



Research paper

## Explicit correlation factors

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## ABSTRACT

We analyze the performance of 17 different correlation factors in explicitly correlated second-order many-body perturbation calculations for correlation energies. Highly performing correlation factors are found to have near-universal shape and size in the short range of electron-electron distance ( $0 < r_{12} < 1.5$  a.u.). The long-range behavior ( $r_{12} > 1.5$  a.u.) is insignificant insofar as the factor becomes near constant, leaving an orbital expansion to describe decoupled electrons. An analysis based on a low-rank Taylor expansion of the correlation factor seems limited, except that a negative second derivative with the value of around  $-1.3$  a.u. correlates with high performance.

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## 1. Introduction

The explicitly correlated extension [1–4] of an *ab initio* electron-correlation method captures a much greater portion of the exact correlation energy with the aid of a correlation factor (a function of the interelectronic distance,  $r_{12}$ ) than the same correlation method using an orbital basis set alone. Kutzelnigg [5] introduced the so-called R12 ansatz of explicitly correlated method, using the simplest correlation factor that satisfies Kato's cusp condition [6], namely, the one that is linear in  $r_{12}$ . Klopper and Kutzelnigg [7] developed the first generally applicable R12 method with second-order many-body perturbation (MP2) theory using Gaussian-type orbital (GTO) basis sets. Insofar as the GTO basis set is large (so as to yield, e.g., 87% of the exact MP2 limit for Ne), MP2-R12 is shown to recover an even greater portion of the exact correlation energy (99% for Ne).

One of the present authors [8–10] proposed the use of the Slater-type geminal (STG), which has the form  $(1 - e^{-\gamma r_{12}})/\gamma$  and thus satisfies the cusp condition [6] at  $r_{12} = 0$ , but becomes flat as  $r_{12} \rightarrow \infty$ . This was shown to systematically and significantly outperform the linear factor [8–10]. Tew and Klopper [11] considered the Slater-linear factor, error function factor, error function-linear factor, and observed their equally good (if not better) performance. In analogy with the contracted GTO approximation of a Slater-type orbital, Valeev [12] explored a correlation factor that was a linear combination of Gaussian-type geminals (GTG), and observed the near-optimal performance of a single STG. Indeed, a

STG seems to resemble the cusped hole of a pair function of the Hylleraas functional (see, e.g., Ref. [13]) so closely that its associated excitation amplitudes (geminal amplitudes) can be held fixed at values dictated by the singlet and triplet cusp conditions [6,14,15], leading to the SP ansatz [9]. Today, a nonlinear correlation factor such as STG has completely replaced the linear factor in explicitly correlated methods, and those using the former are distinguished from the R12 methods as the F12 methods.

From these studies, it is evident that the shape of a correlation factor *away from*  $r_{12} = 0$  is equally important for the performance as the shape at  $r_{12} = 0$ . Exact pointwise satisfaction of the cusp condition seems immaterial [16], judging from the fact that a GTG expansion of a STG works well [11,12] despite GTG's violation of the cusp condition. Klopper et al. [1] speculated the importance of a nonzero second derivative of the correlation factor with respect to  $r_{12}$ , which the linear factor lacks. However, the value of the second derivative (i.e., the second-order cusp condition [17]) is system- and state-dependent and is not known *a priori*, making it hard to judge the correctness of this speculation. Rasolov and Chipman [18] derived an equality obeyed by the second and third derivatives, the significance of which is yet to be determined.

Monkhorst [19] also analyzed the asymptotic forms of pair functions under various conditions and argued that two electrons should 'decouple' at large  $r_{12}$ . This may explain the excellent performance of STG, which becomes constant at  $r_{12} \rightarrow \infty$ , and the poor performance of the linear factor, which grows indefinitely. On the other hand, the correct long-range asymptote in a homogeneous electron gas was shown to be a screened Coulomb decay, supporting the Yukawa-Coulomb factor [20], whose superior performance

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was numerically demonstrated by Grüneis et al. [21,22]. In quantum Monte Carlo, which has extraordinary flexibility in the choice of correlation factors, the Jastrow factor [23] is preferred, which differs from either STG or Yukawa–Coulomb.

In this study, we exploit the same extraordinary flexibility of the Monte Carlo MP2-F12 (MC-MP2-F12) method [24,25] to numerically compare the performance of 17 correlation factors for small molecules. On this basis, we investigate the validity of the aforementioned claims concerning the shape of the correlation factor in determining the performance of the F12 method in the SP ansatz.

## 2. Computational details

Using the SP ansatz [9] and generalized and extended Brillouin conditions [26,27], the F12 correction [5,28] to the MP2 energy consists of two parts:

$$E_{\text{F12}}^{\text{VBX}} = 2E_{\text{F12}}^{\text{V}} + E_{\text{F12}}^{\text{BX}} \quad (1)$$

with

$$E_{\text{F12}}^{\text{V}} = \frac{5}{8} \sum_{ij}^{\text{occ}} V_{ij}^{ij} - \frac{1}{8} \sum_{ij}^{\text{occ}} V_{ji}^{ij}, \quad (2)$$

$$E_{\text{F12}}^{\text{BX}} = \frac{7}{32} \sum_{ij}^{\text{occ}} (\text{BX})_{ij}^{ij} + \frac{1}{32} \sum_{ij}^{\text{occ}} (\text{BX})_{ji}^{ij}, \quad (3)$$

and

$$V_{mn}^{ij} = \langle ij | r_{12}^{-1} \hat{Q}_{12} f_{12} | mn \rangle, \quad (4)$$

$$(\text{BX})_{mn}^{ij} = \langle ij | f_{12} \hat{Q}_{12} [\hat{F}_1 + \hat{F}_2, f_{12}] | mn \rangle, \quad (5)$$

where  $f_{12}$  is the correlation factor,  $\hat{F}_n$  is the Fock operator for electron  $n$ , and  $\hat{Q}_{12}$  is the strong-orthogonality projector [29]:

$$\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2) - \hat{V}_1 \hat{V}_2, \quad (6)$$

in the standard notation. The VBX expression [Eq. (1)] is variational with respect to the size and shape of the correlation factor. At its minimum,  $E_{\text{F12}}^{\text{B}} + E_{\text{F12}}^{\text{X}} = -E_{\text{F12}}^{\text{V}}$  and, therefore,

$$E_{\text{F12}}^{\text{VBX}} = E_{\text{F12}}^{\text{V}}. \quad (7)$$

The overall size of the correlation factor (the geminal amplitudes) is held fixed in the SP ansatz. However, the shape of the correlation factor can usually be adjusted by varying some parameters, which are denoted by  $\gamma$  and  $\beta$  in this Letter. Eq. (7) is expected to hold accurately at the minimum of  $E_{\text{F12}}^{\text{VBX}}$  with respect to  $\gamma$  and  $\beta$  if and only if the shape of the correlation factor is sufficiently close to that of the cusped hole of a pair function.

The total VBX energy can be divided into a sum over orbital-pair contributions as follows:

$$E_{\text{F12}}^{\text{VBX}} = \sum_{i \leq j}^{\text{occ}} e_{ij} \quad (8)$$

with

$$e_{ij} = (2 - \delta_{ij}) \left[ \frac{5}{4} V_{ij}^{ij} - \frac{1}{4} V_{ji}^{ij} + \frac{7}{32} (\text{BX})_{ij}^{ij} + \frac{1}{32} (\text{BX})_{ji}^{ij} \right]. \quad (9)$$

In this work, the high-dimensional integrals arising from Eqs. (2) and (3) were evaluated by the Monte Carlo (MC) method [24,25]. It has the unique ability to handle virtually any integrand and thus any correlation factor, which is essential for our purpose. More specifically, the VBX formalism can treat any correlation factor that is analytic (having at least first and second derivatives with respect to  $r_{12}$ ), whereas the V formalism can use any factor including numerically defined ones.

We considered 17 analytic correlation factors in Table 1 including 6 that had been studied in Ref. [25] for H<sub>2</sub>O and CH<sub>4</sub>

**Table 1**  
Correlation factors.

Correlation factor	Name	$\gamma$ / a.u. <sup>a</sup>	$\beta$ / a.u. <sup>a</sup>	%CBS <sup>b</sup>	$\partial f_{12}/\partial r_{12} _0$	$\partial^2 f_{12}/\partial r_{12}^2 _0$ / a.u.	$\partial^3 f_{12}/\partial r_{12}^3 _0$ / a.u.
$f_{12}^{(0)} = 0$	None	...	...	70.4	0	0	0
$f_{12}^{(1)} = (1 - e^{-\gamma r_{12}})/\gamma$	Slater (STG)	1.2	...	96.1	1	$-\gamma = -1.2$	$\gamma^2 = 1.4$
$f_{12}^{(2)} = (1 - e^{-\gamma r_{12}})/(\gamma r_{12})$	Cusped Gaussian	1.2	...	82.4	1	0	$-3\gamma = -3.6$
$f_{12}^{(3)} = \gamma r_{12}/(\gamma + r_{12})$	Rational	1.2	...	95.9	1	$-2/\gamma = -1.7$	$6/\gamma^2 = 4.2$
$f_{12}^{(4)} = \ln(1 + \gamma r_{12})/\gamma$	Logarithm	2.0	...	95.3	1	$-\gamma = -2.0$	$2\gamma^2 = 8.0$
$f_{12}^{(5)} = \arctan(\gamma r_{12})/\gamma$	Arctangent	1.6	...	96.0	1	0	$-2\gamma^2 = -5.1$
$f_{12}^{(6)} = f_{12}^{(1)}/2 + f_{12}^{(3)}/2$	Hybrid	1.2	...	96.1	1	$-1/\gamma - \gamma/2 = -1.4$	$3/\gamma^2 + \gamma^2/2 = 2.8$
$f_{12}^{(7)} = r_{12}$	Linear	...	...	21.3	1	0	0
$f_{12}^{(8)} = \gamma r_{12}/(2\gamma + 2r_{12}) + \beta^2 r_{12}/\{2(\beta + r_{12})^2\}$	Higher rational	1.6	3.0	96.4	1	$-2/\beta - 1/\gamma = -1.3$	$9/\beta^2 + 3/\gamma^2 = 2.2$
$f_{12}^{(9)} = 1 - e^{-\gamma r_{12}^2}$	Gaussian (GTG)	0.5	...	80.9	0	$2\gamma = 1.0$	0
$f_{12}^{(10)} = (2e^{-\gamma r_{12}} - 2)/(\gamma^2 r_{12})$	Yukawa–Coulomb	2.0	...	96.4	1	$-2\gamma/3 = -1.3$	$\gamma^2/2 = 2.0$
$f_{12}^{(11)} = r_{12} e^{-\gamma r_{12}}$	Slater–linear	0.5	...	94.2	1	$-2\gamma = -1.0$	$3\gamma^2 = 0.8$
$f_{12}^{(12)} = e^{r_{12}/(1+\gamma r_{12})}$	Jastrow	1.2	...	96.0	1	$1 - 2\gamma = -1.4$	$1 - 6\gamma + 6\gamma^2 = 2.4$
$f_{12}^{(13)} = e^{U_{12}/(1+\gamma U_{12})}$ $U_{12} = (1 - e^{-\beta r_{12}})/\beta$	Higher Jastrow	0.8	0.75	96.2	1	$1 - \beta - 2\gamma = -1.4$	$1 - 6\gamma + 6\gamma^2 + \beta^2 + \beta(6\gamma - 3) = 2.0$ $-2\gamma^2 = -2.9$
$f_{12}^{(14)} = -\sqrt{\pi} \text{erfc}(\gamma r_{12})/(2\gamma)$	Error function	1.2	...	92.6	1	0	$-2\gamma^2 = -2.9$
$f_{12}^{(15)} = r_{12} \text{erfc}(\gamma r_{12})$	Error function–linear	0.4	...	88.2	1	$-4\gamma/\pi = -0.5$	0
$f_{12}^{(16)} = \tanh(\gamma r_{12})/\gamma$	Hyperbolic tangent	1.2	...	94.1	1	0	$-2\gamma^2 = -2.9$
$f_{12}^{(17)} = (1 - e^{-\gamma r_{12}})/\gamma + e^{-\beta r_{12}^2}$	Slater–cubic exponential	1.2	0.003	94.9	1	$-\gamma = -1.2$	$\gamma^2 - 6\beta = 1.42$
$f_{12}^{(17)} = (1 - e^{-\gamma r_{12}})/\gamma + e^{-\beta r_{12}^3}$	Slater–cubic exponential	1.2	0.006	93.5	1	$-\gamma = -1.2$	$\gamma^2 - 6\beta = 1.40$
$f_{12}^{(17)} = (1 - e^{-\gamma r_{12}})/\gamma + e^{-\beta r_{12}^3}$	Slater–cubic exponential	1.2	0.012	91.3	1	$-\gamma = -1.2$	$\gamma^2 - 6\beta = 1.37$

<sup>a</sup> Near-optimal values of  $\gamma$  and  $\beta$  in the case of H<sub>2</sub>O using the cc-pVDZ basis set.

<sup>b</sup> The recovery ratio of the MP2 correlation energy in the complete-basis-set (CBS) limit averaged over H<sub>2</sub>O and CH<sub>4</sub> using the cc-pVDZ basis set. Statistical uncertainties alone cause an error up to a few tenths of 1%.

using the cc-pVDZ basis set. The MC-MP2-F12 calculations used the implementation reported in Ref. [25] with  $8.65 \times 10^7$  MC steps ( $3.74 \times 10^6$  steps for Fig. 4), 40 redundant walkers for both one-electron and two-electron walkers [30], and 6 blocking transformations [31] for statistical uncertainties. In all cases, the statistical uncertainties were small enough to not alter the conclusions drawn below (the statistical uncertainty with 99% confidence for the CBS recovery ratios was 0.1–0.4% with the maximum being 0.43% for correlation factor 3). The MP2 energies with the cc-pVDZ basis set and in the complete-basis-set (CBS) limits (see Ref. [25] for more details) were obtained with NWChem [32]. The core electrons were excluded in correlation calculations.

### 3. Results

Table 1 compiles the CBS recovery ratios (averaged over  $\text{H}_2\text{O}$  and  $\text{CH}_4$ ) for all 17 correlation factors at values of  $\gamma$  and  $\beta$  that are near optimal (the latter are also listed in the table for  $\text{H}_2\text{O}$ ). For correlation factor 17, the results for 3 different values of  $\beta$  are given. The first, second, and third derivatives of the correlation factor with respect to  $r_{12}$  at  $r_{12} = 0$  are also shown. The value of unity for the first derivative means that the correlation factor satisfies Kato's cusp condition; only GTG (besides null correlation factor listed as  $f_{12}^{(0)}$ ) does not satisfy the condition. Correlation factor 17 (STG–cubic exponential) reduces to a single STG as  $\beta \rightarrow 0$ . With decreasing  $\beta$ , the performance (CBS recovery ratio) of this correlation factor increases toward that of STG. This means that the cubic exponential part of this correlation factor acts to only spoil the high performance of STG.

Fig. 1 plots the CBS recovery ratios for  $\text{H}_2\text{O}$  and  $\text{CH}_4$  separately for the correlation factors listed in Table 1. The ratios for  $\text{CH}_4$  are higher than those for  $\text{H}_2\text{O}$  by a few percents, the cause of which is unknown. From this figure and Table 1, we divide the correlation factors into two groups: the highly performing ones that capture 90% or above of the correlation energies in the CBS limit, and the poorly performing ones that fail to do so. The poorly performing factors are 2 (cusped Gaussian), 7 (linear), 9 (GTG), and 15 (error function–linear), while the rest are in the highly performing group. For this small dataset, the five best performing factors are 8 and 10 (tie by higher rational and Yukawa–Coulomb), 13 (higher Jastrow), 1 and 6 (tie by STG and hybrid) in this order, although the differences among them are not statistically significant.

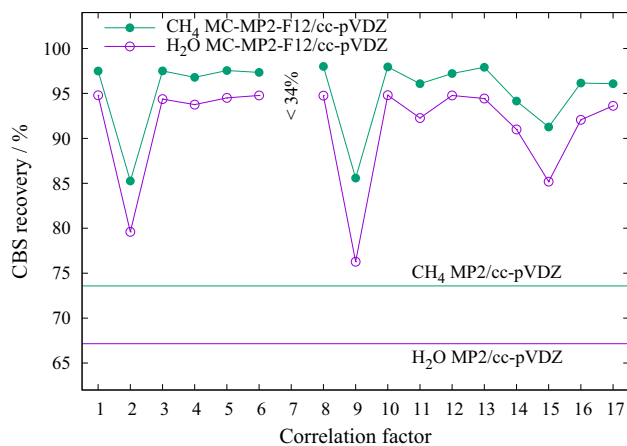


Fig. 1. The CBS recovery ratios of the MC-MP2-F12/cc-pVDZ calculations for  $\text{H}_2\text{O}$  and  $\text{CH}_4$  using the correlation factors listed in Table 1 at their respective near-optimal  $\gamma$  and  $\beta$  values. Correlation factor 17 used  $\beta = 0.003$  a.u.

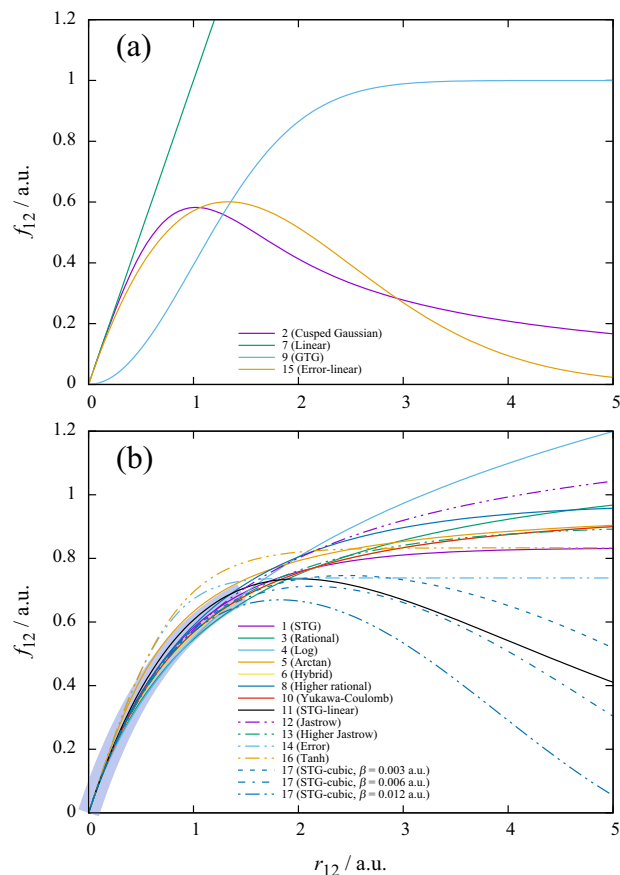
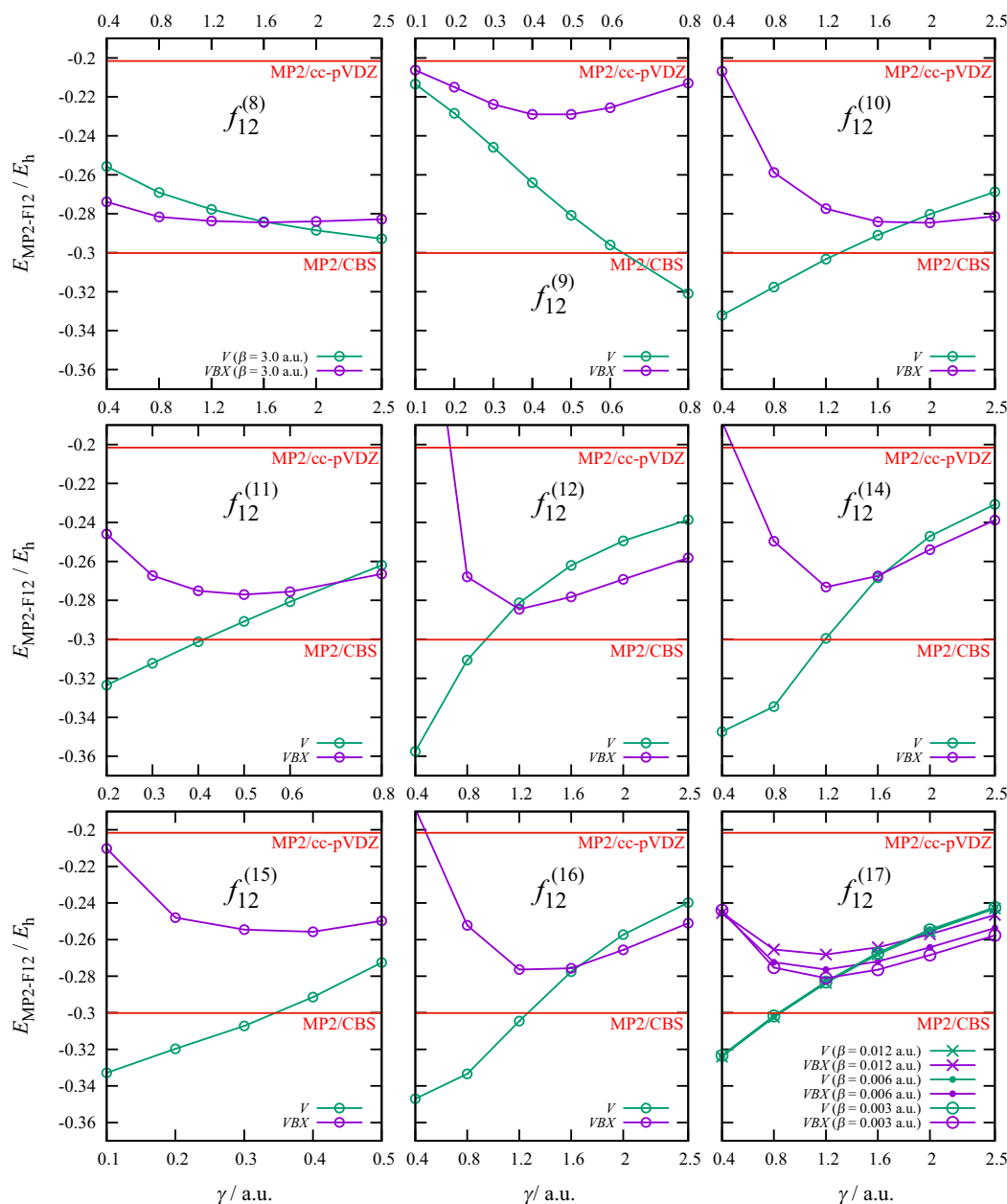


Fig. 2. Plots of (a) poorly performing correlation factors and (b) highly performing ones at the values of  $\gamma$  and  $\beta$  given in Table 1. The blue-shaded area likely reflects the universal shape of the cusped holes of pair functions. Some curves are displaced vertically to cross the origin. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 2 plots the correlation factors in these two groups as a function of  $r_{12}$ . Note that the values of  $\gamma$  used in this plot are near optimal for  $\text{H}_2\text{O}$  (given in Table 1). Common features observed in the shapes of the highly performing correlation factors will likely reflect the near-universal shape of the cusped hole in a pair function, which cannot be described well by an orbital expansion. It is striking to observe the convergence of the functional forms of many best-performing correlation factors in the range of  $0 < r_{12} < 1.5$  a.u. For instance, with increasing  $\beta$ , correlation factor 17 (STG–cubic exponential) decays more rapidly with  $r_{12}$  and deviates more greatly from STG. As a result, this factor with  $\beta = 0.012$  a.u. (the lowest-lying curve) does not differ much in the functional form from correlation factor 15 (error function–linear), which is among the poorly performing group. Correspondingly, its CBS recovery ratio is also the lowest among the highly performing group.

Fig. 3 draws the MP2-F12 energies in the variational  $VBX$  and nonvariational  $V$  formalisms as a function of  $\gamma$ , complementing a similar figure for correlation factors 1 through 6 in Ref. [25]. Correlation factor 7 (linear) is excluded because it has no  $\gamma$  dependence, and the plot for correlation factor 13 (higher Jastrow) is also omitted as it is similar to the one for correlation factor 12 (Jastrow). We observe that with the poorly performing correlation factors 9 and 15, the  $VBX$  and  $V$  curves do not even cross in the chosen domain of  $\gamma$ . With the best performing correlation factors 10 (Yukawa–Coulomb) and 12 (Jastrow), in contrast, these two curves cross near the minima of the  $VBX$  curves, satisfying Eq. (7). This, in turn,



**Fig. 3.** The MC-MP2-F12/cc-pVDZ correlation energy as a function of  $\gamma$  (and  $\beta$ ) in the variational VBX and nonvariational V formalisms of H<sub>2</sub>O. See Ref. [25] for the corresponding plots for correlation factors 1 through 6.

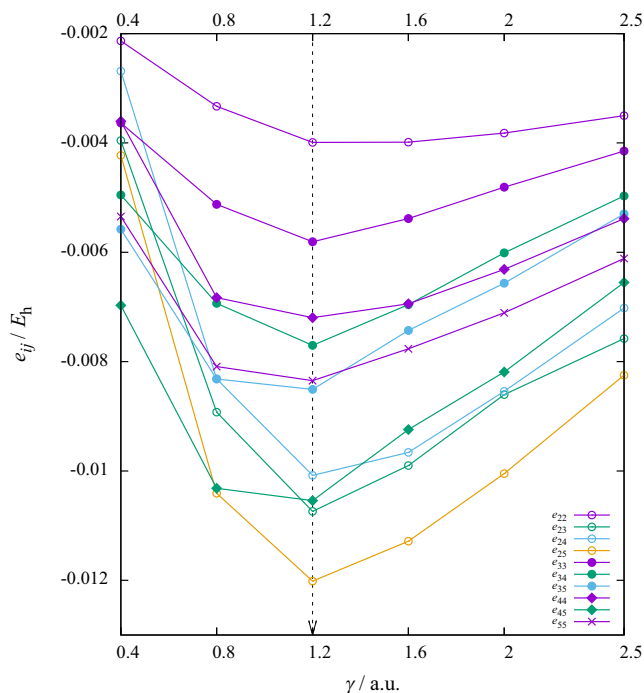
means that only when correlation factors have the right shape does the SP ansatz work exceedingly well. The appropriateness of the shape of a correlation factor can, therefore, be detected by the way these two curves intersect (in addition to the CBS recovery ratio). The  $\beta$ -dependence in the plot of correlation factor 17 (STG–cubic exponential) is a case in point. With decreasing  $\beta$ , this correlation factor approaches STG, improving its CBS recovery ratio. Correspondingly, the intersection of the VBX and V curves also shifts toward the minimum of the VBX curve, attesting to the gradual improvement of the functional form.

Fig. 4 shows the breakdown of the F12 correction (using correlation factor 1 or STG) into its orbital-pair contributions [Eqs. (8) and (9)] as a function of  $\gamma$ . It can be seen that all valence-orbital-pair F12 corrections have a minimum at a similar optimal value of  $\gamma$  around 1.2 a.u.

## 4. Discussion

### 4.1. Cusp ( $r_{12} = 0$ )

Prendergast et al. [16] argued that satisfying the cusp condition pointwise (at  $r_{12} = 0$ ) alters the correlation energy only in the  $\mu E_h$ -accuracy range, and is rather insignificant, the assertion also supported (qualitatively) by Valeev’s work [12]. Our results are not inconsistent with this conclusion in the sense that there are several correlation factors (such as 2, 7, and 15) that satisfy the cusp condition but perform extremely poorly in the SP ansatz. There is only one correlation factor (9 or GTG) in our list that does not satisfy the cusp condition. It also performs poorly, but this is likely traced to the wrong short-range shape (see below) rather than to the lack of cusp. Therefore, our results do not contain discerning



**Fig. 4.** The F12 corrections using STG (correlation factor 1) for orbital pairs [ $e_{ij}$  of Eq. (9)] in  $\text{H}_2\text{O}$  as a function of  $\gamma$ .

(let alone quantitative) information about this conclusion, but they do not contradict it. Taken together with the other observations (see below) about the correct shape of the correlation factor, our results seem supportive of the notion that the pointwise (i.e., at  $r_{12} = 0$ ) satisfaction of the cusp condition is not important for energetics, which may be self-evident because of the infinitesimally small volume element of the cusp. However, the cusp condition remains crucial as it dictates the correct short-range shape of a correlation factor *near* (if not *at*) the cusp (see below).

#### 4.2. Long-range shape ( $r_{12} > 1.5$ a.u.)

Fig. 2 rather decisively shows that correlation factors that are equally highly performing can have qualitatively different long-range behavior at  $r_{12} > 1.5$  a.u. Some (e.g., correlation factor 4) continue to increase with  $r_{12}$ , while others become constant (e.g., correlation factor 1) or turn to decrease (e.g., correlation factor 11), with no drastic effect on the CBS recovery ratios. We, therefore, argue that the long-range behavior of a correlation factor is not too important for the performance of the correlation factor, insofar as it does not distort its behavior in the short range ( $r_{12} < 1.5$  a.u.) or grow indefinitely. This is consistent with Monkhurst's argument [19] that two electrons should decouple its correlation in the long range; a good correlation factor should be constant or only moderately dependent on  $r_{12}$  in the long range, so as not to interfere with the ability of an orbital expansion to accurately describe pair functions there. The linear factor (7) is the worst performer in the SP ansatz partly because of its inappropriately strong coupling at large  $r_{12}$ .

The Yukawa–Coulomb factor (10), which is said to have the physically correct  $-2/(\gamma^2 r_{12})$  decay in the homogeneous electron gas, is found to be the best performer, which may be taken to support the claim of Grüneis et al. [21,22] for molecules as well as for homogeneous electron gases. However, the higher rational (8), which is tied for the highest CBS recovery ratio, has the  $\beta^2/(2r_{12})$

long-range behavior, but with the opposite sign. Furthermore, the differences in the CBS recovery ratios between these two and STG (correlation factor 1, which becomes constant at  $r_{12} \rightarrow \infty$ ) are small and not statistically significant. Therefore, we are inclined to stand by the conclusion about the relative insignificance of the long-range behavior at  $r_{12} > 1.5$  a.u.

The long-range asymptote of a pair function is expected to depend on the highest occupied orbital energy and thus on the system [19]. The fact that the F12 method with the same correlation factor (with the same  $\gamma$  in the SP ansatz) works well for a variety of molecules [8–10] also suggests that the long-range part of pair functions is described well by an orbital expansion; a correlation factor should be near constant there not to spoil this expansion.

#### 4.3. Short-range shape ( $0 < r_{12} < 1.5$ a.u.)

The most striking result of this work is the convergence of all high-performance correlation factors in the short range ( $0 < r_{12} < 1.5$  a.u.) as seen in Fig. 2(b). The dense manifold of curves (indicated by a blue shade in Fig. 2(b) in this  $r_{12}$  range should represent the common feature of the cusped hole in a pair function with the radius of approximately 1.5 a.u., which is not dissimilar to the ones observed in grid-based MP2 calculations [13]. Pair functions outside this range are more strongly dependent on system and state, but are reasonably accurately describable by an orbital expansion. A few curves that are slight outliers of the manifold, such as correlation factors 14 (error function) and 16 (hyperbolic tangent), are also the ones with slightly lower CBS recovery ratios (92.6% and 94.1%, respectively). Correlation factor 17 with the largest value of  $\beta = 0.012$  a.u. seems to decay too early (at  $r_{12} < 1.5$  a.u.), which may explain the penalty in its performance (the CBS recovery ratio of 91.3%). The poorly performing correlation factors in Fig. 2(a) have vastly different shapes in this  $r_{12}$  range.

We, therefore, conclude that the correct shape of the correlation factor in  $0 < r_{12} < 1.5$  a.u. is crucial for the performance of the F12 method in the SP ansatz.

#### 4.4. Second-order cusp and Rassolov–Chipman conditions

The correct shape of the correlation factor is cusped at  $r_{12} = 0$  and concave with a radius of approximately 1.5 a.u. This is consistent with the speculation of Klopper et al. [1] about the significance of a nonzero second derivative of the correlation factor with respect to  $r_{12}$ . Table 1 indicates that the highly performing correlation factors tend to have the second derivatives of around  $-1.2$  to  $-1.4$  a.u. It is possible for a correlation factor to have the correct shape in the short range with zero second derivative by having a compensating third derivative (such as in correlation factors 5 and 16). However, all poorly performing factors have zero or positive second derivative, making their shapes too linear or convex in the short range.

The above observation notwithstanding, the second derivative does not obey a simple, universal condition independent of system or state [17,18]. Rassolov and Chipman [18], however, found the following condition to be met by the second and third derivatives:

$$\left. \frac{\partial^3 f_{12}}{\partial r_{12}^3} \right|_{r_{12}=0} = \left. \frac{\partial^2 f_{12}}{\partial r_{12}^2} \right|_{r_{12}=0} - \frac{1}{4}. \quad (10)$$

None of the correlation factors we studied satisfies this condition; in most cases, including highly performing correlation factors, the left- and right-hand sides of the condition even have the opposite signs. This may mean that the third-order Taylor expansion of



the correlation factor is too approximate and does not discern the short-range shape up to  $r_{12} = 1.5$  a.u., not to mention whether it has the near-constant behavior in the long range.

#### 4.5. Orbital-pair dependence

Fig. 4 testifies that the  $\gamma$  values at which valence-orbital-pair F12 corrections [ $e_{ij}$  of Eq. (9)] in  $\text{H}_2\text{O}$  are at minimum are essentially unchanged from one pair to another. A similar result was obtained for  $\text{CH}_4$  (not shown). This suggests that cusped holes in pair functions have the universal shape seen in Fig. 2(b) across valence orbital pairs (although core orbital pairs may have tighter cusps [8]). We argue that this relative invariance in the size and shape of the cusped holes is what makes the SP ansatz with a non-linear correlation factor a great success. It may be recalled that the second-order cusp condition is system- and orbital-pair-dependent [17], whereas the appropriate form of the correlation factor seems the same for all valence orbital pairs. This may also be viewed as the limitation of the analysis of the correlation factor by its Taylor expansion.

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