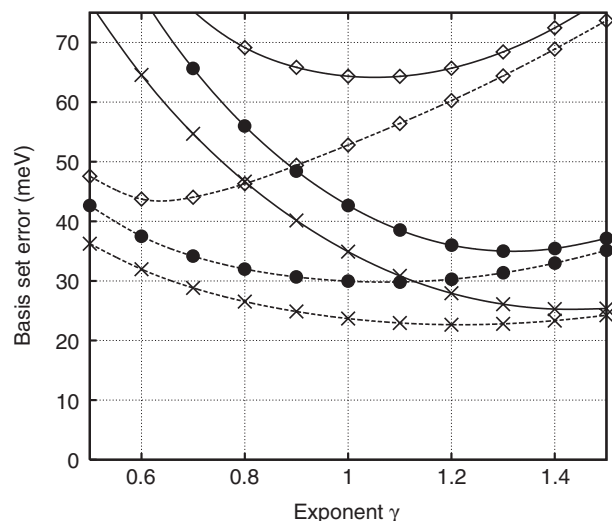


Figure 3. The  $\gamma$  dependence of MP2-F12-*o* (dashed line) and MP2-F12-*sp* (solid line) basis set errors (meV) in the doubles correlation energies for  $F^+$  ( $\times$ ),  $F$  ( $\bullet$ ) and  $F^-$  ( $\diamond$ ), using the cc-pVTZ-F12 orbital basis.

Table 4. Basis set error statistics for the fc-CCSD(F12) correlation contribution to atomisation energies ( $\text{kJ mol}^{-1}$  per valence electron).

CCSD(F12)	cc-pVDZ-F12		cc-pVTZ-F12		cc-pVQZ-F12	
	$\bar{\Delta}$	$\sigma$	$\bar{\Delta}$	$\sigma$	$\bar{\Delta}$	$\sigma$
$\tilde{sp}$	0.37	0.59	0.12	0.14	0.07	0.07
<i>sp</i>	-0.24	0.33	-0.06	0.07	0.02	0.04
$\tilde{o}$	0.23	0.43	0.08	0.07	0.09	0.04
<i>o</i>	0.04	0.37	0.03	0.04	0.07	0.03

singles contributions is not available for the molecules and we are unable to examine these separately. This is possible for our current calculations on atoms and ions and we investigate the singles and doubles contributions separately for IPs and EAs in the next section.

#### 4.2. Ionisation potentials and electron affinities

In Table 5 we present the basis set errors for ionisation potentials and electron affinities for the CCSD(F12)- $\tilde{sp}$ , CCSD(F12)-*sp*, CCSD(F12)- $\tilde{o}$  and CCSD(F12)-*o* methods, computed using fc-UCCSD(F12) with semi-canonical ROHF orbitals. We partition the CCSD(F12) energy into  $HF_+$  and the doubles correlation contribution, where  $HF_+$  is the sum of the HF energy, the singles correlation, and the CABS singles correction. Just as for the atomisation energies, we find that the effect of spin-flip on the CCSD energies is very similar to that of the MP2 energies, discussed in

Table 5. Basis set errors in the CCSD(F12) HF<sub>+</sub> and correlation contributions to ionisation potentials and electron affinities (meV).

Basis	CCSD(F12)	IP				EA			MAD
		C	N	O	F	C	O	F	
cc-pVDZ-F12	HF <sub>+</sub>	6.5	6.5	11.7	4.8	0.9	1.7	-8.2	5.7
	$\tilde{sp}$	13.3	20.6	83.5	16.5	42.3	30.3	-22.1	32.6
	$sp$	7.1	11.5	69.2	59.4	38.6	64.0	51.6	43.1
	$\tilde{o}$	16.3	24.2	51.5	22.8	48.6	44.0	20.3	32.5
	$o$	12.9	17.4	49.6	34.5	44.7	54.2	37.6	35.8
cc-pVTZ-F12	HF <sub>+</sub>	1.7	2.1	2.6	3.2	0.4	3.1	0.6	2.0
	$\tilde{sp}$	3.4	4.5	23.0	4.3	28.7	23.1	4.4	13.1
	$sp$	1.5	2.1	19.0	15.0	27.7	33.0	22.4	17.2
	$\tilde{o}$	3.6	4.7	12.4	6.5	30.0	25.7	13.4	13.8
	$o$	2.9	3.4	10.6	9.4	29.4	28.7	19.8	14.9
cc-pVQZ-F12	HF <sub>+</sub>	0.3	0.3	0.9	0.5	-0.2	0.9	-1.0	0.6
	$\tilde{sp}$	0.8	1.5	8.8	1.9	12.8	22.0	8.1	8.0
	$sp$	0.2	0.7	7.4	5.0	12.5	24.6	13.6	9.1
	$\tilde{o}$	0.6	1.3	3.1	0.5	13.0	20.4	8.6	6.8
	$o$	0.4	0.9	2.6	1.6	12.8	21.3	10.7	7.2

Section 3.2. Comparing the HF<sub>+</sub> and doubles components of the CCSD energies with the MP2 equivalents, we find that the singles contributions converge at similar rates. The basis set errors from the doubles are larger on average for CCSD than MP2 for the cc-pVDZ-F12 basis, but are similar to MP2 for the cc-pVQZ-F12 basis. This is consistent with the effect of the singles basis set incompleteness on the doubles, through the coupling which is present in CCSD but not in MP2.

## 5. Conclusion

For closed-shell calculations, the geminal basis functions are chosen as  $f(r_{12})|ij\rangle$ , where  $ij$  are spin-orbitals, occupied in the HF reference. These are sufficient to exactly satisfy the  $s$ - and  $p$ -wave MP2 coalescence conditions and thus accelerate the basis set convergence from  $X^{-3}$  to  $X^{-7}$ . As first noted by Bokhan *et al.*, spin-flipped geminal functions are required to achieve this for open-shell calculations. In this work, we have defined a hierarchy of open-shell F12 methods with and without spin-flipped functions, which we have used to investigate the numerical importance of the spin-flipped functions for atomisation energies, ionisation potentials and electron affinities at the MP2 and CCSD levels of theory. In particular, we have solved the issue of redundancy or near linear dependency in the normal and spin-flipped basis by using contracted geminals with contraction coefficients determined from the coalescence conditions. Furthermore, we have used an analysis of the spin-orbital MP2 coalescence conditions to establish

the correct choice of fixed amplitudes when no spin-flipped functions are used in the calculation. All of the methods we present are orbital invariant, size extensive and size consistent when combined with UHF references and reduce to either the  $sp$  or original orbital-invariant ansatz for the closed-shell case.

Our calculations on a set of 106 molecules of H, C, N, O and F convincingly demonstrate that spin-flipped functions are important for atomisation energies, where a balanced treatment of open- and closed-shell species is necessary. The basis set errors are approximately halved by including the spin-flipped functions for both MP2 and CCSD calculations. Furthermore, we find that our contracted geminal approach is superior to optimising the amplitudes for both the normal and spin-flipped geminals, since the number of variational parameters is then proportional to the number of correlated electron pairs. For ionisation potentials and electron affinities, we find that including spin-flipped geminals improves the consistency of the energies, but that the accuracy is limited due to difficulties in selecting an appropriate exponent for the correlation factor and the need for diffuse functions for electron affinities.

In conclusion, we find that spin-flipped geminals are very important for open-shell F12 calculations and recommend that they be used. For the fixed-amplitude approach, the  $sp$  ansatz should be used as proposed by Bokhan *et al.* [35], and if the F12 amplitudes are to be optimised, our contracted geminal approach should be used. If the MP2 method is desired and computational cost is an issue, then our  $\tilde{sp}$  method is recommended. For coupled-cluster calculations, the additional cost of

incorporating them in either the *sp* or optimised amplitude method is only at the level of the F12 integrals and is thus minimal.

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### References

- [1] W. Kutzelnigg, *Theor. Chim. Acta* **68**, 445 (1985).
- [2] W. Klopper and W. Kutzelnigg, *Chem. Phys. Lett.* **134**, 17 (1987).
- [3] W. Klopper, F.R. Manby, S. Ten-no, and E.F. Valeev, *Int. Rev. Phys. Chem.* **25**, 427 (2006).
- [4] W. Klopper and C.C.M. Samson, *J. Chem. Phys.* **116**, 6397 (2002).
- [5] E.F. Valeev, *Chem. Phys. Lett.* **395**, 190 (2004).
- [6] S. Ten-no, *Chem. Phys. Lett.* **398**, 56 (2004).
- [7] S. Ten-no, *Chem. Phys. Lett.* **447**, 175 (2007).
- [8] D.P. Tew, W. Klopper, C. Neiss, and C. Hättig, *Phys. Chem. Chem. Phys.* **9**, 1921 (2007).
- [9] D.P. Tew, W. Klopper, C. Neiss, and C. Hättig, *Phys. Chem. Chem. Phys.* **10**, 6325 (2008).
- [10] A. Köhn, *J. Chem. Phys.* **130**, 131101 (2009).
- [11] T. Shiozaki, M. Kamiya, S. Hirata, and E.F. Valeev, *J. Chem. Phys.* **130**, 054101 (2009).
- [12] F.R. Manby, *J. Chem. Phys.* **119**, 4607 (2003).
- [13] S. Ten-no and F.R. Manby, *J. Chem. Phys.* **119**, 5358 (2003).
- [14] H.-J. Werner, T.B. Adler, and F.R. Manby, *J. Chem. Phys.* **126**, 164102 (2007).
- [15] J. Noga, S. Kedžuch, and J. Šimunek, *J. Chem. Phys.* **127**, 034106 (2007).
- [16] F.R. Manby, H.-J. Werner, T.B. Adler, and A.J. May, *J. Chem. Phys.* **124**, 094103 (2006).
- [17] H.-J. Werner and F.R. Manby, *J. Chem. Phys.* **124**, 054114 (2006).
- [18] H.-J. Werner, *J. Chem. Phys.* **129**, 101103 (2008).
- [19] T.B. Adler, H.-J. Werner, and F.R. Manby, *J. Chem. Phys.* **130**, 054106 (2009).
- [20] K.A. Peterson, T.B. Adler, and H.-J. Werner, *J. Chem. Phys.* **128**, 084102 (2008).
- [21] K.E. Yousaf and K.A. Peterson, *J. Chem. Phys.* **129**, 184108 (2008).
- [22] K.E. Yousaf and K.A. Peterson, *Chem. Phys. Lett.* **476**, 303 (2009).
- [23] S. Ten-no, *J. Chem. Phys.* **121**, 117 (2004).
- [24] T. Kato, *Commun. Pure Appl. Math.* **10**, 151 (1957).
- [25] R.T. Pack and W. Byers Brown, *J. Chem. Phys.* **45**, 556 (1966).
- [26] D.P. Tew and W. Klopper, *J. Chem. Phys.* **125**, 094302 (2006).
- [27] G. Knizia and H.-J. Werner, *J. Chem. Phys.* **128**, 154103 (2008).

- [28] D.P. Tew, W. Klopper, and C. Hättig, *Chem. Phys. Lett.* **452**, 326 (2008).
- [29] T.B. Adler, G. Knizia, and H.-J. Werner, *J. Chem. Phys.* **127**, 221106 (2007).
- [30] G. Knizia, T.B. Adler, and H.-J. Werner, *J. Chem. Phys.* **130**, 054104 (2009).
- [31] M. Torheyden and E.F. Valeev, *Phys. Chem. Chem. Phys.* **10**, 3410 (2008).
- [32] D. Bokhan, S. Ten-no, and J. Noga, *Phys. Chem. Chem. Phys.* **10**, 3320 (2008).
- [33] A. Köhn, *J. Chem. Phys.* **130**, 104104 (2009).
- [34] M. Hanauer and A. Köhn, *J. Chem. Phys.* **131**, 124118 (2009).
- [35] D. Bokhan, S. Bernadotte, and S. Ten-no, *J. Chem. Phys.* **131**, 084105 (2009).
- [36] W. Klopper, *Chem. Phys. Lett.* **186**, 583 (1991).
- [37] W.M.C. Foulkes, L. Mitas, R.J. Needs, and G. Rajagopal, *Rev. Mod. Phys.* **73**, 33 (2001).
- [38] J. Noga, W. Kutzelnigg, and W. Klopper, *Chem. Phys. Lett.* **199**, 497 (1992).
- [39] D.P. Tew, *J. Chem. Phys.* **129**, 014104 (2008).
- [40] F.A. Bischoff, S. Wolfsegger, D.P. Tew, and W. Klopper, *Mol. Phys.* **107**, 963 (2009).
- [41] C. Hättig, *Phys. Chem. Chem. Phys.* **7**, 59 (2005).
- [42] F. Weigend, *J. Comp. Chem.* **29**, 167 (2008).
- [43] D.P. Tew and W. Klopper, *J. Chem. Phys.* **123**, 074101 (2005).
- [44] J. Noga and J. Šimunek, *Chem. Phys.* **356**, 1 (2009).
- [45] A. Köhn and D.P. Tew to be published.

### Appendix A: UMP2 coalescence conditions

The exact solution to the Born–Oppenheimer, non-relativistic Schrödinger equation may always be expressed as a sum of products of spatial and spin eigenfunctions. Correspondingly, Kato’s proof of the cusp condition at electron coalescence [24] and the subsequent analysis of Pack and Byers Brown [25] were concerned with spatial eigenfunctions only. For approximate wave functions that are not eigenfunctions of spin, such as UMP2, the analysis leading to the coalescence conditions must be repeated in terms of spin-orbitals. Fortunately, this is relatively straightforward, at least at the level of UMP2, and follows the analysis in Refs. [32,39] for RHF references rather closely.

Consider canonical or semi-canonical orbitals, which are exact eigenfunctions of the zeroth-order operator. The equation for the first-order wave function separates into equations for each pair,

$$\hat{V}_1 \hat{V}_2 (\hat{f}_1^0 + \hat{f}_2^0 - \varepsilon_i - \varepsilon_j) |u_{ij}\rangle + \hat{V}_1 \hat{V}_2 \frac{1}{r_{12}} |ij\rangle = 0. \quad (\text{A1})$$

Here,  $|u_{ij}\rangle = (1 - \hat{P}_{12})u_{ij}/\sqrt{2}$  and  $|ij\rangle = (1 - \hat{P}_{12})\phi_i\phi_j/\sqrt{2}$ , where  $\phi_i$  and  $\phi_j$  are occupied spin-orbitals and  $\hat{P}_{12}$  is the permutation operator.  $\hat{V}_1\hat{V}_2$  is the strong orthogonality projector  $(1 - \hat{O}_1)(1 - \hat{O}_2)$ , where  $\hat{O}$  projects onto the space of occupied spin-orbitals. For the ROHF case,  $\hat{f}^0 = \hat{f} - \hat{f}^1$ , where  $\hat{f}^1 = \hat{O}\hat{f}\hat{V} + \hat{V}\hat{f}\hat{O}$  and the  $\hat{f}^1$  terms drop out since they do not connect the space  $V_1\hat{V}_2$  with  $|u_{ij}\rangle$ . For the UHF case,  $\hat{f}^0$  is the usual Fock operator ( $\hat{f}^1 = 0$ ). The presence of  $\hat{f}^1$  for

ROHF leads to an equation for single excitations in addition to Equation (A1), but this does not affect the nature of the first-order wave function at electron coalescence and we do not consider it further.

The analysis of Pack and Byers Brown proceeds by transforming to centre of mass,  $\mathbf{s} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ , and relative coordinates,  $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$ , and equating powers of  $r_{12}$  as far as possible. To manipulate Equation (A1) into a form amenable to such an analysis, we follow Ref. [39] and introduce a pair function  $w_{ij}$  that has no orthogonality constraints, such that  $u_{ij} = \hat{V}_1 \hat{V}_2 w_{ij}$ . For UHF,  $[\hat{f}, \hat{V}] = 0$  and we may drop the strong orthogonality projector from the equation. For ROHF,  $[\hat{f}, \hat{V}] = \hat{O} \hat{f} \hat{V} - \hat{V} \hat{f} \hat{O}$ . Finally, we remove spin by left projecting onto the spin function  $\alpha\alpha$ ,  $\beta\beta$  or  $\alpha\beta$ . In place of Equation (A1), we now have

$$(\hat{f}_1 + \hat{f}_2 - \varepsilon_i - \varepsilon_j) \omega_{ij} + \frac{1}{r_{12}} \Theta_{ij} = 0, \quad (\text{A2})$$

where  $\hat{f}$  is replaced by  $\hat{f} - \hat{f} \hat{O}$  for ROHF. Note that, for same-spin pairs,  $\hat{P}_{12} \Theta_{ij} = -\Theta_{ij}$  and  $\hat{P}_{12} \omega_{ij} = -\omega_{ij}$ , but for spin-opposite pairs,  $\Theta_{ij}$  and  $\omega_{ij}$  are just the spatial components of  $\phi_i \phi_j$  and  $w_{ij}$ , respectively. Expanding the Fock operator  $\hat{f}$  in powers of  $r_{12}$ , we obtain

$$\hat{f}_1 + \hat{f}_2 = -\nabla_{r_{12}}^2 + \mathcal{O}(r_{12}^0) Y_{00} + \mathcal{O}(r_{12}^1), \quad (\text{A3})$$

where  $Y_{lm}$  are the surface harmonics for the angular dependence of  $\mathbf{r}_{12}$  in spherical coordinates. This differs from the closed-shell case in that the  $\mathcal{O}(r_{12}^1)$  terms, which are angle dependent, do not cancel. To obtain this, we have used

$$\frac{1}{r_{i1}} = \frac{1}{r_{is}} + \frac{r_{12}}{r_{is}^2} \cos \theta_i + \mathcal{O}(r_{12}^2), \quad (\text{A4})$$

$$\frac{1}{r_{i2}} = \frac{1}{r_{is}} - \frac{r_{12}}{r_{is}^2} \cos \theta_i + \mathcal{O}(r_{12}^2), \quad (\text{A5})$$

where  $r_{is}$  is the distance between  $\mathbf{s}$  and the centre  $\mathbf{r}_i$  and  $\cos \theta_i$  is the cosine between the vectors  $\mathbf{r}_{is}$  and  $\mathbf{r}_{12}$ . For ROHF, the presence of  $\hat{f} \hat{O}$  does not change Equation (A3). The spatial components of the zeroth- and first-order pair functions are now expanded in radial and angular functions of  $\mathbf{r}_{12}$ , with a Taylor expansion for the radial functions, whose coefficients depend on  $\mathbf{s}$

$$\Theta_{ij}(\mathbf{r}_{12}, \mathbf{s}) = \sum_{l=0}^{\infty} r_{12}^l \left\{ \sum_{k=0}^v \sum_{m=-l}^l r_{12}^k f_{lm}^k(\mathbf{s}) Y_{lm} + \mathcal{O}(r_{12}^{v+1}) \right\}, \quad (\text{A6})$$

$$\omega_{ij}(\mathbf{r}_{12}, \mathbf{s}) = \sum_{l=0}^{\infty} r_{12}^l \left\{ \sum_{k=0}^v \sum_{m=-l}^l r_{12}^k g_{lm}^k(\mathbf{s}) Y_{lm} + \mathcal{O}(r_{12}^{v+1}) \right\}. \quad (\text{A7})$$

Note that, for same-spin pairs, only terms with odd  $l$  survive, but for  $\alpha\beta$  pairs, all  $l$  are present. Following Pack and Byers Brown, Equation (A2) becomes

$$\sum_{k=0}^v (k(k+2l+1) g_{lm}^k - f_{lm}^{k-1} + \mathcal{O}(r_{12}^0) g_{lm}^{k-2}) r_{12}^{k-2} = 0. \quad (\text{A8})$$

Equating terms in  $r_{12}^{-1}$  gives the familiar  $s$ - and  $p$ -wave coalescence conditions ( $l=0$  and 1, respectively),

$$g_{lm}^1 = \frac{1}{2(l+1)} f_{lm}^0. \quad (\text{A9})$$

For the same-spin pairs, the  $p$ -wave conditions apply. This result is of course well known. For spin-opposite pairs, both the  $s$ - and  $p$ -wave conditions apply, so that

$$\omega_{ij} = g_{00}^0 + \frac{1}{2} r_{12} f_{00}^0 + \mathcal{O}(r_{12}^2) + r_{12} \sum_{m=-1}^1 \left( g_{1m}^0 + \frac{1}{4} r_{12} f_{1m}^0 + \mathcal{O}(r_{12}^2) \right) Y_{1m}. \quad (\text{A10})$$

Since the  $Y_{00}$  terms are symmetric with respect to the operator  $\hat{P}_{12}$ , we may identify

$$\varphi_i \varphi_j(0, \mathbf{s}) = (\varphi_i \varphi_j(0, \mathbf{s}) + \varphi_j \varphi_i(0, \mathbf{s}))/2 = f_{00}^0(\mathbf{s}), \quad (\text{A11})$$

where  $\varphi_i$  is the spatial component of  $\phi_i$ . Similarly, since the  $Y_{1m}$  terms are antisymmetric, we may identify

$$(\varphi_i \varphi_j - \varphi_j \varphi_i)/2 = r_{12} \sum_{m=-1}^1 f_{1m}^0 Y_{1m} + \mathcal{O}(r_{12}^2). \quad (\text{A12})$$

For the same-spin (triplet) pairs, the  $p$ -wave coalescence conditions are satisfied if

$$|u_{ij}\rangle = \frac{1}{4} \hat{V}_1 \hat{V}_2 r_{12} |ij\rangle. \quad (\text{A13})$$

For the  $\alpha\beta$  pairs, the  $s$ -wave cusp conditions are satisfied if

$$|u_{ij}\rangle = \frac{1}{2} \hat{V}_1 \hat{V}_2 r_{12} |ij\rangle. \quad (\text{A14})$$

Both the  $s$ - and  $p$ -wave coalescence conditions are met for the  $\alpha\beta$  pairs if

$$|u_{ij}\rangle = \frac{3}{8} \hat{V}_1 \hat{V}_2 r_{12} |ij\rangle + \frac{1}{8} \hat{V}_1 \hat{V}_2 r_{12} |\bar{j}\bar{i}\rangle, \quad (\text{A15})$$

where the second term is a spin-flipped determinant, for example, with the  $\alpha$  spin-orbital  $\phi_{\bar{j}} = \varphi_j \alpha$ , where  $\varphi_j$  is the spatial component of the  $\beta$  spin-orbital  $\phi_j$ . From Equation (A11) it is clear that any linear combination of  $\varphi_i(\mathbf{r}_1) \varphi_j(\mathbf{r}_2)$  and  $\varphi_j(\mathbf{r}_1) \varphi_i(\mathbf{r}_2)$  can be used to satisfy the  $s$ -wave cusp and Equations (A14) and (A15) are not unique solutions. However, the above choice for Equation (A15) corresponds to the correct formula for the case of identical  $\alpha$  and  $\beta$  spatial orbitals, where spin and space symmetry are properly coupled. The choice in Equation (A14) does not require any spin-flipped functions.