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We have investigated the correlation factors $\exp(-\zeta r_{12})$, $r_{12}\exp(-\zeta r_{12})$, $\text{erfc}(\zeta r_{12})$, and $r_{12}\,\text{erfc}(\zeta r_{12})$ in place of the linear-r_{12} term for use in explicitly correlated electronic-structure methods. The accuracy obtained with all of these correlation factors is significantly greater than that obtained with the plain correlation factor r_{12}. Polarization functions that are more diffuse than those of standard basis sets give even better results. The correlation factor $\exp(-\zeta r_{12})$ is very close to the optimum correlation factor for helium and outperforms the others. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1999632]

I. INTRODUCTION

The quantum chemical methods that expand the wave function in terms of products of one-particle basis functions converge very slowly with the size of the one-particle basis.[1] The smooth one-particle basis functions are unable to efficiently describe the cusps in the wave function that appear at the coalescence of two electronic coordinates.[2] Twenty years ago the linear-r_{12} methods were introduced in order to overcome this deficiency.[2,3] In linear-r_{12} methods additional two-particle basis functions are used to expand the wave function. The two-particle functions depend explicitly on the interelectronic distance r_{12} and describe the electronic cusps efficiently. This dramatically improves the convergence behavior with the one-particle basis, enabling the computation of energies with near basis-set limit accuracy at an accessible computational cost. The linear-r_{12} methods have been very successful in the accurate calculation of the electronic structure of small molecules, and have been used extensively.[4–7] These benchmark results have been used to calibrate other numerical methods of quantum chemistry, in particular, they have been instrumental in the development of basis-set extrapolation techniques.[8–16]

Due to the slow convergence with one-particle basis it is necessary to use basis sets of at least quadruple-zeta quality in order to recover 90% of the correlation energy of a conventional method. In linear-r_{12} methods the improved convergence means that the same accuracy can be achieved with a much smaller basis. Since r_{12} methods exhibit the same scaling with basis-set size as the corresponding conventional methods, linear-r_{12} methods have the potential to be more efficient than conventional methods even when moderate accuracy is required.

The early implementations of linear-r_{12} theory were only appropriate for use with very large basis sets. The three- and four-electron integrals, which arise due to the geminal basis functions, are computed through the insertion of an approximate resolution of the identity (RI), which is only valid for large basis sets. More recently this constraint has been removed by two sets of workers via independent routes. Taylor, Persson, and Dahle replaced the linear-r_{12} term with a linear combination of Gaussian-type geminals, fitted to linear r_{12}. In this way they were able to compute all the necessary many-electron integrals exactly, avoiding the use of the approximate resolution of the identity.[17–20] Klopper and Samson provided an alternative solution by introducing a sufficiently large auxiliary basis for the RI approximation so that the integrals are always evaluated accurately, independent of the size of basis used to expand the Hartree-Fock orbitals used in the correlation method.[21] However, the results of both of these linear-r_{12} methods were disappointing for small basis sets.

In their investigations on the valence-shell MP2 correlation energy of a selection of small molecules, Klopper and Samson showed that the MP2-R12 energies calculated with a correlation-consistent polarized valence double-zeta (cc-pVDZ) basis set are of similar quality to those calculated using standard MP2 with a correlation-consistent polarized valence triple-zeta (cc-pVTZ) basis. The improvement of MP2-R12 over standard MP2 is equivalent to increasing the cardinal number of the standard MP2 basis by one unit only, which is a much smaller effective gain compared to the improvement of MP2-R12 over standard MP2 for the correlation-consistent polarized valence quintuple-zeta (cc-pV5Z) basis.

The fact that the gain in accuracy due to the linear-r_{12} terms is most significant in the limit of large basis sets may be understood through the following argument. Consider a basis set saturated up to an angular momentum quantum number $L_{\max}$ and then truncated. The error in the correlation energy calculated by standard methods is proportional to $(L_{\max}+1)^{-3}$, whereas for linear-r_{12} methods it is proportional to $(L_{\max}+1)^{-7}$ (cf. Fig. 1 of Ref. 21). The reduction of the error due to the linear-r_{12} terms is therefore proportional to $(L_{\max}+1)^4$. In other words, the gain in accuracy relative to standard electron-correlation methods grows quickly with the size of the basis. In a basis with $L_{\max}=5$, the explicitly

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correlated linear-r_{12} calculation is as much as three orders of magnitude more accurate than the corresponding standard electron-correlation method ($6^4 = 1296$).

Much effort has been spent on improving the efficiency of linear-r_{12} methods, for example, through using density-fitting techniques,[22] numerical quadratures,[23] and better RI approximations.[24,25] However, in order for the explicitly correlated methods to compete with the standard methods aimed at computing 90% of the correlation energy, the poor performance for small basis sets must be addressed. It has recently been shown by Ten-no[26] and shortly thereafter by May and Manby[27,28] that the accuracy of explicitly correlated methods can be greatly improved by replacing the factor r_{12} of the linear-r_{12} methods with the function $\exp(-\zeta r_{12})$. We consider that the question regarding the optimum form for a correlation function is an important one and we have therefore investigated several other correlation factors.

The paper is set out as follows. In Sec. II we discuss the optimum form of correlation factor for use in the r_{12} methods introduced by Kutzelnigg and Klopper. In Sec. III we present a detailed investigation of the optimum correlation factor for helium. In Secs. IV and V we test four correlation factors, the one proposed by Ten-no and three new functions. We present results of MP2 calculations on a series of small molecules using these correlation factors. In Sec. VI we discuss the basis sets appropriate for use with these correlation factors and we summarize the conclusions of all of our investigations in Sec. VII.

II. THE OPTIMUM CORRELATION FACTOR

We know from several studies of the electronic cusp conditions that the wave function at the singlet and triplet cusps, respectively, satisfy[29,30]

$$\psi = \psi_{r_{12}=0}\left(1 + \tfrac{1}{2}r_{12} + O(r_{12}^2)\right), \tag{1}$$

$$\psi = \mathbf{w} \cdot \mathbf{r}_{12}\left(1 + \tfrac{1}{4}r_{12}\right) + O(r_{12}^3), \tag{2}$$

where $\mathbf{w}$ is a vector and is dependent on all the electronic coordinates. The linear behavior at the cusp for the coalescence of a given spin pair of electrons is independent of the molecular system, but the higher-order terms $O(r_{12}^2)$ depend in principle on all of the electronic degrees of freedom and therefore on the physical system. In our linear-r_{12} methods we introduce geminals into the expansion of the wave function through the terms

$$\tilde{\psi}_0\left(1 + \sum_{i<j=1}^{n} cr_{ij}\right). \tag{3}$$

$\tilde{\psi}_0$ is the approximate ground-state Hartree-Fock wave function, r_{ij} is the distance between electrons i and j, and c is a variational parameter. For systems which are well represented by a single reference the $\tilde{\psi}_0$ is a reasonable approximation to the exact wave function and the cusp is well described with $c = \tfrac{1}{2}$ or $\tfrac{1}{4}$. The higher-order terms are missing from these linear correlation factors and at regions further away from the cusp, this description becomes increasingly inappropriate.

It is clear that if we allow the correlation factor J to be a function of all electronic degrees of freedom, then we are free to write the exact wave function as $\psi = \tilde{\psi}_0 J$. The optimum J is then simply $\psi/\tilde{\psi}_0$, and is therefore different for every molecular system and every basis set used to compute $\tilde{\psi}_0$. In order to maintain the computational efficiency of the existing methods we restrict our correlation factors to the form

$$J(\{r_{ij}\}) = \sum_{i<j=1}^{n} c f_{12}(r_{ij}), \tag{4}$$

where f_{12} is the same function for all r_{ij}. We now discuss the optimum function f_{12} for a correlation factor of this form in r_{12} calculations.

In r_{12} methods we subdivide the formal (infinite) set of one-particle solutions to the Fock operator $\{\phi_\lambda\}_\infty$ into two distinct subsets $\{\phi_p\}_N$ and $\{\phi_\alpha\}_\infty$, where $\{\phi_i\}_N$ is spanned by the finite basis set used in a computation and $\{\phi_\alpha\}_\infty$ is the complementary set. $\tilde{\psi}_0$ is the slater determinant of the n orbitals, contained in $\{\phi_p\}_N$, which minimize the energy. Using the notation of second quantization the approximate correlated wave function $\tilde{\psi}$ is expanded as

$$
\tilde{\psi} = \sum_{ijk\cdots\alpha\beta\gamma\cdots} j_{ijk\cdots}^{\alpha\beta\gamma\cdots} a_i^\alpha a_j^\beta a_k^\gamma \cdots \tilde{\psi}_0
$$
$$
+ \sum_{ijk\cdots abc\cdots} t_{ijk\cdots}^{abc\cdots} a_i^a a_j^b a_k^c \cdots \tilde{\psi}_0, \tag{5}
$$

where ijk run over the occupied orbitals, abc run over the unoccupied orbitals contained in $\{\phi_p\}_N$, and $\alpha\beta\gamma$ run over all unoccupied orbitals contained in $\{\phi_\lambda\}_\infty$. The first summation is simply the operator representation of $\tilde{\psi}_0 J(\{r_{ij}\})$ and the second term is that of standard methods. The configurations included in the expansion and the way in which the coefficients t and j are computed depend on the correlation method. There is significant overlap between the two terms in Eq. (5) and in the limit of infinite one-particle basis the first term becomes redundant (indeed in the implementation of r_{12} methods a projection operator is inserted in order to ensure orthogonality between the two terms). The form of J in Eq. (4) means that only single and double excitations are present in the first term. If, for example, we allow J to depend on products of two r_{ij}, or on the distance of the coalescence to a nucleus, then triple excitations would be present.

If we project the exact wave function ψ onto the space spanned by $\tilde{\psi}_0 J(\{r_{ij}\})$ for a given approximate $\tilde{\psi}_0$ and all possible functions $J(\{r_{ij}\})$, then the resulting correlation factor is optimum in the sense that the geminal basis functions $\tilde{\psi}_0 f_{12}(r_{ij})$ are optimally suited to fitting ψ, provided that a sufficiently complete basis is available for the remaining contributions to ψ. For a reasonable basis $\tilde{\psi}_0$ is a good approximation to the exact Hartree-Fock solution ψ_0 and the dependence of J on $\tilde{\psi}_0$ is not strong. Therefore, we define an optimum correlation factor for each molecular system as the projection of ψ onto the space spanned by $\psi_0 J(\{r_{ij}\})$ for all possible J of the form in Eq. (4).

There are several points to be raised concerning the optimum correlation factor. Firstly, we have made no reference to the energy in our definition of J. For r_{12} calculations using a given correlation method and basis set, the optimum J defined above does not guarantee a minimum energy with respect to all correlation factors of the form in Eq. (4). This is because the function space spanned by a finite basis is incomplete, and a lower energy may be obtained by adjusting J to compensate for these basis-set deficiencies (at the electron cusp or otherwise). We also observe that the same function f_{12} is used for singlet and triplet pairs. The optimum f_{12} will be a compromise between these two contributions, but it will be dominated by the singlet pairs since antisymmetry ensures that the wave function vanishes at the triplet pair coalescence. In addition, while the linear r_{12} correlation factor is universally applicable, the quality of a given function f_{12} is likely to depend on the molecular system. Since we desire a single f_{12} for use in all systems we are relying on the assumption that the second- and higher-order terms in Eqs. (1) and (2) are similar in all atoms and molecules. We expect that this is a reasonable assumption for valence-shell electron pairs. Lastly, we note that the optimum correlation factor in the context of the r_{12} methods introduced by Kutzelnigg and Klopper differs slightly from the optimum correlation factor for use in other explicitly correlated methods, such as the trans-correlated method[31,32] or quantum Monte Carlo.[33]

III. A STUDY OF HELIUM

Helium and the isoelectronic series of atomic cations are the simplest atomic systems exhibiting electronic correlation. For this reason they have been the subject of much theoretical study, and highly accurate approximate solutions to the Schrödinger equation have been computed as early as 1929 (due to Hylleraas[34]). The basic physics of correlation in molecules is found in helium, and the singlet and triplet electronic cusps are conveniently exhibited separately by the ^1S and ^3S states, respectively. Helium has been successfully used as an accessible model for more complicated systems, most notably in the construction of correlation energy functionals in density-functional theory,[35,36] and in the basis-set convergence behavior of wave-function-based correlation methods.[37] In this section we study the optimum singlet and triplet correlation factors for helium and the isoelectronic series of atomic cations in order to gain insight into more complex systems. In particular, we are looking for new correlation factors that are much better than linear r_{12}.

A. Optimum correlation factors for two-electron atoms and cations

Following Hylleraas we expand an approximate wave function for helium S states in terms of the coordinates r_1, r_2, and r_{12}, where r_1 and r_2 are the distances of electrons 1 and 2 from the nucleus, and r_{12} is the distance between the electrons. Transforming to elliptic coordinates $s = r_2 + r_1$, $t = r_2 - r_1$, and $u = r_{12}$ we write

$$\widetilde{\psi} = \sum_i c_i s^{p_i} t^{q_i} u^{r_i} \exp(-ks). \tag{6}$$

Singlet states ^1S require that the q_i are even and triplet ^3S states require that the q_i are odd. The basis is defined by n_{sum} such that $p_i + q_i + r_i \leqslant n_{sum}$ and the exponent k and the coefficients c_i are variational parameters. For the details of the Hamiltonian and the required integrals we refer the reader to Ref. 34. The energy of the ground-state ^1S is $-2.903\,724\,337E_h$ and the energy of the lowest ^3S is $-2.175\,229\,378E_h$. The convergence of the energy with n_{sum} is rapid and $n_{sum} = 10$ gives an error of 0.02 μE_h for the ^1S state and 0.5 μE_h for the ^3S state which is essentially exact for our purposes. Using the same basis functions the lowest-energy ^1S and ^3S Hartree-Fock (HF) wave functions are given by

$$^1\widetilde{\psi}_0 = \sqrt{\tfrac{1}{2}}(\varphi_1(r_1)\varphi_1(r_2) + \varphi_1(r_1)\varphi_1(r_2)), \tag{7}$$

$$^3\widetilde{\psi}_0 = \sqrt{\tfrac{1}{2}}(\varphi_1(r_1)\varphi_2(r_2) - \varphi_2(r_1)\varphi_1(r_2)), \tag{8}$$

$$\varphi_b(r_a) = \sum_{i=0}^{n} c_{b,i} r_a^i \exp(-kr_a), \tag{9}$$

and can be computed using the Hamiltonian given by Hylleraas in the usual manner. We do not optimize k, but use the value obtained from the $n_{sum} = 10$ Hylleraas CI calculation. The energy of the ground-state ^1S is $-2.861\,679\,996E_h$ and the energy of the lowest ^3S is $-2.174\,250\,778E_h$. The convergence of the HF energy with n is less rapid than the Hylleraas CI convergence, and $n = 8$ is required to converge to within 0.1 μE_h of the exact value ($n = 8$ corresponds to $n_{sum} = 16$). Using our highly accurate wave functions $\widetilde{\psi}$ and $\widetilde{\psi}_0$ we compute the optimum J as follows.

Let us rewrite Eq. (5) in first quantized form and expand $J(r_{12})$ as a polynomial series of powers of r_{12}, truncated at m,

$$\widetilde{\psi} = \widetilde{\psi}_0 J(r_{12}) + \widetilde{\psi}' \approx \widetilde{\psi}_0 \sum_{i=1}^{m} c_i r_{12}^{i-1} + \widetilde{\psi}'. \tag{10}$$

We are free to define $\widetilde{\psi}'$ such that $\langle \widetilde{\psi}_0 r_{12}^i | \widetilde{\psi}' \rangle = 0$ for all $i = 0, 1, \ldots$. Multiplying on the left by $\widetilde{\psi}_0 r_{12}^{j-1}$ and integrating results in a set of linear equations for the coefficients c_i,

$$a_i = \sum_{j=1}^{m} S_{ij} c_j, \tag{11}$$

$$S_{ij} = \langle \widetilde{\psi}_0 r_{12}^{i-1} | \widetilde{\psi}_0 r_{12}^{j-1} \rangle, \tag{12}$$

$$a_i = \langle \widetilde{\psi}_0 r_{12}^{i-1} | \widetilde{\psi} \rangle. \tag{13}$$

Through increasing n_{sum}, n, and m we obtain convergence of the form of J over the range of r_{12} for which $\widetilde{\psi}$ and $\widetilde{\psi}_0$ are valid. We perform our calculations using 16-byte precision and present results using $n_{sum} = 10$, $n = 12$, and $m = 30$. While the form of J has converged, the individual coefficients in the power-series expansion beyond the quadratic terms are not stable. The resulting optimum correlation factors for the
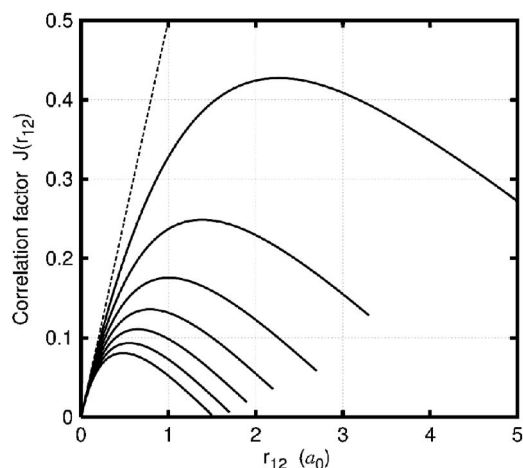
FIG. 1. The optimum correlation factor for the ground-state ^1S of helium and the isoelectronic series of atomic cations from $Z=3,\ldots,8$. The height of the function $J(r_{12})$ decreases as Z increases. The dashed line is the linear correlation factor $\frac{1}{2}r_{12}$.
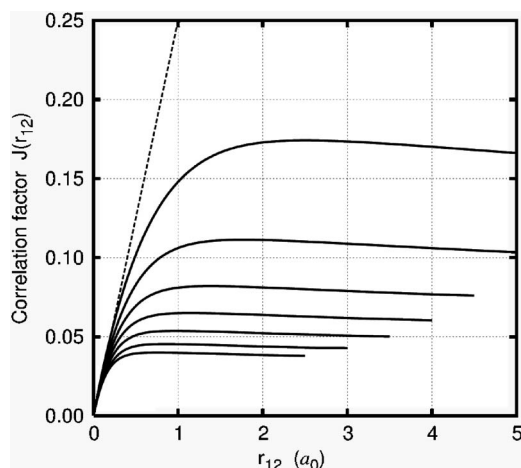

FIG. 2. The optimum correlation factor for the lowest-energy ^3S state of helium and the isoelectronic series of atomic cations from $Z=3,\ldots,8$. The height of the function $J(r_{12})$ decreases as Z increases. The dashed line is the linear correlation factor $\frac{1}{4}r_{12}$.

lowest-energy ^1S and ^3S states of helium and the isoelectronic series of atomic cations, $Z=3,\ldots,8$, are given in Figs. 1 and 2. The magnitude of the correlation factor decreases as the nuclear charge Z increases. The lines are cut at the point beyond which the convergence is less than the width of the lines in the figures and the linear correlation factors are included for comparison.

The optimum correlation factors follow the expected linear behavior at the coalescence $r_{12}\rightarrow 0$, and are damped for large r_{12}. The ^1S correlation factors seem to decay towards zero, while those of the ^3S states seem to tend to a constant. Both the ^1S and ^3S correlation factors have contributions at fairly long range, the maximum of the ^1S correlation factor for helium is at $2.26a_0$. For both the ^1S and ^3S states the form of the correlation factor is insensitive to the nuclear charge. If one scales each correlation function such that the maxima coincide, one sees that the shape of the correlation factors for each atomic cation are very similar, but not identical.

The computed optimum ^1S and ^3S correlation factors

strongly suggest that functions $f_{12}=\exp(-\zeta r_{12})$ and $f_{12}=r_{12}\exp(-\zeta r_{12})$ are likely to perform well in r_{12} calculations. The function $\exp(-\zeta r_{12})$ has already been proposed by Ten-no and is indeed a great improvement on linear r_{12} in MP2 calculations.[26] The short-range region of the ^1S and ^3S correlation factors are well reproduced by both $c\exp(-\zeta r_{12})$ and $cr_{12}\exp(-\zeta r_{12})$, as we illustrate in Table I and Fig. 3. In Table I we present the parameters c and ζ for the two functions fitted to the ^1S and ^3S correlation factors for helium. We give c and ζ resulting from numerical fits over the range $r_{12}=0\rightarrow x$ with $x=0.1a_0,\ldots,2.5a_0$. In Fig. 3 we depict the fits with $x=0.1$. The ^1S correlation factor is particularly well represented by $cr_{12}\exp(-\zeta r_{12})$ at short range. The behavior of the correlation factors beyond $2.0a_0$ is not well reproduced by either function.

In Table II we give the parameters c and ζ for both fitted numerically to the ^1S and ^3S correlation factors for each cation. The exponent for the ^3S correlation factor is larger than that of the ^1S state, indicating that the correlation hole is

TABLE I. Exponents ζ and coefficients c, in atomic units, of numerical fits to the ^1S and ^3S correlation factors for helium over the range $0\rightarrow x$ with $x=0.1a_0\ldots2.5a_0$.

|	Singlet				Triplet			
	$cr_{12}\exp(-\zeta r_{12})$		$c\exp(-\zeta r_{12})$		$cr_{12}\exp(-\zeta r_{12})$		$c\exp(-\zeta r_{12})$	
$0\rightarrow x$	c	ζ	c	ζ	c	ζ	c	ζ
0.1	0.493	0.403	0.607	0.813	0.286	0.691	0.204	1.404
0.2	0.493	0.402	0.603	0.819	0.286	0.689	0.202	1.422
0.3	0.493	0.402	0.598	0.826	0.286	0.686	0.199	1.439
0.4	0.493	0.402	0.593	0.834	0.286	0.682	0.197	1.456
0.5	0.493	0.403	0.586	0.844	0.286	0.678	0.196	1.472
0.6	0.494	0.404	0.580	0.855	0.285	0.673	0.194	1.488
0.8	0.494	0.407	0.565	0.881	0.284	0.663	0.191	1.519
1.0	0.495	0.412	0.551	0.911	0.282	0.651	0.189	1.547
1.2	0.497	0.416	0.536	0.943	0.280	0.637	0.187	1.574
1.5	0.499	0.422	0.517	0.995	0.276	0.616	0.184	1.611
2.0	0.502	0.429	0.489	1.088	0.266	0.577	0.181	1.664
2.5	0.505	0.434	0.466	1.191	0.255	0.539	0.179	1.709
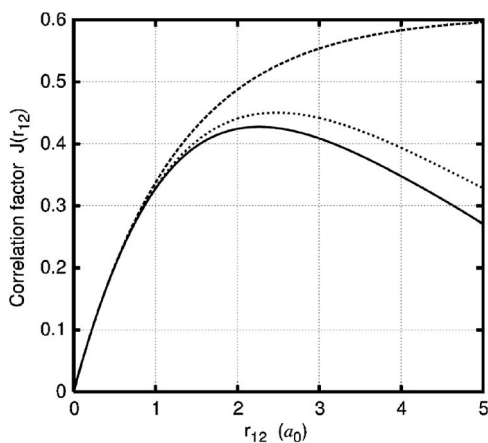
FIG. 3. The functions $c \exp(-\zeta r_{12})$ (dashed line) and $c r_{12} \exp(-\zeta r_{12})$ (dotted line) with c and ζ fitted numerically to the optimum correlation function (solid line) over the range $0 \rightarrow 0.1 a_0$ for the ^1S state of helium.

smaller. The HF ^3S solution is much closer to the exact ^3S wave function than the ^1S HF solution is to the true ground-state wave function due to the presence of the exchange hole. Table II shows that the exponents ζ increase linearly with nuclear charge Z for both the ^1S and ^3S cases. For $c \exp(-\zeta r_{12})$ the prefactor c is related to ζ through the requirement that the linear term is $\frac{1}{2}$ or $\frac{1}{4}$, and is therefore also linearly dependent on Z. This indicates that different exponents are appropriate for core and valence electrons. However, the effective nuclear charge experienced by valence electrons does not vary much between neutral molecules. It is likely that a single exponent will be sufficient for valence-only correlation factors, although anions and cations may require adjusted exponents.

B. Performance of the new correlation factors for helium

It is desirable to investigate the performance of the new correlation factors in the context of CI calculations on helium. Within the Hylleraas framework all integrals are known analytically, and the additional complications of the RI approximation are absent. Also, for CI calculations it is not necessary to project the r_{12} contribution onto specific excitations.

In the Hylleraas coordinate system the conventional CI expansion of the singlet and triplet S states in terms of products of one-electron functions becomes

$$\psi = \sum_{l=0}^{n-1} \sum_{i<j=0}^{n-l-1} c_{lij}(r_1^i r_2^j \pm r_1^j r_2^i)(r_{12}^2 - r_1^2 - r_2^2)^l$$
$$\times \exp(-k(r_1 + r_2)), \tag{14}$$

where c_{lij} are the CI coefficients and the exponent k optimizes the orbitals.[38] The corresponding HF wave functions, $^1\psi_0$ and $^3\psi_0$, are expressed in a similar way and are given in Eqs. (7)–(9). The size of the basis is determined by n, which is the principal quantum number in hydrogen-type functions and determines the maximum angular quantum number $l_{max} = n-1$. We fix the exponent k such that the HF wave function is optimized. In this context the r_{12} method is to add an additional two-particle basis function $\psi_0 J(r_{12})$, where we choose f_{12} in Eq. (4) to be one of

$$f_{12} = \exp(-\zeta r_{12}), \tag{15}$$

$$f_{12} = r_{12} \exp(-\zeta r_{12}). \tag{16}$$

The coefficients c_{lij} and the coefficient in $\psi_0 J(r_{12})$ are determined through solving the secular equations for the ground state, and no difficulties with linear dependencies are encountered.

In Figs. 4 and 5 we present the results of calculations using the two correlation factors in Eqs. (15) and (16) for the basis sets with $l_{max} = 2, 3, 4, 5$, and with varying ζ. The results with a linear correlation factor correspond to the point where $\zeta = 0$ in Fig. 5. We only present the results from calculations on the singlet state. In the above CI expansion there is only one exponent, whereas two exponents are needed for a good representation of the triplet for moderate l_{max}. For the ^3S state the r_{12} contributions are largest when ζ is small, indicating that a diffuse r_{12} term attempts to compensate for the inflexible basis, rather than to fit the cusp. In Fig. 4 the value at $\zeta = 0$ is that of the conventional CI method, which has one less basis function than the f_{12} method. The curve is discontinuous at this point and the conventional CI value does not lie in the range of the graph. The value of the

TABLE II. Exponents ζ and coefficients c, in atomic units, of numerical fits to the ^1S and ^3S correlation factors for the helium and the series of isoelectronic atomic cations. The fitting range is from coalescence to the value of r_{12} at half the maximum height.

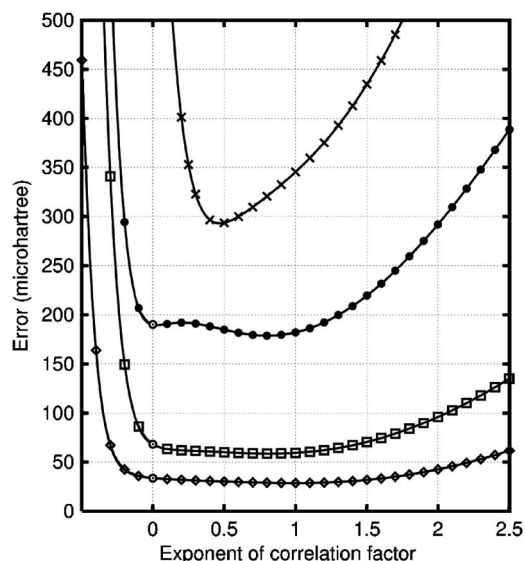| | Singlet | | | | Triplet | | | |
| | $c r_{12} \exp(-\zeta r_{12})$ | | $c \exp(-\zeta r_{12})$ | | $c r_{12} \exp(-\zeta r_{12})$ | | $c \exp(-\zeta r_{12})$ | |
Atomic no.	c	ζ	c	ζ	c	ζ	c	ζ
2	0.496	0.415	0.541	0.932	0.279	0.634	0.186	1.580
3	0.488	0.722	0.303	1.641	0.267	0.947	0.118	2.400
4	0.484	1.030	0.210	2.350	0.262	1.262	0.086	3.235
5	0.482	1.336	0.161	3.057	0.260	1.579	0.068	4.091
6	0.481	1.641	0.131	3.764	0.257	1.884	0.056	4.913
7	0.480	1.947	0.110	4.471	0.250	2.161	0.048	5.636
8	0.479	2.252	0.095	5.178	0.256	2.510	0.042	6.632

FIG. 4. The error in the correlation energy of helium as function of the exponent ζ of the correlation factor $\exp(-\zeta r_{12})$, as obtained with the CI basis with $l_{max}=2,3,4,5$, symbols $\times$, $\bullet$, $\square$, and $\diamond$, respectively.

correlation energy as ζ tends to zero is precisely the value for the linear-r_{12} method, and is the same as in Fig. 5 where there is no discontinuity.

Figures 4 and 5 show that both new correlation factors are significant improvements over the linear-r_{12} correlation factor when an appropriate ζ is used especially for the small basis sets $l_{max}=2,3$. For both correlation factors with small basis sets there are two minima in the correlation energy, one at $\zeta \rightarrow 0$ and one at a positive value. The correlation factors with small ζ are very diffuse, and rather than closely fitting the cusp, make up for the lack of flexibility of the CI basis to describe the longer-range correlation. For the larger basis sets the minima at $\zeta \rightarrow 0$ disappear. At the positive minima the correlation energy computed with a given l_{max} using the two correlation factors is basically the same.
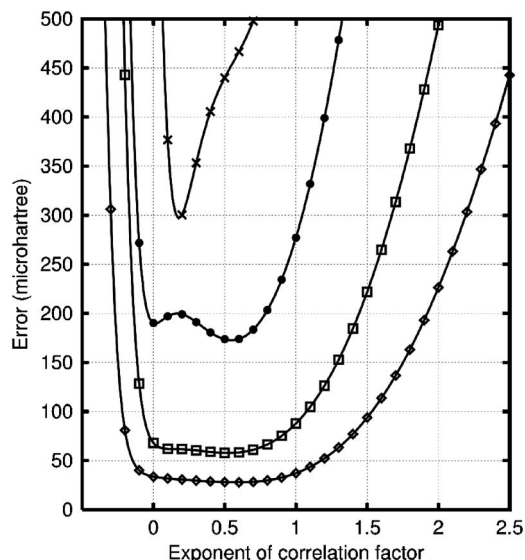

FIG. 5. The error in the correlation energy of helium as function of the exponent ζ of the correlation factor $r_{12}\exp(-\zeta r_{12})$, as obtained with the CI basis with $l_{max}=2,3,4,5$, symbols $\times$, $\bullet$, $\square$, and $\diamond$, respectively.

The values of ζ at the minima for both functions are in most cases slightly larger than the exponent predicted from a fit to the optimum correlation factor. Since the long-range behavior of the functions (15) and (16) differs significantly from the optimum correlation factor, a more compact correlation function is preferred. As one enlarges the basis the region at the cusp that is poorly described by the CI expansion shrinks and the optimum exponent ζ_{opt} increases.

For both functions the correlation energy becomes less sensitive to ζ as the basis set increases, and the range of ζ for which the correlation energy is better than the linear-r_{12} value widens. The dependence of the correlation energy on ζ appears to be fairly similar for the two functions, with a scaling factor of around 1.7 relating them. Taylor expanding each function and fixing both linear terms at $\frac{1}{2}$ reveals that the second-order terms of the two functions are related by scaling ζ by a factor of two, and that the terms of order n are related by scaling ζ by a factor of $n^{1/(n-1)}$. We argue that since the quadratic terms are in part already included in the conventional CI expansion, the cubic terms are responsible for the scaling behavior, with $3^{1/2} \approx 1.7$.

In summary we conclude that both correlation functions are more efficient at describing the cusp than linear r_{12}, and that results of essentially the same quality may be obtained from both. The function $\exp(-\zeta r_{12})$ gives a more compact representation of the cusp than $r_{12}\exp(-\zeta r_{12})$. This leads to a better separation of the short- and long-range correlation effects and less sensitivity to the exponent ζ. This is advantageous since the optimum exponent ζ will depend on the chemical system.

IV. THE MP2-F12 METHOD

Ten-no has demonstrated that the nonlinear correlation factor $\exp(-\zeta r_{12})$ is a great improvement over the linear correlation factor for MP2 calculations.[26] The results of the previous section indicate that the correlation factor $r_{12}\exp(-\zeta r_{12})$ is also likely to perform well in MP2 calculations. Ten-no reports two implementations of the correlation factor $\exp(-\zeta r_{12})$, one where the required integrals are computed explicitly by replacing the Boys function with a novel function and one where $\exp(-\zeta r_{12})$ is fitted with a linear combination of Gaussian-type geminals. The results from both methods are very similar. We would like to test a range of correlation factors and therefore adopt the latter strategy. The acronym MP2-R12 is used exclusively for second-order perturbation theory with linear-r_{12} terms. When we use a nonlinear correlation factor we denote the method MP2-F12.

Motivated by the success of Ten-no's correlation factor Eq. (15) and our new correlation factor Eq. (16) we also investigate two other correlation factors, namely,

$$f_{12} = \text{erfc}(\zeta r_{12}), \tag{17}$$

$$f_{12} = r_{12}\,\text{erfc}(\zeta r_{12}). \tag{18}$$

The error function behaves slightly differently from the exponential function, and we are interested in comparing the performance of the functions, particularly because the error function may be implemented directly if it is successful. The

TABLE III. Exponents α_k and coefficients c_k of fits to the function $\exp(-\zeta r_{12})$ with $\zeta=1.0a_0^{-1}$ in terms of N functions of the form $\exp(-\alpha_k r_{12}^2)$.

Parameter	N	k=1	k=2	k=3	k=4	k=5	k=6
α_k/a_0^{-2}	1	0.6853					
	2	0.4254	4.520				
	3	0.3303	2.321	16.28			
	4	0.2783	1.591	7.637	45.74		
	5	0.2447	1.225	4.924	19.88	112.7	
	6	0.2209	1.004	3.622	12.16	45.87	254.4
c_k	1	0.7354					
	2	0.5640	0.3102				
	3	0.4683	0.3087	0.1529			
	4	0.4025	0.3090	0.1570	0.088 98		
	5	0.3532	0.3072	0.1629	0.093 21	0.056 19	
	6	0.3144	0.3037	0.1681	0.098 11	0.060 24	0.037 26

TABLE V. Exponents α_k and coefficients c_k of fits to the function $\mathrm{erfc}(\zeta r_{12})$ with $\zeta=1.0a_0^{-1}$ in terms of N functions of the form $\exp(-\alpha_k r_{12}^2)$.

Parameter	N	k=1	k=2	k=3	k=4	k=5	k=6
α_k/a_0^{-2}	1	1.701					
	2	1.370	8.312				
	3	1.256	4.702	28.77			
	4	1.198	3.495	14.06	80.56		
	5	1.161	2.888	9.417	35.75	199.1	
	6	1.136	2.521	7.177	22.32	82.04	451.5
c_k	1	0.7658					
	2	0.6232	0.2676				
	3	0.5466	0.2623	0.1308			
	4	0.4948	0.2604	0.1327	0.075 85		
	5	0.4563	0.2577	0.1363	0.078 86	0.047 74	
	6	0.4260	0.2543	0.1393	0.082 44	0.050 94	0.03157

apparent advantage of Eqs. (16) and (18) is that for $\zeta \to 0$, the linear-r_{12} method is obtained, whereas only the standard electron-correlation method is obtained for the correlation factors of Eqs. (15) and (17) in this limit.

We approximate the correlation factors f_{12} of Eqs. (15) and (17) by a linear combination of Gaussian-type geminals, and similarly, the correlation factors f_{12} of Eqs. (16) and (18) by a linear combination of products of r_{12} with Gaussian-type geminals

$$\tilde{f}_{12} = \sum_{k=1}^{N} c_k \exp(-\alpha_k r_{12}^2), \tag{19}$$

$$\tilde{f}_{12} = \sum_{k=1}^{N} c_k r_{12} \exp(-\alpha_k r_{12}^2). \tag{20}$$

The required integrals with the factors $r_{12} \exp(-\beta r_{12}^2)$ were available from earlier work,[39] those with $\exp(-\beta r_{12}^2)$ were implemented in the course of the present work by means of minor modifications of the code developed in Ref. 39.

The expansion coefficients c_k and exponents α_k were determined for $N=1, 2, \ldots, 6$ by minimizing the function

$$T = \int_0^{\infty} \{f_{12} - \tilde{f}_{12}\}^2 \exp(-\beta r_{12}^2) r_{12}^2 dr_{12}. \tag{21}$$

The factor r_{12}^2 is the Jacobian and we include a weighting function $\exp(-\beta r_{12}^2)$ with $\beta=2.0a_0^{-2}$. The corresponding expansion coefficients and exponents for the correlation factors, $\exp(-\zeta r_{12})$, $r_{12} \exp(-\zeta r_{12})$, $\mathrm{erfc}(\zeta r_{12})$, and $r_{12} \mathrm{erfc}(\zeta r_{12})$, are given in Tables III–VI, respectively. In Table VII we present the representative results for how the MP2-F12 energy depends on N, the number of terms in the expansion. For $N \geq 3$, the results are essentially converged. It is interesting to note that the corresponding fits without the weighting function converge much more slowly, indicating that the behavior of f_{12} for small r_{12} is energetically dominant.

In the following, all MP2-R12 and MP2-F12 calculations are performed with $N=6$, for ansatz 2, and almost exclusively in approximation B (see Ref. 21 for details on ansatz 2 and approximation B; we use the hybrid approach of Ref. 40). In ansatz 2, the explicitly correlated pair functions take the form

$$(1 - \hat{O}_1)(1 - \hat{O}_2) f_{12} \varphi_i(1) \varphi_j(2), \tag{22}$$

where $\hat{O} = \sum_k |k\rangle\langle k|$ is the projector onto the space spanned by the occupied Hartree-Fock orbitals and where φ_i and φ_j are

TABLE IV. Exponents α_k and coefficients c_k of fits to the function $r_{12} \exp(-\zeta r_{12})$ with $\zeta=1.0a_0^{-1}$ in terms of N functions of the form $r_{12} \exp(-\alpha_k r_{12}^2)$.

Parameter	N	k=1	k=2	k=3	k=4	k=5	k=6
α_k/a_0^{-2}	1	0.5230					
	2	0.3383	2.652				
	3	0.2670	1.503	7.928			
	4	0.2272	1.077	4.270	18.85		
	5	0.2011	0.8520	2.941	9.710	39.80	
	6	0.1824	0.7118	2.252	6.474	19.66	77.92
c_k	1	0.6498					
	2	0.4806	0.3307				
	3	0.3880	0.3184	0.1768			
	4	0.3259	0.3108	0.1755	0.1102		
	5	0.2804	0.3026	0.1785	0.1100	0.074 50	
	6	0.2454	0.2938	0.1815	0.1128	0.075 02	0.052 80

TABLE VI. Exponents α_k and coefficients c_k of fits to the function $r_{12} \mathrm{erfc}(\zeta r_{12})$ with $\zeta=1.0a_0^{-1}$ in terms of N functions of the form $r_{12} \exp(-\alpha_k r_{12}^2)$.

Parameter	N	k=1	k=2	k=3	k=4	k=5	k=6
α_k/a_0^{-2}	1	1.492					
	2	1.266	5.257				
	3	1.185	3.351	14.61			
	4	1.143	2.643	8.308	34.11		
	5	1.117	2.269	6.008	18.08	71.71	
	6	1.099	2.037	4.815	12.39	36.03	140.5
c_k	1	0.6939					
	2	0.5564	0.2815				
	3	0.4835	0.2677	0.1493			
	4	0.4350	0.2602	0.1460	0.092 97		
	5	0.3993	0.2535	0.1468	0.091 91	0.062 78	
	6	0.3716	0.2472	0.1478	0.093 46	0.062 82	0.044 42

TABLE VII. Valence-shell second-order Møller-Plesset correlation energy $[-E^{(2)}$ in] of the Ne atom, obtained in the aug-cc-pVQZ basis, as function of the number (N) of terms in the expansion of the correlation factor.

| | f_{12} | | | |
| | $\exp(-\zeta r_{12})$ | $r_{12}\exp(-\zeta r_{12})$ | $\mathrm{erfc}(\zeta r_{12})$ | $r_{12}\,\mathrm{erfc}(\zeta r_{12})$ |
N	$\zeta=1.62a_0^{-1}$	$\zeta=0.68a_0^{-1}$	$\zeta=1.51a_0^{-1}$	$\zeta=0.41a_0^{-1}$
1	305.11	316.16	311.88	316.18
2	316.54	317.81	317.17	317.37
3	317.98	318.32	317.68	317.91
4	318.32	318.40	317.74	318.02
5	318.43	318.42	317.75	317.98
6	318.46	318.42	317.75	317.97

two such orbitals. The invocation of approximation B implies that no terms were neglected (but we shall also report a few results for approximation A′, in which terms involving the exchange operator are omitted).

The calculations were performed in the correlation-consistent basis sets cc-pVXZ,[41] aug-cc-pVXZ,[42] or cc-pCVXZ.[43] The auxiliary basis sets for the RI approximation were taken from Ref. 21. We used the different sets of Ref. 21 for calculations with and without frozen core, but in the present work, we used them in the framework of the complementary-auxiliary-basis-set (CABS) approach of Valeev.[25] In this approach, the auxiliary basis is first orthogonalized against the orbital basis and then the remaining functions are mutually orthonormalized. Hence, the final (orthonormal) basis used for the RI approximation consists of the orbital basis plus that part of the auxiliary basis that is orthogonal on the orbital basis. All MP2-F12 as well as all MP2-R12 calculations were carried out with a local version of the DALTON program.[44]

Finally, we note that the evaluation of the necessary integrals is not time consuming. Since we expand the Cartesian overlap distributions in Hermite functions, the sums over the N terms in the fitting function of Eqs. (19) and (20) only occur at the level where the two-electron integrals over Hermite functions are computed. More specifically, only the calculation of the integrals R_k^{tuv} (with $k=2,3,4,6$) as given in Eqs. (25)–(28) of Ref. 39 is affected. The number of integrals R_2^{tuv} and R_3^{tuv} scales linearly with the number N in the expansion while the number of integrals R_4^{tuv} and R_6^{tuv} scales quadratically. However, the latter two types of integrals only occur for the orbital basis, not for the auxiliary basis.

V. THE PERFORMANCE OF THE MP2-F12 METHOD

In Figs. 6 and 7 we present the MP2-F12 valence-shell correlation energy of Ne, calculated using the 2B approach with augmented correlation-consistent basis sets aug-cc-pVXZ with $X=2,\ldots,4$. The results using the correlation factors $\exp(-\zeta r_{12})$ and $r_{12}\exp(-\zeta r_{12})$ are presented in Fig. 6 as a function of ζ, and the corresponding results from $\mathrm{erfc}(\zeta r_{12})$ and $r_{12}\,\mathrm{erfc}(\zeta r_{12})$ are presented in Fig. 7. The points at which the curves for $r_{12}\exp(-\zeta r_{12})$ and $r_{12}\,\mathrm{erfc}(\zeta r_{12})$ touch the ordinate (with zero slope) are the MP2-R12 values.
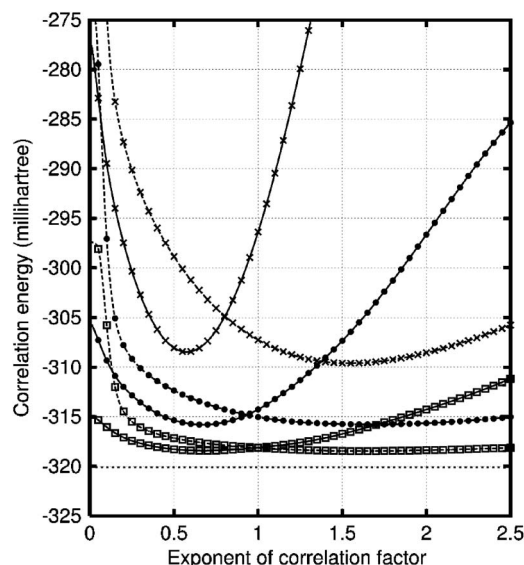

FIG. 6. Valence-shell second-order Møller-Plesset correlation energy of the Ne atom as function of the exponent ζ of the correlation factors $\exp(-\zeta r_{12})$ (dashed lines) or $r_{12}\exp(-\zeta r_{12})$ (solid lines), as obtained in the aug-cc-pVDZ ($\times$), aug-cc-pVTZ ($\bullet$), and aug-cc-pVQZ ($\square$) basis sets.

It is clear that all the MP2-F12 results represent significant improvements over the MP2-R12 energies. The minima of the curves for functions $\exp(-\zeta r_{12})$ and $r_{12}\exp(-\zeta r_{12})$ lie slightly below those of $\mathrm{erfc}(\zeta r_{12})$ and $r_{12}\,\mathrm{erfc}(\zeta r_{12})$. The best MP2-F12/aug-cc-pVXZ energies are below the MP2-R12/aug-cc-pV$(X+1)$Z energies for all X. Hence the gain in accuracy of the correlation factors $\exp(-\zeta r_{12})$ and $r_{12}\exp(-\zeta r_{12})$ over MP2-R12 is greater than that of increasing the cardinal number of the basis in MP2-R12 calculations by one unit.

From Fig. 6 we see that for the functions $\exp(-\zeta r_{12})$ and $r_{12}\exp(-\zeta r_{12})$ the dependence of the correlation energy with ζ is very similar to that of the CI calculations in Sec. III B.
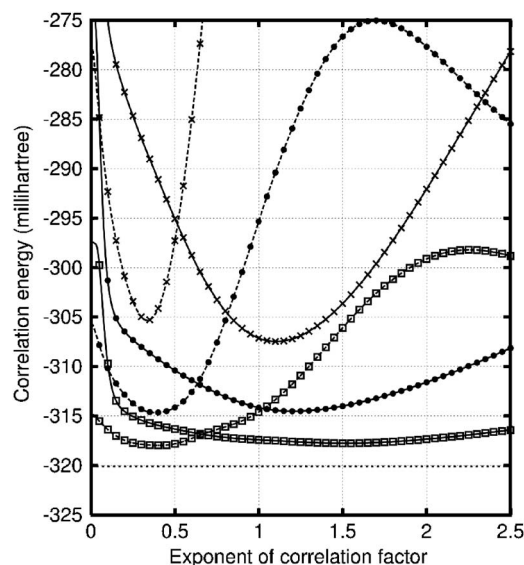

FIG. 7. Valence-shell second-order Møller-Plesset correlation energy of the Ne atom as function of the exponent ζ of the correlation factors $\mathrm{erfc}(\zeta r_{12})$ (dashed lines) or $r_{12}\,\mathrm{erfc}(\zeta r_{12})$ (solid lines), as obtained in the aug-cc-pVDZ ($\times$), aug-cc-pVTZ ($\bullet$), and aug-cc-pVQZ ($\square$) basis sets.

TABLE VIII. Valence-shell second-order Møller-Plesset correlation energy $[-E^{(2)}$ in $]$ of the Ne atom, as obtained at the MP2 and MP2-R12 levels. The basis-set limit is $E^{(2)}=-320.1$ (Ref. 21).

Basis	MP2	MP2-R12	
		2A′	2B
aug-cc-pVDZ	206.87	291.17	277.31
aug-cc-pVTZ	272.52	309.74	305.61
aug-cc-pVQZ	297.24	316.40	314.84
aug-cc-pV5Z	307.97	318.63	318.15
aug-cc-pV6Z	312.87	319.48	319.27

Energetically there is very little to choose between the two correlation factors, but the MP2 correlation energy computed using $\exp(-\zeta r_{12})$ is less sensitive on the exponent ζ. From Fig. 7 we see that the dependence of the correlation energy with ζ for the functions $\mathrm{erfc}(\zeta r_{12})$ and $r_{12}\,\mathrm{erfc}(\zeta r_{12})$ follows a similar pattern, with tighter curves than the corresponding exponential functions, as one would expect.

For each correlation factor and basis we determine the optimal exponents ζ_{opt} by locating the minima of the curves in Figs. 6 and 7. In Tables VIII–X we report ζ_{opt} and the corresponding MP2-F12/2B energies. We also include the MP2-F12/2A′ energy at ζ_{opt} and the corresponding MP2-R12 and standard MP2 results. The results become less dependent on the exponent ζ for larger basis sets and the aug-cc-pV5Z and augmented correlation-consistent polarized valence sextuple-zeta (aug-cc-pV6Z) curves are very flat. Taking the function $r_{12}\exp(-\zeta r_{12})$ as an example (Table IX), in the aug-cc-pVDZ basis, the MP2-R12/2B error amounts to 42.8 mE$_h$. It is reduced to only 11.7 mE$_h$ at the MP2-F12/2B level. The same is observed for the larger basis sets, where the MP2-R12/2B error is also reduced by about a factor of three. Furthermore, we observe that energies below the limiting value of $E^{(2)}=-320.1$ mE$_h$ are obtained at the MP2-F12/2A′ level, which is not variational due to the neglect of the terms that involve the exchange operator (cf. Ref. 21). Thus, one should not attempt to optimize the exponent ζ of the new correlation factor at the 2A′ level (the same is true for the 2A level).

Rather than investigating the new approach with very large basis sets, we are particularly interested in whether the new correlation factors give improved results for medium-sized basis sets of triple- and quadruple-zeta quality. The

TABLE IX. Valence-shell second-order Møller-Plesset correlation energy $[-E^{(2)}$ in $]$ of the Ne atom, obtained at the MP2-F12 level with the correlation factors $\exp(-\zeta r_{12})$ and $r_{12}\exp(-\zeta r_{12})$. The basis-set limit is $E^{(2)}=-320.1$ (Ref. 21).

Basis	$\exp(-\zeta r_{12})$			$r_{12}\exp(-\zeta r_{12})$		
	ζ_{opt}[a]	2A′	2B	ζ_{opt}[a]	2A′	2B
aug-cc-pVDZ	1.54	323.97	309.60	0.58	323.72	308.46
aug-cc-pVTZ	1.67	319.51	315.77	0.67	319.85	315.79
aug-cc-pVQZ	1.62	319.71	318.46	0.68	319.73	318.42
aug-cc-pV5Z	1.79	319.94	319.48	0.83	319.97	319.50
aug-cc-pV6Z	1.87	320.08	319.87	0.88	320.09	319.88

[a]In a_0^{-1}, optimized at the MP2-F12/B level.

TABLE X. Valence-shell second-order Møller-Plesset correlation energy $[-E^{(2)}$ in $]$ of the Ne atom, obtained at the MP2-F12 level with the correlation factors $\mathrm{erfc}(\zeta r_{12})$ and $r_{12}\,\mathrm{erfc}(\zeta r_{12})$. The basis-set limit is $E^{(2)}=-320.1$ (Ref. 21).

Basis	$\mathrm{erfc}(\zeta r_{12})$			$r_{12}\,\mathrm{erfc}(\zeta r_{12})$		
	ζ_{opt}[a]	2A′	2B	ζ_{opt}[a]	2A′	2B
aug-cc-pVDZ	1.10	322.61	307.48	0.34	321.06	305.34
aug-cc-pVTZ	1.21	318.58	314.52	0.39	319.19	314.67
aug-cc-pVQZ	1.51	319.06	317.75	0.41	319.43	317.97
aug-cc-pV5Z	1.62	319.65	319.14	0.42	319.84	319.31
aug-cc-pV6Z	1.70	319.93	319.69	0.55	320.02	319.78

[a]In a_0^{-1}, optimized at the MP2-F12/2B level.

results using the four correlation factors in Eqs. (15)–(18) for Ne and a selection of small molecules are reported in Tables XI–XIV. The tables show that the pattern observed for Ne is indeed representative of the molecules investigated. In all cases the MP2-F12 results are great improvements over the MP2-R12 results when ζ is chosen appropriately. The optimum value of ζ changes a little with the molecule being computed, with the same trend for all correlation factors. The greater the electronegativity of the atoms in the molecule, the greater the optimum value of ζ is, as one would expect from the conclusions of Sec. III A.

The functions $\exp(-\zeta r_{12})$ and $r_{12}\exp(-\zeta r_{12})$ perform better than the functions $\mathrm{erfc}(\zeta r_{12})$ and $r_{12}\,\mathrm{erfc}(\zeta r_{12})$ over the set of molecules investigated, and since the performance of $\exp(-\zeta r_{12})$ is less sensitive to the exponent ζ, this seems to be the best choice. For all systems, the MP2-F12/aug-cc-pVTZ energies (with optimized ζ) lie below the MP2-R12/aug-cc-pVQZ energies. The same holds for the MP2-F12/aug-cc-pVQZ energies if we compare them with the energies reported in Ref. 40. These are very encouraging results.

VI. BASIS-SET INVESTIGATIONS

All of the results in the previous section are computed using augmented correlation-consistent basis sets aug-cc-pVXZ, and we recommend that augmented basis sets should be used for MP2-F12 methods, unless a basis set specifically optimized for this purpose is available. We illustrate this point through the following study, taking the correlation factor $r_{12}\exp(-\zeta r_{12})$ applied to Ne as an example.

In Fig. 8 we compare the results of valence-shell MP2-F12/2B calculations for the cc-pVXZ basis sets $(X=3,4)$ with and without augmentation. The effect of the diffuse functions is to lower the energy at every ζ as expected, and also to shift the optimum ζ to larger values. Since a small ζ gives a diffuse correlation factor this indicates that the geminal basis functions attempt to compensate for the lack of diffuse functions in the orbital basis.

If one adds the s, p, and d augmentation functions to the cc-pVDZ basis separately, one finds that the s functions have almost no energetic effect, and that the effect of the d functions is twice that of the p functions. Moreover, one sees that only the d functions are responsible for the change in the

TABLE XI. Valence-shell second-order Møller-Plesset correlation energies $[-E^{(2)}$ in $mE_h]$ as function of ζ for Ne and a selection of small test molecules as obtained from MP2-F12/2B calculations with the correlation factor $f_{12}=\exp(-\zeta r_{12})$ in an augmented correlation-consistent aug-cc-pVXZ basis with cardinal number $X=3$ or $X=4$.

Molecule[a]	X	ζ/a_0^{-1}								Limiting value[c]
		0.0[b]	0.8	1.0	1.2	1.4	1.6	1.8	2.0	
CH_2	3	141.03	154.64	154.80	154.86	154.81	154.68	154.49	154.27	
	4	149.29	155.46	155.51	155.53	155.52	155.50	155.46	155.41	155.9
H_2O	3	268.36	297.10	297.56	297.80	297.90	297.88	297.74	297.52	
	4	285.93	299.33	299.50	299.59	299.62	299.60	299.57	299.51	300.5
NH_3	3	240.19	262.32	262.64	262.79	262.82	262.74	262.56	262.32	
	4	253.78	263.81	263.92	263.97	263.97	263.95	263.92	263.87	264.5
HF	3	279.73	315.09	315.70	316.03	316.17	316.21	316.14	315.98	
	4	301.14	318.07	318.28	318.42	318.49	318.50	318.46	318.40	319.7
N_2	3	379.59	416.48	417.15	417.50	417.60	417.48	417.18	416.74	
	4	401.85	419.30	419.52	419.62	419.64	419.61	419.55	419.46	421.0
CO	3	360.08	399.19	399.92	400.27	400.37	400.29	400.04	399.66	
	4	383.88	402.14	402.38	402.52	402.56	402.54	402.47	402.38	403.9
Ne	3	272.52	314.26	315.03	315.47	315.69	315.76	315.75	315.65	
	4	297.24	317.88	318.13	318.30	318.42	318.46	318.44	318.37	320.1
F_2	3	535.99	602.63	603.90	604.59	604.95	605.10	605.06	604.83	
	4	575.71	608.28	608.70	609.00	609.15	609.18	609.11	609.01	611.7

[a]Geometries as in Ref. 21. Results are reported for CH_2 in its $^1A_1$ state.
[b]Standard MP2 value.
[c]From Ref. 21.

ζ dependence. An examination of the pair energy contributions to the MP2 correlation energy as a function of ζ reveals that the different ζ dependence is almost entirely due to the $2p$-$2p$ electron pairs. This means that there is a redundancy between the configurations with orbital replacements $p \rightarrow d$ and the geminal basis functions. Depending on the exponents, both are attempting to describe either the electron cusp or the outer regions of the wave function. The description of the electron cusp requires large exponents, and small exponents are required for the regions of the wave function away from the nucleus.

The current basis sets are optimized for standard methods,[41] and the exponents of the polarization functions are too large for MP2-F12 calculations, where the geminals take care of the cusp. We have therefore attempted to estimate the effect of optimizing the cc-pVXZ basis set, taking

TABLE XII. Valence-shell second-order Møller-Plesset correlation energies $[-E^{(2)}$ in $mE_h]$ as function of ζ for Ne and a selection of small test molecules as obtained from MP2-F12/2B calculations with the correlation factor $f_{12}=r_{12}\exp(-\zeta r_{12})$ in an augmented correlation-consistent aug-cc-pVXZ basis with cardinal number $X=3$ or $X=4$.

Molecule[a]	X	ζ/a_0^{-1}								Limiting value[c]
		0.0[b]	0.4	0.5	0.6	0.7	0.8	0.9	1.0	
CH_2	3	150.85	154.74	154.77	154.56	154.12	153.52	152.78	151.89	
	4	154.29	155.47	155.50	155.49	155.46	155.39	155.27	155.12	155.9
H_2O	3	290.18	297.41	297.78	297.85	297.61	297.08	296.29	295.32	
	4	297.09	299.41	299.54	299.58	299.56	299.51	299.42	299.28	300.5
NH_3	3	256.68	262.53	262.74	262.67	262.32	261.75	261.01	260.12	
	4	262.12	263.85	263.92	263.94	263.92	263.88	263.79	263.65	264.5
HF	3	307.24	315.45	315.99	316.20	316.13	315.75	315.07	314.1	
	4	315.45	318.18	318.36	318.45	318.46	318.41	318.31	318.19	319.7
N_2	3	405.69	416.90	417.28	417.05	416.26	415.02	413.43	411.53	
	4	415.99	419.38	419.51	419.53	419.47	419.35	419.14	418.82	421.0
CO	3	388.48	399.64	400.11	400.00	399.36	398.25	396.76	394.96	
	4	398.73	402.25	402.42	402.48	402.44	402.33	402.14	401.86	403.9
Ne	3	305.61	314.66	315.36	315.72	315.78	315.56	315.05	314.26	
	4	314.84	318.05	318.28	318.39	318.42	318.36	318.25	318.11	320.1
F_2	3	587.24	603.26	604.32	604.78	604.66	603.95	602.67	600.88	
	4	602.98	608.49	608.84	609.00	609.00	608.88	608.69	608.42	611.7

[a]Geometries as in Ref. 21. Results are reported for CH_2 in its $^1A_1$ state.
[b]MP2-R12/2B value.
[c]From Ref. 21.

TABLE XIII. Valence-shell second-order Møller-Plesset correlation energies $[-E^{(2)}$ in $mE_h]$ as function of ζ for Ne and a selection of small test molecules as obtained from MP2-F12/2B calculations with the correlation factor $f_{12}=\mathrm{erfc}(\zeta r_{12})$ in an augmented correlation-consistent aug-cc-pVXZ basis with cardinal number $X=3$ or $X=4$.

Molecule[a]	X	0.0[b]	0.6	0.8	1.0	1.2	1.4	1.6	1.8	Limiting value[c]
						ζ/a_0^{-1}				
CH_2	3	141.03	154.01	154.44	154.32	153.89	153.29	152.56	151.77	
	4	149.29	155.13	155.26	155.36	155.36	155.26	155.09	154.86	155.9
H_2O	3	268.36	295.33	296.60	297.10	296.94	296.37	295.50	294.39	
	4	285.93	298.61	298.91	299.13	299.26	299.24	299.10	298.86	300.5
NH_3	3	240.19	261.11	262.00	262.19	261.92	261.33	260.49	259.46	
	4	253.78	263.31	263.52	263.69	263.75	263.69	263.54	263.31	264.5
HF	3	279.73	312.74	314.25	315.11	315.20	314.74	313.93	312.87	
	4	301.14	317.08	317.52	317.77	317.95	318.02	317.92	317.71	319.7
N_2	3	379.59	414.33	416.00	416.34	415.82	414.69	413.13	411.27	
	4	401.85	418.30	418.70	419.02	419.14	419.04	418.74	418.30	421.0
CO	3	360.08	396.91	398.75	399.28	398.80	397.68	396.14	394.32	
	4	383.88	400.68	401.64	401.97	401.93	401.56	401.01	400.17	403.9
Ne	3	272.52	311.40	313.06	314.16	314.52	314.29	313.65	312.73	
	4	297.24	316.66	317.17	317.41	317.59	317.73	317.74	317.60	320.1
F_2	3	535.99	598.16	601.19	602.87	603.12	602.35	600.87	598.85	
	4	575.71	606.36	607.20	607.64	608.00	608.13	607.97	607.58	611.7

[a]Geometries as in Ref. 21. Results are reported for CH_2 in its $^1A_1$ state.
[b]Standard MP2 value.
[c]From Ref. 21.

the Ne atom as an example. We have not fully optimized the basis set but rather scaled (with a common factor γ) the exponents of the polarization functions of the cc-pVTZ and cc-pVQZ basis sets of Ne at the MP2-F12/2B level. In Figs. 9 and 10 we present plots of the valence-shell correlation energy as a function of γ and ζ. As the polarization functions become more diffuse, the optimum exponent for the correlation factor increases, and the dependence of the energy on

ζ becomes flatter paralleling that of the aug-cc-pVXZ basis. In absolute terms there is only a slight energy gain in optimizing both γ and ζ, relative to optimizing ζ for the standard basis ($\gamma=1$). However, reducing γ so that the polarization functions are more diffuse makes the correlation energy much less sensitive to the exponent ζ in the correlation factor, and the same optimum ζ is obtained for the cc-pVXZ and aug-cc-pVXZ basis sets. It is certainly desirable that the

TABLE XIV. Valence-shell second-order Møller-Plesset correlation energies $[-E^{(2)}$ in $mE_h]$ as function of ζ for Ne and a selection of small test molecules as obtained from MP2-F12/2B calculations with the correlation factor $f_{12}=r_{12}\,\mathrm{erfc}(\zeta r_{12})$ in an augmented correlation-consistent aug-cc-pVXZ basis with cardinal number $X=3$ or $X=4$.

Molecule[a]	X	0.0[b]	0.1	0.2	0.3	0.4	0.5	0.6	0.7	Limiting value[c]
						ζ/a_0^{-1}				
CH_2	3	150.85	153.15	154.10	154.34	153.66	151.74	149.33	147.06	
	4	154.29	155.01	155.27	155.33	155.21	155.08	154.88	154.41	155.9
H_2O	3	290.18	294.04	296.22	296.94	296.86	295.74	293.13	289.47	
	4	297.09	298.35	299.02	299.23	299.28	299.09	298.80	298.40	300.5
NH_3	3	256.68	259.97	261.61	262.11	261.80	260.31	257.78	254.73	
	4	262.12	263.31	263.52	263.69	263.75	263.69	263.54	263.31	264.5
HF	3	307.24	311.48	313.97	315.02	315.09	314.46	312.42	308.81	
	4	315.45	316.83	317.69	317.97	318.12	317.97	317.53	317.05	319.7
N_2	3	405.69	411.78	415.05	415.93	414.85	411.38	406.40	400.78	
	4	415.99	417.93	418.79	419.04	418.79	418.43	418.02	417.19	421.0
CO	3	388.48	394.47	397.83	398.80	398.08	395.33	390.67	385.07	
	4	398.73	400.68	401.64	401.97	401.93	401.56	401.01	400.17	403.9
Ne	3	305.61	310.19	312.84	314.32	314.66	314.15	312.58	309.58	
	4	314.84	316.37	317.46	317.86	317.97	317.81	317.27	316.65	320.1
F_2	3	587.24	595.48	600.25	602.21	602.65	601.48	597.34	590.31	
	4	602.98	605.79	607.44	608.05	608.31	607.77	606.77	605.84	611.7

[a]Geometries as in Ref. 21. Results are reported for CH_2 in its $^1A_1$ state.
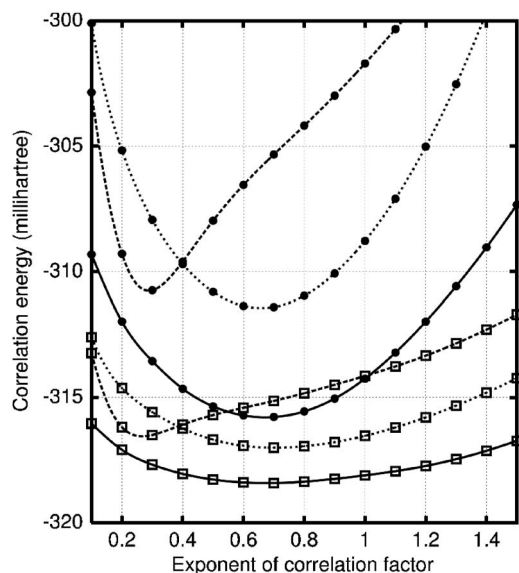[b]MP2-R12/2B value.
[c]From Ref. 21.

FIG. 8. A comparison of the valence-shell second-order Møller-Plesset correlation energy of the Ne atom as function of ζ for the aug-cc-pVXZ (solid line), cc-pVXZ (dashed line), and scaled cc-pVXZ (dotted line) basis sets, with $X=3$ (●) and $X=4$ (□). The scaled cc-pVTZ and cc-pVQZ basis sets are created by scaling the exponents of the polarization functions by 0.55 and 0.60, respectively.

same exponent ζ is applicable to any size of basis set, and any basis sets optimized for the MP2-F12 methods should exhibit this behavior.

VII. CONCLUSIONS

In this paper we have been principally concerned with finding the correlation factors for use in r_{12} methods which are an improvement over the linear function. Through a consideration of the optimum correlation factor for helium we chose to investigate the performance of four functions, Eqs. (15)–(18), in MP2-F12 calculations on a small set of molecules. We find that all of the new correlation functions are great improvements over the linear-r_{12} results and that the
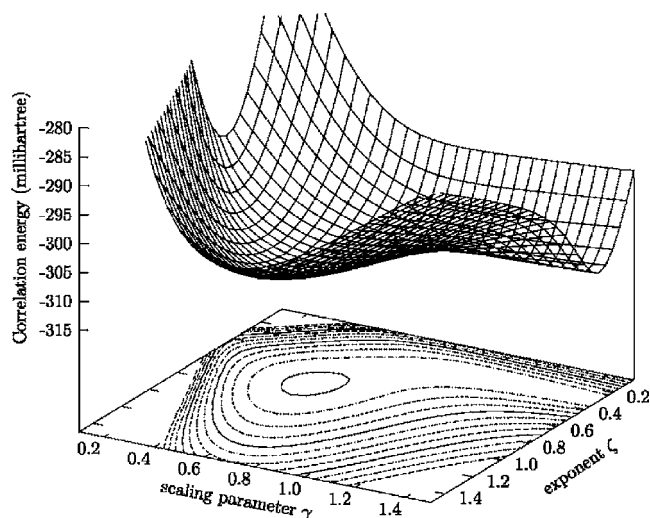

FIG. 9. Valence-shell second-order Møller–Plesset correlation energy of the Ne atom as function of ζ and γ, where ζ is the exponent of the correlation factor $r_{12}\exp(-\zeta r_{12})$ and γ is the scaling parameter of the polarization functions of the aug-cc-pVTZ basis.
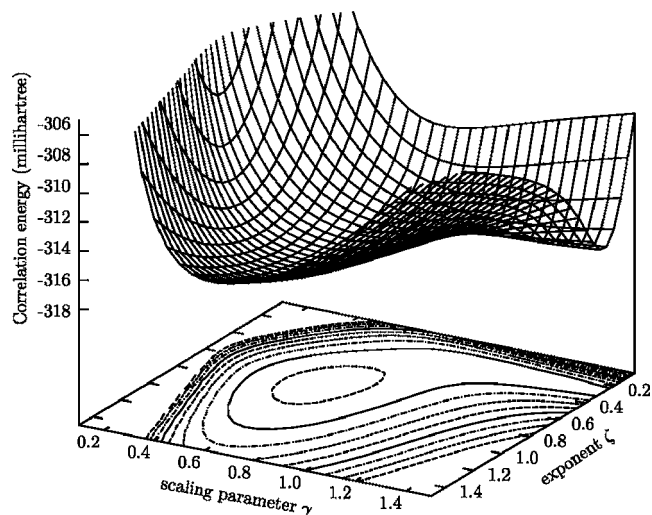

FIG. 10. Valence-shell second-order Møller–Plesset correlation energy of the Ne atom as function of ζ and γ, where ζ is the exponent of the correlation factor $r_{12}\exp(-\zeta r_{12})$ and γ is the scaling parameter of the polarization functions of the aug-cc-pVQZ basis.

substitution of the linear-r_{12} term with any of these functions results in a gain of accuracy equivalent to increasing the basis set of the linear-r_{12} calculation by one cardinal number for all molecules in our set. Due to the relative insensitivity of the results to the exponent ζ we find that the function $c\exp(-\zeta r_{12})$, which was first proposed by Ten-no,[26] is best suited for use in our r_{12} methods.

We interpret the success of the new correlation factors in terms of the computed optimum correlation factor for helium, which we define as the projection of the exact wave function onto the space spanned by $\psi_0 J$, with J constrained to that of Eq. (4). The new correlation factors not only satisfy the universal cusp condition of Kato,[29] but also closely fit the behavior of the correlation hole around the cusp due to the higher-order terms in Eqs. (1) and (2). We find that for helium and its isoelectronic series of cations the size of the correlation factor scales linearly with the nuclear charge, but the shape remains almost constant. We infer that the shape of the optimum correlation factor is very similar in many molecular systems, and that it is contracted depending on the effective nuclear charge experienced by the coalescing electron pairs. Indeed we find that the functions $c\exp(-\zeta r_{12})$ and $cr_{12}\exp(-\zeta r_{12})$, which fit the optimum correlation factor for helium very closely, perform slightly better than $c\,\mathrm{erfc}(\zeta r_{12})$ and $cr_{12}\mathrm{erfc}(\zeta r_{12})$, which diverge from the optimum correlation function sooner. We also observe that the pattern of optimum exponents ζ follows that of the electronegativies of the component atoms in the set of molecules we investigate.

We find from both our CI-F12 and our MP2-F12 calculations that there is a significant redundancy between the geminal basis functions and the CI expansion functions. This redundancy is predominantly in the description of the longer-range correlation. We observe that when the one-particle basis is too small or does not have enough diffuse functions, a correlation factor with small exponent ζ compensates for the inadequate basis. This situation is not desirable because the new correlation factors cannot properly describe both the cusp and the longer-range correlation effects simultaneously.

In the spirit of the r_{12} methodology introduced by Kutzelnigg[2] it is preferable to employ a more compact correlation factor in order to properly describe the cusp, and to ensure that the one-particle basis has sufficiently diffuse functions for the description of the longer-range correlation. We therefore recommend that augmented basis sets are used in f_{12} methods.

Finally we comment that using the conventional MP2 method, 90% of the MP2 correlation energy of Ne is recovered with an aug-cc-pVQZ basis, and an aug-cc-pVTZ basis is required for similar accuracy when using the MP2-R12 method. The MP2-F12 method with any of these correlation factors recovers the same accuracy using only an aug-cc-pVDZ basis. This represents a large saving in computational time, primarily due to the computation of the Hartree-Fock wave function. We conclude that using these new correlation factors the r_{12} methodology is a highly competitive method for obtaining not only very high accuracy results, but also for obtaining the correlation energy to moderate accuracy efficiently. Since the new correlation factors are suitable for use in localization methods, this situation can only improve.

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