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A diagonal orbital-invariant explicitly-correlated coupled-cluster method

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Abstract

We present an orbital-invariant explicitly-correlated coupled-cluster method where we determine the contribution from the geminal pair functions by the known first-order electron coalescence conditions. This method is free from geminal basis set superposition errors and yields quintuple-ζ quality correlation energies using triple-ζ orbital basis sets.
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1. Introduction

The past five years have seen a rapid development in R12 explicitly-correlated methods [1–5], which are designed to overcome the painfully slow basis set convergence of standard orbital based computational approaches [6]. At the level of second order Møller–Plesset perturbation theory (MP2), near basis set limit correlation energies may now be obtained using orbital basis sets of only triple-ζ quality [7]. Similarly, the recently developed explicitly-correlated coupled-cluster method CCSD(F12) yields correlation energies equivalent to quintuple-ζ quality conventional CCSD calculation, with a triple-ζ quality orbital basis [8]. Since each CCSD(F12) iteration requires approximately three times as many floating point operations as that of an orbital-only calculation, the cost to accuracy ratio is favourable and the F12 methods are now an attractive alternative to conventional approaches for many thermochemical applications. However, a number of issues remain to be addressed. One such issue is that of geminal basis set superposition error (BSSE), which has been observed to be critical for MP2 calculations of weak interactions [9]. Geminal BSSE can be removed by excluding inter-fragment F12 excitations, which may be achieved through using the original diagonal (non-invariant) ansatz [1]. Combining the diagonal ansatz with localised orbitals gives much improved predictions of Van der Waals (VdW) binding energies [9] and also for reaction enthalpies [10]. For methods using canonical Hartree–Fock orbitals, however, the orbital variance of the diagonal approach leads to a violation of size consistency [11]. Recently, Ten-no has recommended a further simplification that reintroduces orbital invariance by constraining the coefficients of the F12 geminal basis functions to have the same value, which is chosen such that they obey the coalescence conditions [12,13]. For MP2-F12, Ten-no shows that, although there is a stronger dependence on the exponent of the geminal basis functions, the loss in accuracy due to the reduced variational flexibility is small. Moreover, the diagonal, fixed-amplitude MP2-F12 method scales as n^5 with the size of the one-particle basis, compared to n^8 for the original orbital-invariant method where all F12 excitation coefficients are optimised. In this Letter we extend this approach to the coupled-cluster level. We assess the diagonal, fixed-amplitude method using the same set of 23 molecules and 15 reaction enthalpies as we used in Ref. [8] (Sections 3 and 4) and also investigate its performance for weak VdW interaction energies (Section 5).

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2. Theory

The CCSD-F12 wave function, $\exp(\widehat{S})|\mathrm{HF}\rangle$, is defined by the singles, doubles and F12 doubles excitation operators, $\widehat{S} = \widehat{T}_1 + \widehat{T}_2 + \widehat{T}_{2'}$.

$$\widehat{T}_1 = \sum_{ai} t_i^a E_{ai}, \tag{1}$$

$$\widehat{T}_2 = \frac{1}{4}\sum_{aibj} t_{ij}^{ab} E_{bj}E_{ai}, \tag{2}$$

$$\widehat{T}_{2'} = \frac{1}{4}\sum_{kilj} c_{ij}^{kl} \sum_{\alpha\beta} w_{kl}^{\alpha\beta} E_{\beta j}E_{\alpha i}. \tag{3}$$

The indices $i, j, \cdots$ indicate occupied orbitals and $a, b, \cdots$ refer to virtual orbitals and a formally complete one-electron basis has been introduced to express the F12 double excitations in the occupation vector formalism: $\{\phi\} = \{\phi_i\} \oplus \{\phi_\alpha\} = \{\phi_i\} \oplus \{\phi_a\} \oplus \{\phi_{\alpha_\perp}\}$. The spin-free excitation operators $E_{\alpha i}$ have the usual definitions [14] and

$$w_{ij}^{\alpha\beta} = \langle \phi_\alpha \phi_\beta | \widehat{Q}_{12} \sum_{x=1}^{6} c_x \exp(-\gamma_x r_{12}^2) | \phi_i \phi_j \rangle. \tag{4}$$

The exponents γ_x and contraction coefficients c_x are such that the linear combination of Gaussians reproduces a Slater function $\exp(-\gamma r_{12})$ [4,15,16]. It is now well established that Ansatz 2 is superior to Ansatz 1, particularly for the F12 geminal functions where the coupling with the conventional double excitations is significant. Thus [3],

$$\widehat{Q}_{12} = (1 - \widehat{O}_1)(1 - \widehat{O}_2)(1 - \widehat{V}_1\widehat{V}_2), \tag{5}$$

$$\widehat{O}_1 = \sum_i |\phi_i(1)\rangle\langle\phi_i(1)|, \tag{6}$$

$$\widehat{V}_1 = \sum_a |\phi_a(1)\rangle\langle\phi_a(1)|. \tag{7}$$

The CCSD-F12 energy may be obtained by variationally optimising the Lagrangian

$$E = \langle \mathrm{HF}|\widehat{H}^S|\mathrm{HF}\rangle + \bar{\mathbf{t}}_1\langle\mu_1|\widehat{H}^S|\mathrm{HF}\rangle + \bar{\mathbf{t}}_2\langle\mu_2|\widehat{H}^S|\mathrm{HF}\rangle + \bar{\mathbf{t}}_{2'}\langle\mu_{2'}|\widehat{H}^S|\mathrm{HF}\rangle, \tag{8}$$

with respect to the amplitudes $\mathbf{t}_1 = \{t_i^a\}$, $\mathbf{t}_2 = \{t_{ij}^{ab}\}$ and $\mathbf{t}_{2'} = \{c_{ij}^{kl}\}$ and the multipliers $\bar{\mathbf{t}}_1$, $\bar{\mathbf{t}}_2$ and $\bar{\mathbf{t}}_{2'}$. $\widehat{H}^S = \exp(-\widehat{S})\widehat{H}\exp(\widehat{S})$. In the CCSD(F12) approach, the commutator contributions to the F12 vector function that are second order or higher in the fluctuation potential are neglected [17]. Explicit formulae for the CCSD-R12 method are presented in Refs. [18,19], and the extension to include auxiliary basis functions for the resolution of the identity (RI) and non-linear correlation factors (F12) are found in Refs. [8,2,20,21]. Here, instead of optimising the F12 coefficients $\mathbf{t}_{2'}$ by energy considerations, we follow Ten-no and fix them according to the coalescence conditions for the first-order pair functions:

$$\text{singlet} \qquad \psi^{(1)} = \psi^{(1)}_{r_{12}=0} + \frac{1}{2}\widehat{Q}_{12}r_{12}\psi_{\mathrm{HF}} + \mathcal{O}(r_{12}^2), \tag{9}$$

$$\text{triplet} \qquad \psi^{(1)} = \mathbf{r}_{12}\cdot\frac{\partial\psi^{(1)}}{\partial\mathbf{r}_{12}}|_{r_{12}=0} + \frac{1}{4}\widehat{Q}_{12}r_{12}\psi_{\mathrm{HF}} + \mathcal{O}(r_{12}^3). \tag{10}$$

All off-diagonal F12 excitation coefficients c_{ij}^{kl}, $ij \neq kl$ are zero. To infinite order in perturbation theory the coalescence conditions are

$$\text{singlet} \qquad \psi = \psi_{r_{12}=0}(1 + \frac{1}{2}r_{12}) + \mathcal{O}(r_{12}^2), \tag{11}$$

$$\text{triplet} \qquad \psi = \mathbf{r}_{12}\cdot\frac{\partial\psi}{\partial\mathbf{r}_{12}}|_{r_{12}=0}(1 + \frac{1}{4}r_{12}) + \mathcal{O}(r_{12}^3). \tag{12}$$

For CCSD(F12) calculations, fixing the F12 amplitudes so that $c_{ij}^{ij} + c_{ji}^{ij} = \frac{1}{2\gamma}$ and $c_{ij}^{ij} - c_{ji}^{ij} = \frac{1}{4\gamma}$ is a good approximation if $\psi_{\mathrm{CC}} \approx \psi_{\mathrm{HF}}$. The energy is given by the value of the Lagrangian at the point where it is stationary with respect to $\bar{\mathbf{t}}_2$ and $\bar{\mathbf{t}}_1$, that is, having optimised the singles and doubles amplitudes in the presence of the F12 contributions,

$$E = \langle \mathrm{HF}|\widehat{H}^S|\mathrm{HF}\rangle + \bar{\mathbf{t}}_{2'}\langle\mu_{2'}|\widehat{H}^S|\mathrm{HF}\rangle. \tag{13}$$

Determining the Lagrange multipliers $\bar{\mathbf{t}}_{2'}$ by solving the usual eigenvalue problem [14] gives different values for each excitation and breaks orbital invariance. At the MP2 level of theory, Ten-no chooses $\bar{\mathbf{t}}_{2'} = \mathbf{t}_{2'}$, since this is true for the optimised amplitudes. However, we note that, in the limit of infinite orbital basis, the F12 contributions to the energy disappear and the second term vanishes. The choice of $\bar{\mathbf{t}}_{2'}$ only effects the manner of convergence to this limit. We therefore consider two choices of multipliers. The first is the coupled-cluster analogue of Ten-no's MP2-F12 method where $\bar{\mathbf{t}}_{2'} = \mathbf{t}_{2'}$. Although the optimised coupled-cluster amplitudes and multipliers are not identical, they are approximately equal if the difference between the MP2 and CCSD wavefunctions is relatively small. We will refer to this method as CCSD(F12)-*c*. Note that the F12 vector function need only be evaluated once. Moreover, if one precomputes appropriate intermediates (the disk storage scales as $\mathcal{O}(ON^3)$), the n^6 scaling operations, required for the F12 contributions to the CCSD(F12) conventional amplitude equations, may be removed from the coupled-cluster iterations. The second choice of multipliers is $\bar{\mathbf{t}}_{2'} = 0$, which is even cheaper and is equivalent to solving the coupled-cluster equations without the F12 projection. This may be justified by the same arguments that lead us to exclude triples and higher projections in the CCSD equations. Since the inclusion of the F12 contributions in this way are inconsistent from the point of view of a perturbative analysis, we will refer to this method as CCSD-F12-0. Both of these methods are orbital-invariant and size-extensive. In addition, we will present results using the method CCSD(F12)-c_{ij}^{ij} where the diagonal amplitudes c_{ij}^{ij} are optimised. This method is orbital variant and is size-consistent when local orbitals are used. In this work we use cannonical orbitals exclusively. Finally, we will refer to the method where all amplitudes c_{ij}^{kl} are optimised as CCSD(F12)-c_{ij}^{kl}. The perturbative triples correction for CCSD(T)(F12) is computed using the conventional singles and doubles amplitudes that result from

the CCSD(F12) iterations in the usual way [22], with no additional F12 contribution.

3. Molecular correlation energies

In Fig. 1 we plot the basis set convergence of the frozen-core (fc) CCSD(F12)-c_{ij}^{kl}, -c_{ij}^{ij}, -c and F12-0 correlation energies of H_2O as a function of the geminal exponent γ. For all our computations we use augmented correlation-consistent basis sets [23,24], since previous investigations have revealed that diffuse polarisation functions are important in F12 calculations [16]. As the complementary auxiliary basis set (CABS) for the approximate RI, we used a 21s14p8d7f5g4h3i2k basis constructed from the well tempered basis sets [25,26] as described in Ref. [9]. At the MP2 level of theory, use of the Hylleraas functional ensures that the energy is variational with respect to the F12 amplitudes, and also with respect to γ. For CCSD, however, the energy lies at a saddle point on the Lagrangian, due to the higher order terms. Near variational behaviour of the energy with repect to γ and the F12 amplitudes is expected if the MP2 contributions are dominant. From Fig. 1 we observe the expected energy ordering $c_{ij}^{kl} < c_{ij}^{ij} < c$, following the degree of variational flexibility, which we interpret as an indication that our approximation $\bar{\mathbf{t}}_{2'} = \mathbf{t}_{2'}$ in the -c method is sensible. The -c_{ij}^{ij} correlation energies are essentially the same quality as the -c_{ij}^{kl} values, with the same weak dependence on γ. Diagonal F12 excitations clearly dominate, which is expected because the primary function of the geminal basis is to describe the Coulomb hole for short r_{12} distances. It is remarkable that the fc-CCSD(F12)-c_{ij}^{ij}, -c and F12-0 curves cross at approximately the same γ value. At this γ the norm of the vector function is close to zero and the optimised diagonal amplitudes coincide with those predicted by the coalescence conditions. This underlines the ability of the exponential correlation factor to fit both the cusp and the general shape of the Coulomb hole for the energetically dominant electron pairs. However, the γ dependence of the fc-CCSD(F12)-c method is stronger than when the F12 amplitudes are optimised because of the lack of flexibility for this purpose. The absence of the Lagrangian term in the fc-CCSD-F12-0 leads to an error linear in the F12 amplitudes and a strongly non-variational γ dependence. We exclude this method from further discussion in this work.

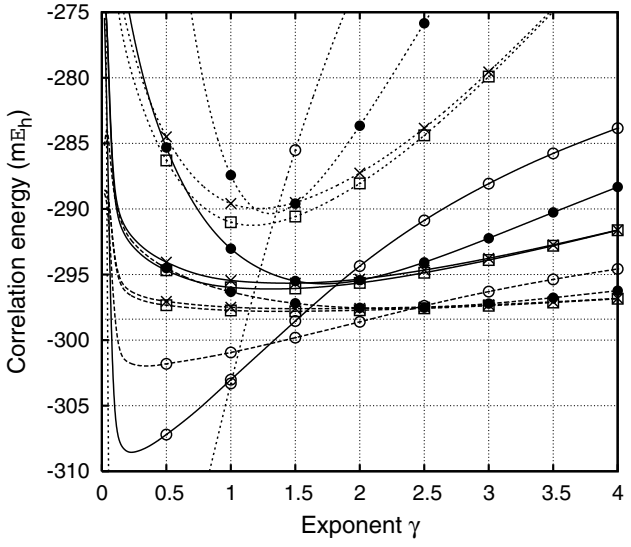


Fig. 1. The fc-CCSD(F12) correlation energy of H_2O, as a function of γ, using c_{ij}^{kl} (□), c_{ij}^{ij} (×), c (●) and 0 (◯) with the aug-cc-pVXZ orbital basis sets, X = D (dotted line), T (solid line) and Q (dashed line).

We have proceeded to assess the performance of the fc-CCSD(T)(F12)-c_{ij}^{ij} and -c methods over a test set of 23 closed-shell molecules of H, C, N, O, S and Cl, developed by Pflüger and Werner [27]. As an independent estimate of the basis set limit we use the two-point extrapolation formula of Helgaker [28]. For the CCSD contribution we extrapolate using the aug-cc-pV5Z and aug-cc-pV6Z orbital basis sets, except for CH_3CHO where values computed in Ref. [29], without augmentation, are used. The reference (T) corrections are extrapolated from aug-cc-pVQZ and aug-cc-pV5Z values. For the S and Cl atoms we use the aug-cc-pV(X+d)Z sets in all our calculations. We compare the fc-CCSD(T)(F12)-c_{ij}^{kl} and -c methods for the aug-cc-pVTZ orbital basis set and present results for $\gamma = 1.0$, $\gamma = 1.3$ and $\gamma = 1.8$. Our fc-CCSD(T)(F12)-c_{ij}^{kl} values differ slightly from those of Ref. [8] because an error has been removed from the program; an erratum is being prepared. The uncontracted aug-cc-pV5Z orbital basis is used as CABS. The mean absolute correlation energy error (mae), the standard deviation (σ_N) and maximum absolute error (max), per correlated electron, are given in Table 1. To assess the sensitivity of our statistical measures to the estimate of the basis set limit, we compared statistics using Q5 and 56 extrapolations as the limit for the fc-CCSD correlation energies. We find that the mae values vary by less than 0.04 mE_h.

As we reported in Ref. [8], the fc-CCSD(F12)-c_{ij}^{kl} ($\gamma = 1.3$) method with an aug-cc-pVTZ basis yields correlation energies of superior quality to orbital-only calculations with an aug-cc-pV5Z basis. In accordance with the discussion for H_2O, the fc-CCSD(F12)-c method has a slightly larger basis set error than -c_{ij}^{kl}. Increasing γ to 1.8 does not significantly improve the performance of this method for the systems

Table 1
Basis set errors of fc-CCSD and (T) correlation energies, per correlated electron (mE_h)

Basis	CCSD			(T)		
	mae	σ_N	max	mae	σ_N	max
aug-cc-pVTZ	2.77	0.82	3.91	0.19	0.07	0.33
aug-cc-pVQZ	1.11	0.35	1.62	0.08	0.03	0.15
aug-cc-pV5Z	0.55	0.18	0.84	0.04	0.02	0.08
F12-c_{ij}^{kl} ($\gamma = 1.0$)	0.29	0.13	0.68	0.24	0.09	0.39
F12-c_{ij}^{kl} ($\gamma = 1.3$)	0.28	0.13	0.67	0.23	0.09	0.39
F12-c ($\gamma = 1.0$)	0.59	0.32	1.00	0.24	0.13	0.41
F12-c ($\gamma = 1.3$)	0.40	0.15	0.77	0.23	0.09	0.39
F12-c ($\gamma = 1.8$)	0.38	0.17	0.91	0.23	0.08	0.38

tested. Since the (T) corrections for the CCSD(T)(F12) methods do not contain any F12 contributions, they are slightly worse than the aug-cc-pVTZ orbital-only value and the basis set error in (T) is the same order of magnitude as the remaining error in the CCSD contribution. However, the accuracy of the fc-CCSD(T)(F12)-c_{ij}^{kl}/aug-cc-pVTZ method remains equivalent to fc-CCSD(T)/aug-cc-pV5Z for total correlation energies and the -c method is almost as good.

4. Reaction enthalpies

To assess the performance of the diagonal, orbital-invariant fc-CCSD(T)(F12)-c method for thermochemistry we use Pflüger and Werner's [27] test set of 15 reactions involving the 23 molecules of Section 3. In Tables 2 and 3 we present basis set errors for the CCSD and (T) correlation contributions to the reaction enthalpies. We report the results of fc-CCSD(T)(F12)-c_{ij}^{kl} and -c calculations using $\gamma = 1.0$, $\gamma = 1.3$ and $\gamma = 1.8$. For reaction 12, the CCSD reference is computed from 56 extrapolation using the values for C_2H_2, H_2O and CH_3CHO in Ref. [29]. The maes are collected in Table 4 and the corresponding fc-CCSD(T)/aug-cc-pVXZ values are also given for X = T, Q and 5. The sensitivity of the CCSD values to the accuracy of the

Table 4
The mean absolute basis set errors of the fc-CCSD, (T) and fc-CCSD(T) correlation contribution to reaction energies (kJ mol^{-1})

Basis	CCSD	(T)	CCSD(T)
aug-cc-pVTZ	4.04	0.38	3.94
aug-cc-pVQZ	1.64	0.18	1.62
aug-cc-pV5Z	0.93	0.09	0.94
F12-c_{ij}^{kl} ($\gamma = 1.0$)	0.63	0.57	0.87
F12-c_{ij}^{kl} ($\gamma = 1.3$)	0.68	0.57	0.82
F12-c ($\gamma = 1.0$)	1.26	0.62	1.64
F12-c ($\gamma = 1.3$)	0.72	0.59	1.15
F12-c ($\gamma = 1.8$)	0.75	0.54	1.09

Table 2
Correlation contributions of aug-cc-pVTZ, fc-CCSD(F12)-c_{ij}^{kl} and -c reaction enthalpies relative to 56 extrapolated fc-CCSD values (kJ mol^{-1})

Reaction	CCSD 56	(F12)-c_{ij}^{kl}		(F12)-c		
		$\gamma = 1.0$	$\gamma = 1.3$	$\gamma = 1.0$	$\gamma = 1.3$	$\gamma = 1.8$
$CO + NH_3 \rightarrow HCONH_2$	−27.87	−0.34	−0.30	−0.93	−0.34	0.36
$H_2C_2O + H_2CO \rightarrow C_2H_4O + CO$	3.01	−0.04	−0.13	0.62	0.17	−0.14
$CS_2 + 2H_2O \rightarrow CO_2 + 2H_2S$	57.27	0.39	0.23	0.73	−0.08	−1.22
$CO + Cl_2 \rightarrow COCl_2$	−48.16	−2.21	−2.38	−1.94	−1.70	−1.82
$NH_3 + 4H_2O_2 \rightarrow HNO_3 + 5H_2O$	17.80	−0.41	−0.12	−2.24	−0.92	0.25
$C_2H_2 + H_2 \rightarrow C_2H_4$	5.68	−0.31	−0.33	−0.37	−0.28	−0.52
$CO + H_2 \rightarrow H_2CO$	−23.43	−0.15	−0.11	−0.87	−0.33	0.00
$H_2O_2 + H_2 \rightarrow 2H_2O$	18.24	0.15	0.28	−1.09	−0.43	−0.18
$H_2CO + H_2 \rightarrow CH_3OH$	−8.18	−0.29	−0.36	−0.77	−0.47	−0.35
$C_2H_6 + H_2 \rightarrow 2CH_4$	10.63	0.16	0.15	0.02	0.04	−0.07
$C_2H_4 + H_2 \rightarrow C_2H_6$	−5.91	−0.62	−0.72	−0.79	−0.69	−0.98
$C_2H_2 + H_2O \rightarrow CH_3CHO$	3.06	3.40	3.27	4.09	3.84	3.38
$CH_4 + 4H_2O_2 \rightarrow CO_2 + 6H_2O$	87.12	0.86	1.34	−2.61	−0.80	0.40
$SO_2 + H_2O_2 \rightarrow SO_3 + H_2O$	16.40	0.11	0.35	−0.58	0.19	1.31
$CO + H_2O_2 \rightarrow CO_2 + H_2O$	1.28	0.02	0.14	−1.31	−0.46	0.32

Table 3
(T) correlation contributions of aug-cc-pVTZ, fc-CCSD(T)(F12)-c_{ij}^{kl} and -c reaction enthalpies relative to Q5 extrapolated fc-CCSD(T) values (kJ mol^{-1})

Reaction	(T) Q5	(F12)-c_{ij}^{kl}		(F12)-c		
		$\gamma = 1.0$	$\gamma = 1.3$	$\gamma = 1.0$	$\gamma = 1.3$	$\gamma = 1.8$
$CO + NH_3 \rightarrow HCONH_2$	−3.73	0.39	0.40	0.37	0.37	0.37
$H_2C_2O + H_2CO \rightarrow C_2H_4O + CO$	4.56	−0.16	−0.16	−0.19	−0.17	−0.13
$CS_2 + 2H_2O \rightarrow CO_2 + 2H_2S$	17.69	−1.91	−1.89	−2.02	−1.81	−1.58
$CO + Cl_2 \rightarrow COCl_2$	−10.15	0.21	0.22	0.24	0.22	0.19
$NH_3 + 4H_2O_2 \rightarrow HNO_3 + 5H_2O$	−5.33	−0.78	−0.77	−0.80	−0.79	−0.78
$C_2H_2 + H_2 \rightarrow C_2H_4$	4.38	−0.38	−0.38	−0.41	−0.38	−0.34
$CO + H_2 \rightarrow H_2CO$	0.74	0.09	0.09	0.06	0.07	0.08
$H_2O_2 + H_2 \rightarrow 2H_2O$	8.12	−0.81	−0.81	−0.89	−0.86	−0.82
$H_2CO + H_2 \rightarrow CH_3OH$	4.63	−0.35	−0.35	−0.42	−0.39	−0.35
$C_2H_6 + H_2 \rightarrow 2CH_4$	2.46	−0.21	−0.21	−0.21	−0.21	−0.21
$C_2H_4 + H_2 \rightarrow C_2H_6$	4.31	−0.38	−0.39	−0.43	−0.40	−0.36
$C_2H_2 + H_2O \rightarrow CH_3CHO$	1.09	−0.17	−0.17	−0.18	−0.15	−0.11
$CH_4 + 4H_2O_2 \rightarrow CO_2 + 6H_2O$	15.02	−2.18	−2.19	−2.39	−2.34	−2.24
$SO_2 + H_2O_2 \rightarrow SO_3 + H_2O$	4.35	−0.30	−0.29	−0.40	−0.36	−0.30
$CO + H_2O_2 \rightarrow CO_2 + H_2O$	−2.04	−0.22	−0.22	−0.27	−0.26	−0.25

basis set limit is estimated in the same way as for the total correlation energies and is as much as 0.2 kJ mol^{-1} in the mae.

From Table 4 we see that the reduced variational flexibility in the fc-CCSD(F12)-c method does not lead to a degredation in energy differences, provided that a suitable γ is chosen. This is perhaps due in part to the absence of geminal BSSE. The -c_{ij}^{kl} and -c methods with $\gamma = 1.3$ both give higher accuracy than orbital-only calculations with an aug-cc-pV5Z basis. For the F12 methods, the remaining basis set error of the CCSD(F12) correlation contribution to the reaction energies is of the same order of magnitude as that of (T). Nevertheless the fc-CCSD(T)(F12)-c_{ij}^{kl} and -c methods perform as well as aug-cc-pV5Z orbital-only calculations with only an aug-cc-pVTZ orbital basis.

5. Van der Waals interactions of He_2 and Ne_2

The basis set limit fc-CCSD(T) spectroscopic parameters for He_2 and Ne_2 have been thoroughly investigated by Cybulski and Toczyłowski using special bond functions [30] and the basis set limit interaction energy of He_2 is known to high accuracy from extrapolations by Van Mourik and Dunning using doubly augmented basis sets [31] and from CCSD(T)-R12 calculations with very large basis sets, performed by one of us [32]. The fc-CCSD(T) equilibrium bond lengths and interaction energies are $5.62\,a_0$ and $-33.7\,\mu E_h$ for He_2 and $5.86\,a_0$ and $-130\,\mu E_h$ for Ne_2. Here we investigate the convergence of the fc-CCSD(T)(F12)-c_{ij}^{kl} and -c interaction energies to the basis set limit, using standard aug-cc-pVXZ orbital basis sets X = D, T, Q and 5. The interatomic separation is fixed at the basis set limit and we use the counter poise correction of Boys and Bernardi to reduce the orbital BSSE [33]. For the CABS we use an 18s10p6d5f4g3h2i for He and a 21s14p8d7f5g4h3i2k basis for Ne, constructed from the well tempered basis sets [25,26], as described in Ref. [9], which is more than sufficient to ensure that the RI error may be neglected [34]. The γ dependence of the fc-CCSD(T)(F12) interaction energies are presented in Figs. 2 and 3 for He_2 and Ne_2 respectively.

For the aug-cc-pVTZ basis, Figs. 2 and 3 show that the geminal BSSE present when all c_{ij}^{kl} are optimised leads to drastic overbinding at large values of γ. This tendency is naturally much more severe for Ne than He and diminishes when larger orbital basis sets are used. This instability in the interaction energy prediction is completely absent when the diagonal, orbital-invariant method is used due to the negation of geminal BSSE. The fc-CCSD(T)(F12)-c interaction energies converge from above and the best predictions are obtained with a value of γ close to 1.0. The detailed dependence of the fc-CCSD(T)(F12) interaction energies on γ is very similar to that observed for MP2-F12 calculations and a thorough discussion on this topic may be found in Ref. [9].

The HF, CCSD and (T) components of the interaction energy for the two fc-CCSD(T)(F12) methods, using

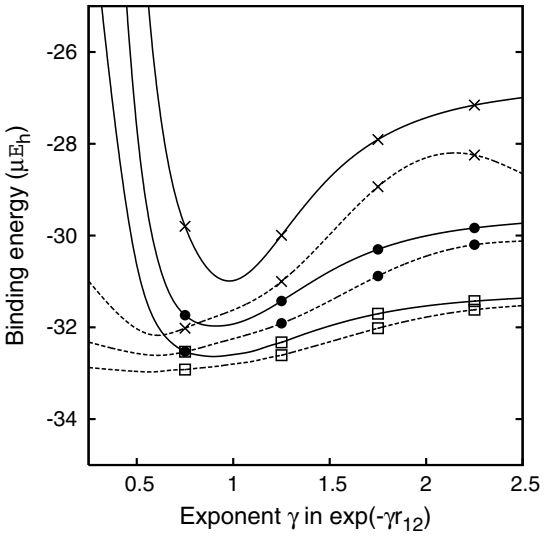


Fig. 2. The fc-CCSD(T)(F12) interaction energy of He_2 ($r_e = 5.62\,a_0$) as a function of γ, using c_{ij}^{kl} (dashed line) and c (solid line) with aug-cc-pVXZ orbital basis sets, X = T (×), Q (●) and 5 (□).

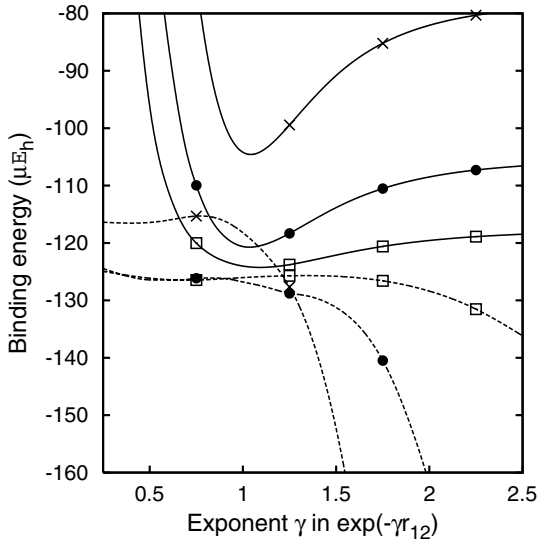


Fig. 3. The fc-CCSD(T)(F12) interaction energy of Ne_2 ($r_e = 5.86\,a_0$) as a function of γ, using c_{ij}^{kl} (dashed line) and c (solid line) with aug-cc-pVXZ orbital basis sets, X = T (×), Q (●) and 5 (□).

$\gamma = 1.0$, are presented in Table 5 for He_2 and Table 6 for Ne_2. The conventional, orbital-only values are also presented for comparison. Although the fc-CCSD(T)(F12)-c_{ij}^{kl} method appears to already be very close to the basis set limit for Ne_2 even with the aug-cc-pVDZ basis set and $\gamma = 1.0$, this is due to the fortuitous error cancellation between the overestimation of the CCSD contribution (due to geminal BSSE) and the underestimation of the (T) contribution. The convergence of the fixed-amplitude method is more reliable and using the aug-cc-pVQZ basis 95% and 93% of the basis set limit interaction energy is obtained for He_2 and Ne_2 respectively, compared to and 94% and 96% for TQ extrapolation. The accuracy of the F12 calcu-

Table 5
The HF, CCSD and (T) components of the interaction energy of He_2 ($r_e = 5.62\,a_0$) using aug-cc-pVXZ orbital basis sets and $\gamma = 1.0$ for the geminal basis

X	Orbital-only				F12-c_{ij}^{kl}			F12-c		
	HF	CCSD	(T)	Total	CCSD	(T)	Total	CCSD	(T)	Total
D	28.86	−40.05	−2.75	−13.95	−53.52	−2.59	−27.25	−50.73	−2.55	−24.42
T	27.65	−50.22	−3.95	−26.53	−55.38	−3.89	−31.62	−54.76	−3.87	−30.98
Q	27.80	−52.95	−4.31	−29.46	−55.76	−4.29	−32.25	−55.45	−4.28	−31.93
5	27.83	−54.55	−4.49	−31.20	−56.15	−4.48	−32.80	−55.96	−4.47	−32.59
6	27.81	−55.73	−4.62	−32.54	−56.62	−4.61	−33.42	−56.49	−4.60	−33.28

The basis set limit is $-33.7\,\mu E_h$.

Table 6
The HF, fc-CCSD and (T) components of the interaction energy of Ne_2 ($r_e = 5.86\,a_0$) using aug-cc-pVXZ orbital basis sets and $\gamma = 1.0$ for the geminal basis

X	Orbital-only				F12-c_{ij}^{kl}			F12-c		
	HF	CCSD	(T)	Total	CCSD	(T)	Total	CCSD	(T)	Total
D	93.2	−97.1	−10.4	−14.3	−204.8	−9.6	−121.2	−145.7	−8.9	−61.5
T	89.7	−146.9	−19.0	−76.3	−188.8	−19.1	−118.2	−175.3	−18.5	−104.2
Q	88.4	−169.3	−23.7	−104.6	−191.9	−23.3	−126.8	−185.7	−23.3	−120.6
5	89.9	−181.0	−26.0	−117.2	−190.2	−25.7	−126.0	−188.2	−25.7	−124.0

The basis set limit is $-130\,\mu E_h$.

lations is likely to improve upon optimisation of the orbital basis sets. This should also remove the inconsistency that different values of γ are required for VdW interactions and reaction enthalpies.

6. Conclusion

By building on Ten-no's fixed-amplitude MP2-F12 approach, we have introduced a diagonal orbital-invariant explicitly-correlated coupled-cluster method where the F12 amplitudes are fixed according to the coalescence conditions. This method is free from geminal BSSE and provides stable predictions for weak VdW interactions and yields aug-cc-pV5Z quality reaction enthalpies using aug-cc-pVTZ basis sets. The slow convergence of the (T) contribution with orbital basis appears to be a limiting factor in the accuracy of the CCSD(T)(F12) methods, which could be improved by including an F12 triples projection. The systems considered in this work are predominantly single-reference and the approximations made, namely $\psi \approx \psi_{r_{12}\to 0} + cr_{12}\psi_{\mathrm{HF}r_{12}\to 0}$ and $\bar{\mathbf{t}}_{2'} = \mathbf{t}_{2'}$, are likely be valid. Since the results of the diagonal fixed-amplitude approach are encouraging, this method should be more thoroughly tested on a wider range of molecules.

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