AIP | The Journal of Chemical Physics

On the large interelectronic distance behavior of the correlation factor for explicitly correlated wave functions

Michał Lesiuk, Bogumił Jeziorski, and Robert Moszynski

Citation: The Journal of Chemical Physics **139**, 134102 (2013); doi: 10.1063/1.4822045
View online: http://dx.doi.org/10.1063/1.4822045
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/139/13?ver=pdfcov
Published by the AIP Publishing

THE JOURNAL OF CHEMICAL PHYSICS **139**, 134102 (2013)

On the large interelectronic distance behavior of the correlation factor for explicitly correlated wave functions

Michał Lesiuk,[a] Bogumił Jeziorski, and Robert Moszynski
Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

(Received 17 July 2013; accepted 10 September 2013; published online 1 October 2013)

In currently most popular explicitly correlated electronic structure theories, the dependence of the wave function on the interelectronic distance r_{ij} is built via the correlation factor $f(r_{ij})$. While the short-distance behavior of this factor is well understood, little is known about the form of $f(r_{ij})$ at large r_{ij}. In this work, we investigate the optimal form of $f(r_{12})$ on the example of the helium atom and helium-like ions and several well-motivated models of the wave function. Using the Rayleigh-Ritz variational principle, we derive a differential equation for $f(r_{12})$ and solve it using numerical propagation or analytic asymptotic expansion techniques. We found that for every model under consideration, $f(r_{12})$ behaves at large r_{ij} as $r_{12}^{\rho}\, e^{Br_{12}}$ and obtained simple analytic expressions for the system dependent values of ρ and B. For the ground state of the helium-like ions, the value of B is positive, so that $f(r_{12})$ diverges as r_{12} tends to infinity. The numerical propagation confirms this result. When the Hartree-Fock orbitals, multiplied by the correlation factor, are expanded in terms of Slater functions $r^n e^{-\beta r}$, $n = 0,\ldots,N$, the numerical propagation reveals a minimum in $f(r_{12})$ with depth increasing with N. For the lowest triplet state, B is negative. Employing our analytical findings, we propose a new "range-separated" form of the correlation factor with the short- and long-range r_{12} regimes approximated by appropriate asymptotic formulas connected by a switching function. Exemplary calculations show that this new form of $f(r_{12})$ performs somewhat better than the correlation factors used thus far in the standard R12 or F12 theories. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4822045]

I. INTRODUCTION

It is well known that the slow convergence of the standard, orbital based methods of the electronic structure theory is due to the difficulties to model the exact wave function in the regions of the configurations space where electrons are close to each other.[1,2] It was shown by Kato[3] and later elaborated by Pack and Byers Brown,[4] and Hoffman-Ostenhofs and co-workers[5,6] that in the vicinity of points where the positions of two electrons coincide, the wave function behaves linearly in the interelectronic distance r_{12}. Such a behavior, referred often to as the *cusp condition*, cannot be modeled by a finite expansion in terms of orbital products.[7] The solution to this problem is to include the interelectronic distance dependence directly into the wave function. This is the main idea of the so-called *explicitly correlated methods* of the electronic structure theory.[1,2,8] It should be noted, however, that the explicit dependence on r_{12} is advantageous even if the cusp condition is not fulfilled exactly as in the Gaussian geminal[7,9] or the ECG[10,11] (explicitly correlated Gaussian) approaches. This is due to the fact that the correlation hole, i.e., the decrease of the wave function amplitude when the electrons approach each other, is much easier to model with basis functions depending explicitly on r_{12} than with the orbital products.[7]

The simplest way to make the wave function r_{12} dependent is to multiply some or all orbital products in its conventional configuration-interaction-type expansion by a *correlation factor* $f(r_{12})$. In this way, all r_{12} dependence is contracted in one function of single variable. The idea of the correlation factor is very old one. It can be traced back to the late 1920s work of Slater[12] and of Hylleraas,[13,14] who showed great effectiveness of including the linear r_{12} term in the helium wave function. More than two decades later Jastrow[15] proposed to use the correlation factor to construct a compact form of correlated wave function for an N-particle quantum system. The wave function form proposed by Jastrow became popular in the electronic structure theory as the guide function in diffusion-equation Monte Carlo calculations.[16,17]

The concept of the correlation factor is now most widely used in the context of many-body perturbation theory[18] (MBPT) and coupled cluster[19] (CC) approach. It was first observed by Byron and Joachain,[20] and later by Pan and King,[21,22] Szalewicz and co-workers,[23–27] and Adamowicz and Sadlej[28–30] that the pair functions appearing in the energy expressions of the MBPT or CC theory can be very efficiently approximated when expanded in terms of explicitly correlated basis functions. In the investigations of Refs. 21–30, the dependence on the r_{12} coordinate was introduced through the Gaussian factors, $\exp(-\gamma_i r_{12}^2)$, with different γ_i for different basis functions (Gaussian geminals). Thus, the pair functions were not represented with a single, universal correlation factor. Massive optimizations of thousands of nonlinear parameters defining the Gaussian geminals (γ_i and orbital exponents) made these calculations very time consuming, limiting

---

[a] E-mail: lesiuk@tiger.chem.uw.edu.pl

applications of this approach to very small systems such as Be, Li^-, LiH, He_2, Ne, or H_2O.[31–35]

An important advance in the field of explicitly correlated MBPT/CC theory came with the seminal 1985 work of Kutzelnigg[36] and the subsequent development of the so-called R12 method by Kutzelnigg, Klopper, and Noga.[37–41] In this work, a simple linear correlation factor $f(r_{12}) = r_{12}$ was used to multiply products of occupied Hartree-Fock (HF) orbitals ϕ_i, $i = 1, \ldots n$. The resulting set of explicitly correlated basis functions $f(r_{12})\phi_i\phi_j$, supplemented by products of all virtual orbitals, was then used to expand the pair functions of the MBPT/CC theory. The necessity to calculate three and four-electron integrals, resulting from the Coulomb and exchange operators and the strong orthogonality projectors, was eliminated by suitable resolution of identity (RI) insertions. Kutzelnigg and Klopper introduced also some useful approximations[37,38] to the expression for the commutator of the Fock operator with $f(r_{12})$ which significantly simplified calculations. The practical implementation of the original R12 scheme was, however, not free from problems. Most importantly, in order to make the RI approximation accurate enough the one-electron basis set used in calculations had to be very large. This constraint was alleviated by Klopper and Samson[42] who introduced auxiliary basis sets for the RI approximation which are saturated independently from the size of the basis set that is used in the preceding Hartree-Fock calculations. During the past two decades, the R12 technology was progressively refined by the use of many tricks such as the density fitting,[43] numerical quadratures,[44] improvements in the RI approximations,[45,46] or efficient parallel implementations.[47,48] A generalization to multi-reference configuration interaction problems (MRCI-R12) has been developed by Gdanitz.[49,50] One should also mention the work of Taylor and co-workers[51–53] who expanded the linear correlation factor r_{12} as a combination of the Gaussian functions, and evaluated the necessary many-electron integrals analytically.

Despite this progress, the results of R12 calculations using small basis sets were not fully satisfying. In particular, it was shown that the results of R12 calculations with a correlation-consistent polarized valence double-zeta (cc-pVDZ) basis set were of similar quality as ordinary orbital based calculations with a triple-zeta cc-pVTZ basis set.[42] This is a rather small gain when compared to the accuracy improvement in calculations with the quintuple-zeta basis sets when the R12 method gives almost saturated results. In 2005, May and co-workers[54] reported a careful analysis of the errors in R12 theory at the second-order Møller-Plesset (MP2-R12) level. They concluded that the most significant source of these errors are defects inherent in the R12 *ansatz* and it is essential that r_{12} is replaced by a more accurate correlation factor $f(r_{12})$. Actually, a generalization of the R12 theory, referred to as the F12 theory, allowing an arbitrary, nonlinear correlation factor $f(r_{12})$ was formulated by May and Manby[55] already in 2004. In the same year, Ten-no[56] proposed the use of the exponential correlation factor $[1 - \exp(-\gamma r_{12})]/\gamma$ (Slater-type geminal) and showed that it leads to much better results than the linear one. This launched rapid development of the F12 methods, which are now almost exclusively based on the application of the exponential correlation factor.[2,8] This correlation factor turned out to be effective not only in the conventional single-reference MBPT/CC theory but was also successfully applied to improve the basis set convergence of multireference methods: MRCI,[57,58] multireference perturbation theory,[59–61] multireference CC approach,[62] and even the multiconfiguration SCF procedure.[63]

It is clear that the shape of the correlation factor is important for the high quality of the results. One may, thus, ask what is the optimal form of $f(r_{12})$ that is correct not only in the vicinity of the electrons coalescence points, but also at arbitrary distance between electrons. This question has been considered by Tew and Klopper[64] who have investigated the shape of the correlation factor for the helium atom and for helium-like ions and compared it with several simple analytic forms. These authors expanded $f(r_{12})$ as a polynomial in r_{12} and determined its coefficients by minimizing the distance (in the Hilbert space) between the exact wave function and its approximate form constructed using $f(r_{12})$. They found that the exponential correlation factor proposed by Ten-no[56] is close to optimal.

It should be pointed out that the method used by Tew and Klopper[64] is not accurate at larger values of r_{12} and does not give any information about the asymptotic behavior of $f(r_{12})$ at large r_{12}. This is a consequence of the assumed polynomial form for $f(r_{12})$, which prejudges the asymptotic behavior of $f(r_{12})$ and makes the obtained approximation to the optimal $f(r_{12})$ less reliable at larger r_{12}. Moreover, the optimum $f(r_{12})$ as defined by Tew and Klopper does not guarantee the minimum energy with respect to a variation of a fully flexible form of the correlation factor.

In the present communication, we propose an alternative method to determine the optimal form of $f(r_{12})$, which is free from the above drawbacks. We do not expand $f(r_{12})$ in a basis set but derive a differential equation for $f(r_{12})$, resulting from the unconstrained minimization of the Rayleigh-Ritz energy functional. This differential equation can be solved by a numerical propagation or using analytic, asymptotic expansion techniques. In this way, the problems with the stability of the optimal $f(r_{12})$ at large r_{12}, experienced by Tew and Klopper,[64] are avoided and we obtain a reliable information on the large r_{12} behavior of $f(r_{12})$. This information, combined with the well known information about the short-range behavior of $f(r_{12})$, gives us a possibility to propose a new form of the correlation factor which is correct at small and large values of r_{12}. One may hope that the correlation factor more adequate at large r_{12} will make up for the lack of flexibility of the orbital basis to describe the long-range correlation and will reduce the basis-set requirements of F12 calculations.

The paper is organized as follows. In Secs. II A and II B, we analyze the simplest models of the correlated wave functions for the ground and the lowest triplet state of the helium atom and helium-like ions. In both cases, we establish differential equations for the correlation factor $f(r_{12})$ and solve them exactly in the large-r_{12} domain. In Sec. II C, we investigate another model for the singlet ground state when the 1*s* Slater orbital is replaced by a single Gaussian function. In Sec. II D, we move on to the case of a self-consistent-field (SCF) determinant multiplied by the correlation factor. In this case, we were not able to derive an explicit differential equation but we present equations sufficient to determine the leading term of the asymptotic expansion for $f(r_{12})$. In Sec. II E, we report changes that occur when a set of excited state determinants is added to the approximate wave functions considered previously. In Sec. III, we propose a new analytical form of the correlation factor and give results of simple numerical calculations, followed by a short discussion. The paper ends with conclusions in Sec. III C.

In our work, we use several special functions. The definition of these functions is the same as in Ref. 65. Atomic units are used throughout the paper.

II. THEORY

A. Correlated Slater orbitals: Singlet state

We first consider a very simple model, a particular case of the Slater-Jastrow wave function[15,17] for helium-like ions:

$$\Psi = \Psi_0(r_1, r_2) f(r_{12}), \tag{1}$$

where r_1 and r_2 are the electron-nucleus distances, r_{12} is the interelectronic distance, $\Psi_0(r_1, r_2) = e^{-\alpha r_1} e^{-\alpha r_2}$, and $f(r_{12})$ is the correlation factor. The orbital exponent α is left unfixed — it can be later optimized without or with the correlation factor. We determine $f(r_{12})$ by unconstrained minimization of the Rayleigh-Ritz energy functional,

$$E[f] = \frac{\langle \Psi_0 f | \hat{H} | \Psi_0 f \rangle}{\langle \Psi_0 f | \Psi_0 f \rangle}. \tag{2}$$

The requirement that the functional derivative of $E[f]$ is zero,

$$\frac{\delta E}{\delta f(r_{12})} = 0, \tag{3}$$

or equivalently that

$$\frac{\partial E[f + \mu \delta f]}{\partial \mu}\Big|_{\mu=0} = 0, \tag{4}$$

for every variation δf of f, leads to a differential equation for $f(r_{12})$. This equation has a unique solution (up to a phase) if we assume that f is regular at $r_{12} = 0$ and that $\Psi = \Psi_0 f$ is square integrable.

To evaluate the functional derivative of Eq. (3), it is convenient to integrate over Euler angles first and perform the integral over r_{12} at the end. This can be done by means of the formula,

$$\iint \mathcal{F}(r_1, r_2, r_{12}) d\mathbf{r}_1 d\mathbf{r}_2 = 8\pi^2 \int_0^\infty \int_0^\infty \int_{|r_1 - r|}^{r_1 + r} r_1 r_2 r \, \mathcal{F}(r_1, r_2, r) \, dr_2 \, dr_1 \, dr, \tag{5}$$

where $\mathcal{F}(r_1, r_2, r_{12})$ is any function for which the integral on the left exists. For states of S^e symmetry and wave functions expressed through interparticle distances r_1, r_2, and $r_{12} \equiv r$, the Hamiltonian can be taken in the form

$$\hat{H} = -\frac{1}{2}(1 + \mathcal{P}_{12}) \left[\frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1}\frac{\partial}{\partial r_1} + \frac{r^2 + r_1^2 - r_2^2}{r r_1} \frac{\partial^2}{\partial r_1 \partial r} + \frac{2Z}{r_1} \right] - \frac{\partial^2}{\partial r^2} - \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r}, \tag{6}$$

where $\mathcal{P}_{12}$ denotes permutation of the indices 1 and 2, and Z is the nuclear charge. In Eq. (6) and in the following text, we denote r_{12} by r to make equations more transparent and more compact. Recently, Pestka[66] presented generalizations of this Hamiltonian valid for two-electron states of arbitrary angular momentum. His results can be used to extend our approach to states of higher angular momenta.

Evaluating the lhs of Eq. (4) with the help of Eq. (5) and assuming that it vanishes for every variation δf, one obtains the following equation for f,

$$\int_0^\infty \int_{|r_1 - r|}^{r_1 + r} r_1 r_2 e^{-\alpha(r_1 + r_2)} (\hat{H} - E) e^{-\alpha(r_1 + r_2)} f(r) dr_2 dr_1 = 0. \tag{7}$$

To obtain the explicit form of this equation, we have to perform integration over the variables r_1 and r_2. Using Eq. (6) and the integral formulas from Appendix A, one finds

$$\begin{aligned} &[-3 + 3(4\alpha Z - 2\alpha - 3\alpha^2 + E) r + 2\alpha(12\alpha Z - 2\alpha - 9\alpha^2 + 3E) r^2 \\ &+ 4\alpha^2(\alpha^2 + E) r^3] f(r) + [6 + 12\alpha r + 4\alpha^2 r^2 - 8\alpha^3 r^3] f'(r) \\ &+ r[3 + 6\alpha r + 4\alpha^2 r^2] f''(r) = 0. \end{aligned} \tag{8}$$

Equation (8) is a second-order linear differential equation for $f(r)$. To the best of our knowledge, its solution cannot be expressed as a combination of the known elementary and/or special functions. Since $r = 0$ is a regular singular point,[67] at least one solution can be found by using the following substitution:

$$f(r) = \sum_{k=0}^{\infty} c_k r^{k+\rho}. \tag{9}$$

Inserting Eq. (9) into the differential equation, collecting terms with the same power of r, and requiring the corresponding coefficients to vanish identically, one obtains the indicial equation:

$$3\rho(\rho + 1) c_0 = 0, \tag{10}$$

that is used to determine the value of ρ. Since $f(r)$ must be finite at $r = 0$, we reject $\rho = -1$ and pick up $\rho = 0$. Setting $\rho = 0$, one obtains the first three coefficients:

$$\begin{aligned} c_1 &= \frac{1}{2} c_0, \\ c_2 &= \frac{1}{12}\left(6\alpha^2 - 8\alpha Z - 2E + 1\right) c_0, \\ c_3 &= \frac{1}{144}\left(32\alpha^2 - 32\alpha Z - 8E + 1\right) c_0, \end{aligned} \tag{11}$$

and the recursion relation for the remaining ones

$$\begin{aligned} &\frac{4}{3} c_n \alpha^2 (E + 1) + \alpha c_{n+1} \left[-\frac{4}{3}\alpha - \alpha^2 \left(\frac{26}{3} + \frac{8}{3} n \right) + 2E + 8\alpha Z \right] \\ &+ c_{n+2} \left[-2\alpha + \frac{1}{3}\alpha^2 (2n + 1)(2n + 7) + E + 4\alpha Z \right] \\ &+ c_{n+3}[-1 + 2\alpha(n + 3)(n + 4)] + c_{n+4}(n + 4)(n + 5) = 0. \end{aligned} \tag{12}$$

The value of c_0 is arbitrary and can be fixed by imposing a normalization condition for the wave function. For the sake of convenience, we put $c_0 = 1$. The first equality in the system (11) is the cusp condition. It turns out that the correlation factor obtained from the differential equation (8) automatically satisfies the electronic cusp, independently of the values of α and Z, so that for small r the correlation factor behaves as $f(r) \sim 1 + \frac{1}{2}r$. This result is not surprising. The wave function Ψ depends on r through $f(r)$ only, so that the factor $f(r)$ alone is responsible for the cancellation of the $1/r$ singularity between the potential and kinetic energy terms.

To obtain the asymptotic form of the solution of the differential equation (8), we keep only the terms proportional to the highest (the third) power of r. The resulting equation

$$4\alpha^2 f''(r) - 8\alpha^3 f'(r) + 4\alpha^2 \left(\alpha^2 + E\right) f(r) = 0 \tag{13}$$

has two linearly independent solutions $e^{(\alpha-\sqrt{-E})r}$ and $e^{(\alpha+\sqrt{-E})r}$. The acceptable solution is the one with the exponent equal to $\alpha - \sqrt{-E}$. This suggests the following substitution:

$$f(r) = e^{Br} g(r), \tag{14}$$

where $B = \alpha - \sqrt{-E}$. The differential equation for $g(r)$, obtained from Eqs. (8) and (14), is

$$\begin{aligned}
&g''(r)[3r+6\alpha r^2+4\alpha^2 r^3]+g'(r)[6+(18\alpha-6\sqrt{-E})r\\
&\quad+(16\alpha^2-12\alpha\sqrt{-E})r^2-8\alpha^2\sqrt{-E}\,r^3]\\
&\quad+g(r)[-3+6\alpha-6\sqrt{-E}+(6\alpha^2-18\alpha\sqrt{-E}\\
&\quad+12\alpha Z-6\alpha)r+(24\alpha^2 Z-8\alpha^3-16\alpha^2\sqrt{-E}-4\alpha^2)r^2]=0.
\end{aligned} \tag{15}$$

We shall present a general method of deriving the first term in the asymptotic expansion of $f(r)$ by using the information about the asymptotic behavior of the confluent hypergeometric functions. When the differential equation is given explicitly, as in the present section, and we know the leading term of the asymptotic expansion of $f(r)$, it becomes easy to derive the complete asymptotic series. Method based on the hypergeometric functions is even more useful in further sections, where the complete form of the corresponding differential equation cannot be simply obtained so we confine ourselves merely to the derivation of the leading term in the asymptotic expansion. For mathematical details of the asymptotic expansion around an irregular singular point and the dominant balance method we refer to the book of Bender and Orszag.[68]

We start by neglecting in Eq. (15) the terms proportional to r^0 and r^1. After simple rearrangements, one arrives at the following differential equation:

$$\begin{aligned}
&(2\alpha r+3)h''(r)+2[4\alpha-(2\alpha r+3)\sqrt{-E}\,]h'(r)\\
&\quad-2\alpha\,(1+2\alpha+4\sqrt{-E}-6Z)h(r)=0.
\end{aligned} \tag{16}$$

The next step is a simple linear change of variable $s = \sqrt{-E}\,(3+2\alpha r)/\alpha$. The differential equation in the new variable s reads

$$s\,h''(s) + (4-s)h'(s) + \rho h(s) = 0, \tag{17}$$

where

$$\rho = -\frac{1+2\alpha-6Z+4\sqrt{-E}}{2\sqrt{-E}}. \tag{18}$$

Equation (17) is a special case of the confluent hypergeometric equation and has two linearly independent solutions expressed usually in terms of Kummer's function[65] $M(-\rho, 4, s)$ [denoted also by ${}_1F_1$] and Tricomi's function[65] $U(-\rho, 4, s)$. The leading terms of the large-s ($s > 0$) asymptotic expansions of these functions are[65]

$$M(a,b,s) = \frac{\Gamma(b)}{\Gamma(a)}\, e^s s^{a-b}\left[1+\mathcal{O}\left(\frac{1}{s}\right)\right], \tag{19}$$

$$U(a,b,s) = s^{-a}\left[1+\mathcal{O}\left(\frac{1}{s}\right)\right]. \tag{20}$$

We pick up the normalizable solution $U(-\rho, 4, s)$ and by returning to the initial variable r,

$$\begin{aligned}
U(-\rho,4,s) &= \left[\frac{\sqrt{-E}}{\alpha}\,(3+2\alpha r)\right]^{\rho}\left[1+\mathcal{O}\left(\frac{1}{r}\right)\right]\\
&\sim r^{\rho}\left[1+\mathcal{O}\left(\frac{1}{r}\right)\right],
\end{aligned} \tag{21}$$

where the multiplicative constant was neglected since it is irrelevant in the present context. By combining this result with Eq. (14), one finds that for large r,

$$f(r) = r^{\rho} e^{(\alpha-\sqrt{-E})r}\left[1+\mathcal{O}\left(\frac{1}{r}\right)\right]. \tag{22}$$

Once the leading term of the asymptotic expansion is known, it becomes quite straightforward to obtain the complete asymptotic series. By inserting the following ansatz:

$$f(r) = r^{\rho}\, e^{(\alpha-\sqrt{-E})r}\sum_{k=0}^{\infty}\frac{d_k}{r^k}, \tag{23}$$

into the differential equation (8) and collecting the same powers of r^{-1}, one finds that the indicial equation is automatically satisfied by the choice of ρ given by Eq. (18). The recurrence relation determining the d_k coefficients is given by

$$\begin{aligned}
&d_n[3n(n-1)-(6n-3)\rho+3\rho^2]\\
&\quad+d_{n+1}[-3-12n\alpha\rho+6\alpha(n^2+\rho^2)+6(n-\rho)\sqrt{-E}]\\
&\quad+d_{n+2}[6(2\alpha Z-1)+2\alpha^2(2n^2+2n-1)\\
&\quad-\alpha^2(8n+4)\rho+4\alpha^2\rho^2+6\alpha(2n-1)\sqrt{-E}]\\
&\quad+d_{n+3}[4\alpha^2(6Z-2\alpha-1)+8\alpha^2(n+1-\rho)\sqrt{-E}]=0,
\end{aligned} \tag{24}$$

with d_0 arbitrary. Equation (24) is also valid for $n = -1$ and $n = -2$ provided that we assume that $d_n = 0$ for $n < 0$. The asymptotic series for the second (unphysical) solution of Eq. (8), behaving at large r as $r^{-\rho-4}\, e^{(\alpha+\sqrt{-E})r}\,[1+\mathcal{O}(1/r)]$, can be obtained in the same way.

Summarizing, we found that the correlation factor in Eq. (1) possesses large-r asymptotic expansion given by Eq. (23) with all parameters known analytically as functions of α, Z, and $\sqrt{-E}$. To determine numerical values of B and ρ, we performed variational calculations on the series of helium-like ions using the trial wave function of the form of Eq. (1), with $f(r)$ represented as a 15th order polynomial in r. In this

TABLE I. The values of the parameters B and ρ determining the asymptotic behavior of $f(r)$, Eq. (23). Two approaches were used to fix the exponent α: optimization of the energy obtained with the correlated wave function of Eq. (1) and the "bare-nucleus" value $\alpha = Z$.

Z	α	E	B	ρ
		Energy optimized α		
1	0.84267	− 0.509378	0.128966	0.322138
2	1.84833	− 2.891254	0.147959	0.147577
3	2.85039	− 7.268487	0.154375	0.095543
4	3.85144	− 13.64459	0.157585	0.070615
5	4.85208	− 22.02025	0.159510	0.055997
6	5.85251	− 32.39568	0.160792	0.046391
7	6.85282	− 44.77099	0.161707	0.039598
8	7.85305	− 59.14622	0.162393	0.034540
		$\alpha = Z$		
1	1.00000	− 0.498452	0.293989	0.124612
2	2.00000	− 2.879363	0.303131	0.062623
3	3.00000	− 7.256353	0.306238	0.041754
4	4.00000	− 13.63235	0.307799	0.031309
5	5.00000	− 22.00795	0.308737	0.025041
6	6.00000	− 32.38335	0.309363	0.020864
7	7.00000	− 44.75863	0.309811	0.017880
8	8.00000	− 59.13384	0.310147	0.015643

way, we obtained sufficiently accurate values of E and, consequently, of $B = \alpha - \sqrt{-E}$ and of ρ [employing Eq. (18)]. For the value of the screening parameter α, we adopted (i) an optimal value for the wave function of Eq. (1), or (ii) the value $\alpha = Z$ corresponding to the solution for the "bare-nucleus" Hamiltonian. Table I summarizes the results. We see that, independently of the choice of α, the parameters B and ρ are positive, albeit small. Therefore, somewhat surprisingly, the correlation factor at large r neither decreases to zero as predicted by Bohm and Pines[69] for the homogeneous electron gas, nor tends to a constant value as in the standard versions of F12 theory.[2,8] In fact, it tends to infinity even faster than the linear correlation factor of the R12 theory of Kutzelnigg and Klopper.[36,37]

It has to be mentioned that throughout the paper, E is treated as a constant. However, E is a functional of f evaluated with the optimal form of f, and thus a function α. Nonetheless, this dependence is rather weak when one is limited to a reasonable vicinity of the optimal value of α.

The differential equation (8) also gives an opportunity to obtain the correlation factor with a controlled accuracy for an arbitrary value of r. It is clear that the expansion of $f(r)$ in the powers of r and the variational minimization gives an access to the short-range part of $f(r)$ but cannot describe its long-range part with a satisfactory accuracy. On the other hand, the numerical propagation of the differential equation (8) can be performed very accurately up to very large distances r. Also the energy E can be determined very accurately in this way by adjusting it such that the solution diverging as $r^{-\rho-4}\, e^{(\alpha+\sqrt{-E})}$ does not show up at large r. We used a high-order Runge-Kutta propagation with a variable step size and checked carefully the convergence of the solution. Figure 1 shows the result of the propagation of the differential equation (8) for the helium atom ($\alpha = 1.84833$). This numerical propagation result is compared with the variational solution expanded in powers of r up to r^{15}. The agreement is very good up to about $r = 8$ (the curves in Fig. 1 are indistinguishable at $r < 6$). At larger distances, the variational solution becomes completely unrealistic and becomes negative at $r > 14$.

At large r, the propagation curve agrees very well with the first term of Eq. (23). It is remarkable that the leading term of this asymptotic expansion gives reasonable approximation to $f(r)$ even for r as small 0.5, where the remaining error is slightly less than 7%. We also found that adding two more terms from expansion (23) significantly improves the approximation around $r = 1$, reducing the error from about 4% to less than 0.8%. Moreover, the reliability of this three-term asymptotic expansion extends to $r = 0.2$, where the remaining error is about 5% (the approximation by the leading term only gives 15% error at this distance). These results confirm the validity of the differential equation (8) as well as of the asymptotic form of $f(r)$ given by Eq. (23).

B. Correlated Slater orbitals: Triplet state

In this section, we consider a slightly more complicated model, namely, the simplest wave function for the lowest triplet state of a helium-like ion,

$$\Psi(r_1, r_2, r) = \left(e^{-\alpha r_1 - \beta r_2} - e^{-\beta r_1 - \alpha r_2}\right) f(r). \tag{25}$$

The implicit differential equation for $f(r)$ takes the form analogous to Eq. (7),

$$\int_0^\infty \int_{|r_1 - r|}^{r_1 + r} r_1 r_2\, e^{-\alpha r_1 - \beta r_2} (\hat{H} - E)(e^{-\alpha r_1 - \beta r_2} - e^{-\beta r_1 - \alpha r_2}) \times f(r)\, dr_2 dr_1 = 0. \tag{26}$$

The explicit form of this equation, obtained easily using the integral formulas of Appendix A, splits naturally into three components proportional to the exponential factors $e^{-2\alpha r}$, $e^{-2\beta r}$, and $e^{-2(\alpha+\beta)r}$, respectively. Since the differential equation (26) is symmetric with respect to the exchange $\alpha \leftrightarrow \beta$, we can assume that $\alpha < \beta$. With this assumption, the component proportional to the factor $e^{-2\alpha r}$ dominates at large r. Neglecting the two (exponentially) small components, one obtains the following equation for $f(r)$:

$$\begin{aligned} f(r)\{&4\alpha\beta + 2r\,[(\beta - \alpha Z - \beta Z)(\alpha^2 - \beta^2) \\ &- \alpha\beta(\alpha^2 + \beta^2) - 2\alpha\beta E\,] + r^2(\beta^2 - \alpha^2) \\ &\times [\alpha(3\beta^2 - \alpha^2) + 2\alpha E + 2Z(\alpha^2 - \beta^2)]\} \\ &+ f'(r) 4\alpha[-\beta + (\alpha^2 + \beta^2) r + \beta(\beta^2 - \alpha^2) r^2] \\ &+ f''(r) 2\alpha[-2\beta r - (\beta^2 - \alpha^2) r^2\,] = 0. \end{aligned} \tag{27}$$

Neglecting for the moment terms proportional to r^0 and r^1, we obtain the equation

$$\begin{aligned} f(r)[&-\alpha(3\beta^2 - \alpha^2) - 2\alpha E + 2Z(\beta^2 - \alpha^2)] \\ &+ 4\alpha\beta f'(r) - 2\alpha f''(r) = 0, \end{aligned} \tag{28}$$

which has two linearly independent solutions in the form e^{Br} but the only physically acceptable solution is the one with the

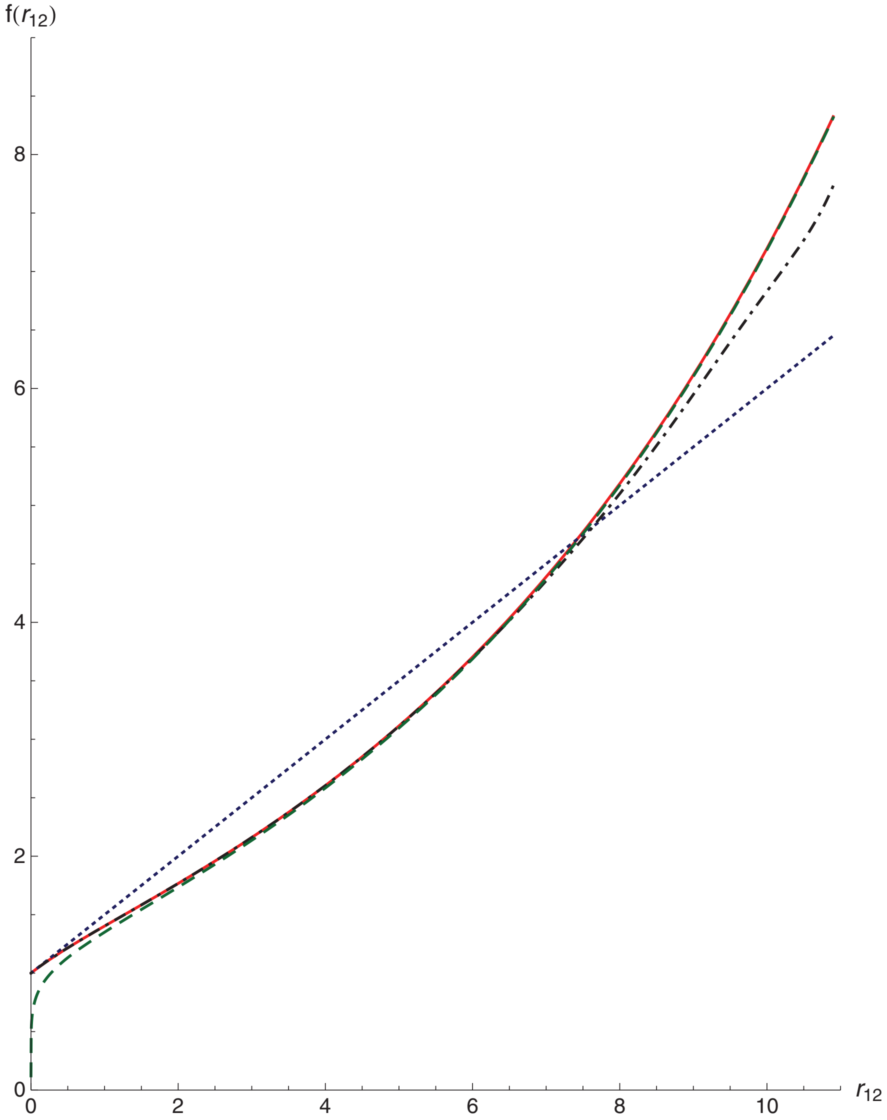

FIG. 1. The correlation factor $f(r)$ calculated for the helium atom using the wave function of Eq. (1) and $\alpha = 1.84833$. Red solid line is the result of numerical propagation of Eq. (8). Black dash-dotted line is the variational solution with $f(r)$ expanded as a polynomial of order 15. Green dashed line is the first term of the asymptotic expansion of $f(r)$. Blue dotted line is used for the short-range factor $1 + \frac{1}{2}r$.

exponent $B = \alpha - \gamma$, where

$$\gamma = \sqrt{(\alpha^2 - \beta^2)\left(\frac{2Z - \beta}{2\beta}\right) - E}. \tag{29}$$

Knowing the value of B, we can follow the hypergeometric function approach presented in Sec. II A and find that the leading term of the asymptotic expansion for $f(r)$ is $r^\rho e^{Br}$ with $B = \alpha - \gamma$ and

$$\rho = \frac{\alpha + \beta}{2\beta\gamma}Z - \frac{1}{2\gamma} - 1. \tag{30}$$

Now keeping all terms in Eq. (27) and using the ansatz (23), one obtains the following recursion relation determining the complete asymptotic expansion for $f(r)$:

$$\begin{aligned}
&d_{n+3}(\alpha^2 - \beta^2)[2Z(\alpha^2 - \beta^2) \\
&\quad - 2\beta(E + B^2 - 2\alpha B) + \beta^2(\beta^2 - 3\alpha^2)] \\
&+ d_{n+2}[2(\alpha^2 - \beta^2)(\alpha - \beta)(2B\rho + Z - 4n\beta B - 4\beta B) \\
&- 4\alpha\beta(E + B^2 - 2\alpha B)] \\
&+ d_{n+1}[8\alpha\beta\rho(\alpha - B) + (4nB + 2B - 2\beta\rho)\rho(\alpha^2 - \beta^2) \\
&+ 4(2n + 1)\alpha\beta B - 2n(n + 1)\beta(\alpha^2 - \beta^2) \\
&- 8(n + 1)\alpha^2\beta + 4\alpha\beta] - 4\alpha\beta(n - \rho)^2 d_n = 0,
\end{aligned} \tag{31}$$

where the value of d_0 is arbitrary.

To confirm the validity of formulas derived in this section, we performed variational calculations using the wave function of Eq. (25) and $f(r)$ expanded in powers of r up to r^{15}. We used the optimized parameters $\alpha = 0.321454$ and $\beta = 1.968451$ which give the energy of 2^3S state -2.170104. This value compares reasonably with the exact energy of this state equal to -2.175229. With the adopted values of α and β, the values of B and ρ, calculated according to Eqs. (29) and (30) are -0.151753 and 0.40172, respectively. Therefore, in the case of the triplet state 2^3S, the correlation factor in the

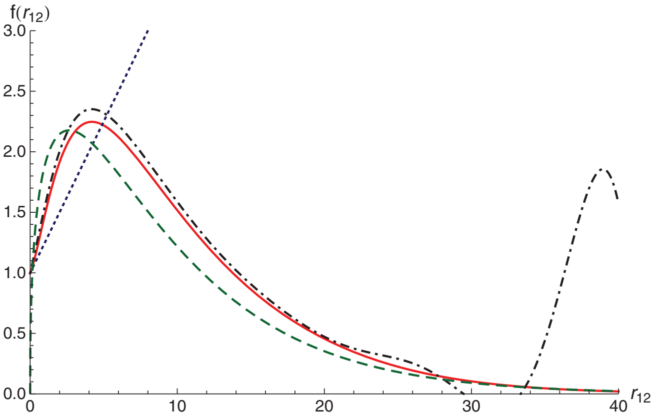

FIG. 2. The correlation factor $f(r)$ calculated for the helium atom using the wave function of Eq. (25) with $\alpha = 0.321454$ and $\beta = 1.968451$. The explanation of lines is the same as in Fig. 1, except that the short-range correlation factor, marked by the blue dotted line, is now $1 + \frac{1}{4}r$.

wave function (25) vanishes exponentially at large distances r. This can be understood by invoking the argument that in the 2^3S state the electrons occupy two different shells, so that correlation between them is asymptotically weaker. Moreover, the Fermi part of the correlation is already included in the zero-order wave function. In Fig. 2, we present a comparison of the correlation factors obtained from the numerical propagation and variational calculation with the leading term of the asymptotic expansion. The agreement between the variational result and the numerical propagation is not as good as in Sec. II A. This is due to the slow convergence of the variational result when increasing the number of powers of r included in the expansion of $f(r)$. Indeed, even with the 15th power included, the ratio of first two coefficients in the expansion of $f(r)$ is equal to 0.367, while it should be 0.25 (the cusp condition for triplet states). We were not able to include more powers of r in the variational calculations since the overlap matrix becomes ill conditioned, and even in the octuple arithmetic precision the results obtained by symmetric orthogonalization were not reliable. The reason for this slow convergence is that for $r = 0$, the wave function (25) vanishes. Therefore, the energy values are not sensitive to the quality of the trial wave function in the regions close to the coalescence points of the electrons. Again we find it remarkable that the first term in the asymptotic expansion represents $f(r)$ reasonably well in a wide range of distances, although the agreement at intermediate r is not as good as for the singlet state.

C. Correlated Gaussian orbital: Singlet state

Since the vast majority of calculations in quantum chemistry are performed employing the basis of Gaussian orbitals, one may ask how the results of Secs. II A and II B are modified when the orbital basis changes from Slater to Gaussian functions. To investigate this problem, we use the Gaussian analogue of the model from Sec. II A. Namely, we consider the following approximation to the wave function:

$$\Psi(r_1, r_2, r) = e^{-\alpha r_1^2}\, e^{-\alpha r_2^2}\, f(r). \tag{32}$$

It is perfectly clear that the above wave function is a very crude approximation to the exact one. One can expect, however, that this model captures the essential features of more accurate approximations when the atomic orbitals are expanded as linear combinations of Gaussian functions. The results obtained for such model extensions can easily be deduced from the equations presented here.

To derive a differential equation for $f(r)$, we start from a suitable modification (the replacement of $r_1 + r_2$ by $r_1^2 + r_2^2$) of Eq. (7). After changing the variables to $\xi = (r_1 + r_2)/r$, $\eta = (r_1 - r_2)/r$ and using well-known Gaussian integrals, we find that $f(r)$ satisfies the equation

$$\begin{aligned}&[16\,\mathrm{Erf}\left(\sqrt{\alpha} r\right) - 2 + (2E - 9\alpha)r + 2\alpha^2 r^3]\,f(r)\\&\quad + (4 - 4\alpha r^2)f'(r) + 2rf''(r) = 0,\end{aligned} \tag{33}$$

where Erf(x) is the error function. Since we are interested in the large-r behavior of $f(r)$, we can invoke the asymptotic form of the error function, $\mathrm{Erf}(x) = 1 - e^{-x^2}/(x\sqrt{\pi}) + \ldots$, and replace Eq. (33) by a simpler one

$$\begin{aligned}&[14 + (2E - 9\alpha)r + 2\alpha^2 r^3]\,f(r)\\&\quad + (4 - 4\alpha r^2)f'(r) + 2rf''(r) = 0.\end{aligned} \tag{34}$$

This equation can be solved exactly in terms of Kummer and Tricomi functions. To obtain its solutions, we make the substitution

$$f(r) = e^{\frac{\alpha}{2}r^2 - \gamma r}k(r), \tag{35}$$

where the parameter γ is yet undetermined. By inserting the above from of $f(r)$ into Eq. (34), one arrives at the following differential equation for $k(r)$:

$$\begin{aligned}&[r(-3\alpha + 2E + 2\gamma^2) + 14 - 4\gamma]k(r)\\&\quad + 4(1 - \gamma r)k'(r) + 2rk''(r) = 0.\end{aligned} \tag{36}$$

The value of γ can be now fixed by requiring that the coefficient proportional to $rk(r)$ vanishes identically. Choosing

$$\gamma = \sqrt{\frac{3}{2}\alpha - E}, \tag{37}$$

Eq. (36) then takes the form:

$$rk''(r) + 2\,(1 - \gamma r)\,k'(r) + (7 - 2\gamma)\,k(r) = 0. \tag{38}$$

Finally, by change of variable $x = 2\gamma r$, we transform Eq. (38) into the standard from of the Kummer equation[65]

$$xk''(x) + (2 - x)k'(x) - \left(1 - \frac{7}{2\gamma}\right)k(x) = 0. \tag{39}$$

The two linearly independent solutions of Eq. (39) are the Kummer and Tricomi functions, $M(1 - \frac{7}{2\gamma}, 2, x)$ and $U(1 - \frac{7}{2\gamma}, 2, x)$, respectively. For the same reason as in Sec. II A, we pick up the Tricomi function. Thus, the exact solution of Eq. (34) reads

$$f(r) = e^{\frac{\alpha}{2}r^2 - \gamma r}\, U\left(1 - \frac{7}{2\gamma}, 2, 2\gamma r\right). \tag{40}$$

The asymptotic expansion of the Tricomi function is well-known [cf. Eq. (20)], so the leading term in the large-r

expansion of $f(r)$ is

$$f(r) \sim r^{\frac{7}{2\gamma}-1}\, e^{\frac{\alpha}{2}r^2-\gamma r}. \tag{41}$$

Since α is positive, $f(r)$ diverges to infinity large r.

We performed numerical calculations for the helium atom to verify our findings. We found variationally that the optimized parameter α for the wave function (32) is equal to 0.859802. The corresponding energy value is $E = -2.339039\ldots$. The values of the parameters in Eq. (41) that define the asymptotic expansion are

$$\gamma = 1.90493, \tag{42}$$

$$\frac{7}{2\gamma} - 1 = 0.837342. \tag{43}$$

Figure 3 shows the result of the propagation of the differential equation (33) compared with the leading term of the asymptotic expansion of $f(r)$. We see a very good agreement between these two curves at large interelectronic distances. For comparison, we also plot the correlation factor obtained from variational calculations when $f(r)$ is expanded in powers of r. We conclude that the numerical results presented in Figure 3 confirm the analytical results derived in this section.

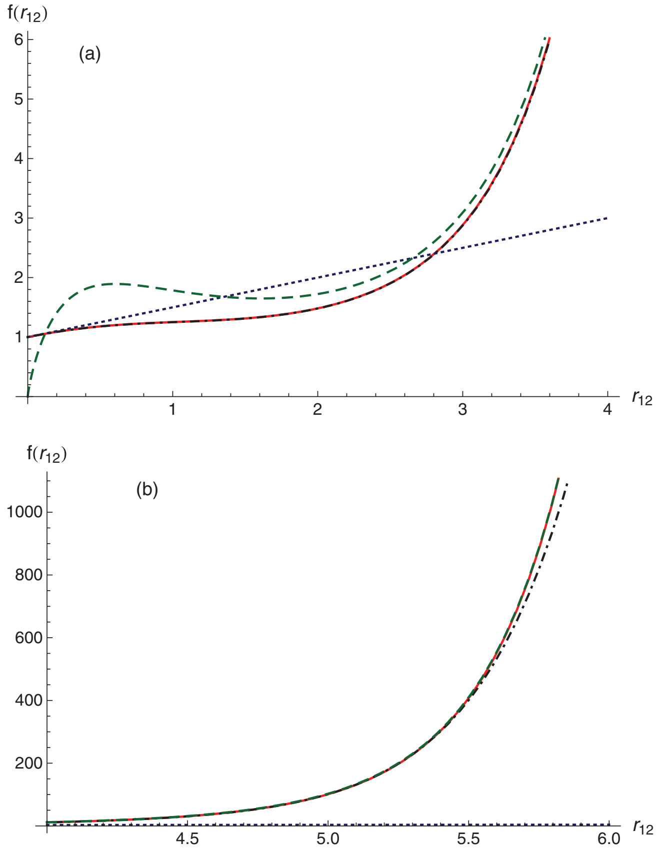

FIG. 3. The correlation factor $f(r)$ calculated for the helium atom by using the Gaussian wave function of Eq. (32) and $\alpha = 0.8598$. Red solid line is the result of numerical solution of the differential equation (33). Black doted-dashed line is the variational solution with $f(r)$ expanded in the powers of r. Green dashed line is the leading term of the asymptotic expansion of $f(r)$ calculated for the relevant values of parameters. Blue dotted line $(1 + \frac{1}{2}r)$ is plotted for the comparison purposes. Two different plot ranges are given separately to improve the readability.

D. Correlated SCF orbitals: Singlet state

We now consider a more complicated model wave function — an SCF determinant multiplied by the correlation factor $f(r)$. For simplicity, we will consider only the ground state of the helium like ions. However, the method developed here can be extended with minor modifications to other states of a two-electron atomic system. We found it too tedious to derive recurrence relations for the coefficients appearing in the asymptotic expansion for $f(r)$. However, we obtained a relatively compact expression for the first term in this expansion and developed a method to obtain in principle as many other terms as desired. The results of this section can be expressed using the following theorem.

Theorem. *If the wave function for a helium-like ion with charge Z has the form*

$$\Psi(r_1, r_2, r) = \phi(r_1)\phi(r_2)f(r), \tag{44}$$

where

$$\phi(r) = e^{-\alpha r}\sum_{k=0}^{N} c_k r^k, \tag{45}$$

then the optimal correlation factor $f(r)$ behaves at large r as $r^\rho e^{Br}$, with

$$B = \alpha - \sqrt{-E} \tag{46}$$

and

$$\rho = \frac{2N(4Z-\alpha-1)+6Z-2\alpha-1}{2(2N+1)\sqrt{-E}} - 2N - 2, \tag{47}$$

where E is the variational energy obtained with the wave function $\Psi(r_1, r_2, r)$.

Note that we do not assume here that the coefficients c_k are obtained from the solution of the matrix SCF equations. The theorem applies to an arbitrary product of one-electron functions of the form of (45). In fact, the coefficients c_k do not even appear explicitly in the equations for the parameters B and ρ.

We begin the proof by writing down the analogue of Eq. (7). It reads

$$\sum_{k,l,m,n=0}^{N} c_k c_l c_m c_n \int_0^\infty \int_{|r_1-r|}^{r_1+r} r_1^{k+1} r_2^{l+1} e^{-\alpha(r_1+r_2)} \times (\hat{H}-E) r_1^n r_2^m e^{-\alpha(r_1+r_2)} f(r)\, dr_2\, dr_1 = 0. \tag{48}$$

Similarly as in the derivations in Secs. II A and II B, we shall identify the coefficients that multiply the two highest powers of r in the differential equation defining $f(r)$. Using Eq. (6) and Eq. (A8), we find that these two highest powers of r are r^{4N+3} and r^{4N+2}. This kind of terms can be produced only by five components of the sum in Eq. (48). The component $k = l = m = n = N$ produces terms of the order $4N + 3$ and $4N + 2$, while the four components for which $k + l + m + n = 4N - 1$ produce terms of the order $4N + 2$. As a result, we need to analyze only the following two integrals:

$$M_1 = \int_0^\infty \int_{|r_1-r|}^{r_1+r} r_1^{N+1} r_2^{N+1} e^{-\alpha(r_1+r_2)} \times (\hat{H}-E) r_1^N r_2^N e^{-\alpha(r_1+r_2)} f(r)\, dr_2\, dr_1, \tag{49}$$

$$M_2 = \int_0^\infty \int_{|r_1-r|}^{r_1+r} r_1^N r_2^{N+1} e^{-\alpha(r_1+r_2)} \times (\hat{H}-E) r_1^N r_2^N e^{-\alpha(r_1+r_2)} f(r) dr_2 dr_1, \tag{50}$$

which correspond to the $k=l=m=n=N$ and $l=m=n=N$, $k=N-1$ case, respectively. The remaining three combinations of indexes lead to the same matrix element as the one given above due to the indistinguishability of electrons and the hermiticity of the Hamiltonian.

The integrals (49) and (50) can be expressed through the integrals $I_{mn}(2\alpha, 2\alpha) \equiv I_{mn}$ of Appendix A. Making use of the asymptotic relation (A8), one easily finds that

$$\begin{aligned} M_1 = &-f''(r) I_{2N+1,2N+1} - r^{-1} f'(r) \\ &\times [-\alpha I_{2N+2,2N+1} - \alpha r^2 I_{2N,2N+1} + \alpha I_{2N,2N+3}] \\ &- f(r)(\alpha^2+E) I_{2N+1,2N+1} + \mathcal{R}_{4N+2}, \end{aligned} \tag{51}$$

where $\mathcal{R}_{4N+2}$ collects terms involving r^{4N+2} and lower powers of r. More explicitly,

$$\begin{aligned} M_1 = &-\frac{e^{-2\alpha r}}{2\alpha} r^{4N+3} [f''(r) C_{2N+1,2N+1} + \alpha f'(r) \\ &\times (C_{2N,2N+3} - C_{2N+2,2N+1} - C_{2N,2N+1}) \\ &+ (\alpha^2+E) C_{2N+1,2N+1} f(r) + \mathcal{O}(r^{-1}),], \end{aligned} \tag{52}$$

where C_{nm} are the coefficients appearing in Eq. (A8) and given by Eq. (A12). Noting that

$$C_{2N+2,2N+1} + C_{2N,2N+1} - C_{2N,2N+3} = 2C_{2N+1,2N+1} \tag{53}$$

end equating the coefficient at r^{4N+3} to zero, we obtain the equation

$$0 = f''(r) - 2\alpha f'(r) + f(r)(\alpha^2 + E), \tag{54}$$

which is a strict analogue of Eq. (13). Its solutions are $e^{(\alpha+\sqrt{-E})r}$ and $e^{(\alpha-\sqrt{-E})r}$, the latter one being the only acceptable choice.

To obtain the pre-exponential factor, we follow the method used in Sec. II A and make the substitution $f(r) = e^{Br} g(r)$, where $B = \alpha - \sqrt{-E}$. To derive a useful equation for $g(r)$, we need a more accurate representation of the the lhs of Eq. (48) than that given by Eq. (52). The required equation, including the next lower power of r, has been derived in Appendix B. It has the form

$$\begin{aligned} & r[f(r)(\alpha^2+E) - 2\alpha f'(r) + f''(r)](2N+1) \\ &+ f(r)\left\{(4N+3)\left[2Z - \frac{\alpha}{2}(2N+3) \right.\right. \\ &\left.\left. + \frac{E}{2\alpha}(2N+1) + 4b_N(\alpha^2+E)\right]\right\} \\ &+ f'(r)[(2N+1) - 8\alpha b_N(4N+3)] \\ &+ f''(r)(4N+3)\left[\frac{2N+1}{2\alpha} + 4b_N\right] = 0, \end{aligned} \tag{55}$$

where $b_N = c_{N-1}/c_N$. After the substitution $f(r) = e^{Br} g(r)$, we obtain the following differential equation for $g(r)$:

$$\begin{aligned} &-2\alpha[1 + 4\sqrt{-E} + 2\alpha(N+1) \\ &\quad + 4N(2N+3)\sqrt{-E} - 2Z(4N+3)]g(r) \\ &\quad - 2[(4N+3)\sqrt{-E}(2N+1+8\alpha b_N) \\ &\quad - 2\alpha(2N+1)(2N+2-\sqrt{-E}\, r)]g'(r) \\ &\quad + [8\alpha b_N(4N+3) + (2N+1)(4N+3+2\alpha r)]g''(r) = 0. \end{aligned} \tag{56}$$

If we now introduce a new variable $x = 2\sqrt{-E}(r+a)$, where

$$a = \frac{(4N+3)(2N+1+8\alpha b_N)}{2\alpha(2N+1)}, \tag{57}$$

then Eq. (56) reduces to the standard Kummer's differential equation

$$x g''(x) + (4N+4-x) g'(x) + \rho g(x) = 0, \tag{58}$$

with ρ given now by Eq. (47). Note that when $N = 0$, Eq. (58) reduces to Eq. (17) with ρ given by Eq. (18). Using the asymptotic representation of the Tricomi function, Eq. (20), we find that $g(r) \sim r^\rho$ and $f(r) \sim r^\rho e^{Br}$ at large r, where B and ρ are given by Eqs. (46) and (47). The complete large-r asymptotic expansion of $f(r)$ can be obtained by inserting the ansatz of Eq. (23), with B and ρ given by Eqs. (46) and (47), into the differential equation for $f(r)$ and deriving recurrence relation for the coefficients d_n. Because of its great complexity, we did not attempt to carry out this procedure except for $N = 1$ and $N = 2$. This completes the proof of the theorem formulated at the beginning of this section.

We find it remarkable that the value of B does not depend explicitly on N. One might expect that an increase of N changes the orbital part of the wave function significantly at large r and, in turn, changes the rate of the asymptotic growth of $f(r)$. This intuition seems to be invalid and B is found to be a universal parameter, dependent on the orbital part of the wave function through the values of α and E only. There is of course an implicit dependence on N through the value of E. This dependence is found to be very weak since the energy saturates very quickly with increasing N. For example, for the helium atom with the optimized parameter $\alpha = 1.84833$ our best theoretical value of B, based on the energy extrapolation toward the complete basis (i.e., infinite N) is 0.148505, while the values obtained with $N = 2$, 3, and 4 are 0.148463, 0.148521, and 0.148504, respectively. Even the value corresponding to $N = 0$ (0.147961) compares well with the estimated limit. Similar conclusions can be drawn from the calculations on the helium-like ions. Therefore, the parameter B seems to be universal and weakly dependent on the quality of the "orbital" part of the wave function.

The dependence of ρ on N appears to be rather strong. At large N, this parameter decreases linearly with N with the slope of -2:

$$\rho = -2N - 2 + \frac{4Z - 1 - \alpha}{2\sqrt{-E}} + \mathcal{O}\left(\frac{1}{N}\right). \tag{59}$$

This result is independent of the values of E, α, and Z. Figure 4 presents the shape of $\rho(N)$ calculated for the helium

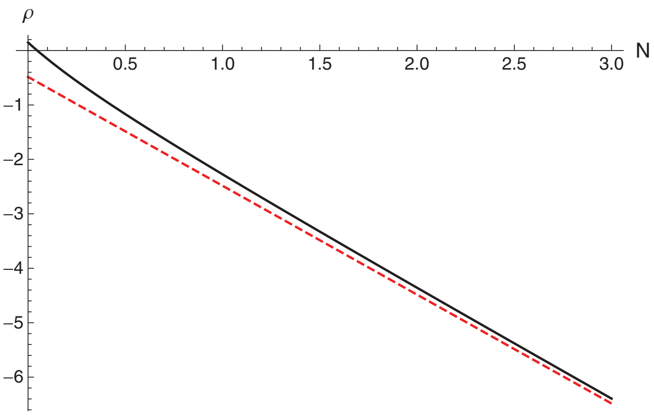

FIG. 4. Plot of $\rho(N)$ parameter calculated for the helium atom [black curve, Eq. (18)] compared to its large-N asymptote [red line, Eq. (59)]. The corresponding curves for the other helium-like ions were not included since they are barely distinguishable with the adopted scale of the plot.

atom with an optimized parameter α. One can see that the convergence toward the linear asymptote is fast, so that even for N being as small as 3.0 the error resulting from the use of Eq. (59) is of the order of 1%. Therefore, for longer expansions of $\phi(r)$, the approximation (59) is sufficiently accurate for all practical purposes.

To verify our findings numerically, we derived explicit differential equation for $f(r)$ in the case of $N = 2$, i.e., a three-term SCF orbital used with in Eq. (45). With the optimized parameter $\alpha = 1.920904$ and $N = 2$, we obtained the SCF energy equal to -2.86159 which compares well with the Hartree-Fock limit[70] of -2.86168. Figure 5 presents results of the numerical propagation of the differential equation for $f(r)$ in the described case. For comparison, we plot the results of the variational calculations with $f(r)$ expanded in a basis set of the powers of r. Excellent agreement between those curves is found for small r albeit for a medium range the variational result becomes unstable and progressively less accurate. A new feature of the correlation factor in the present example is that it is no longer monotonic over the whole domain, as found in the previous models. Instead, it possesses a single maximum for a small r value and then a shallow minimum somewhere at the medium large. The leading term of the asymptotic expansion of $f(r)$ is $r^\rho e^{Br}$ with $B = 0.220361$ and $\rho = -4.38436$, calculated according to Eqs. (46) and (47). Satisfactory agreement between this term and the propagation curve is found for larger values of r.

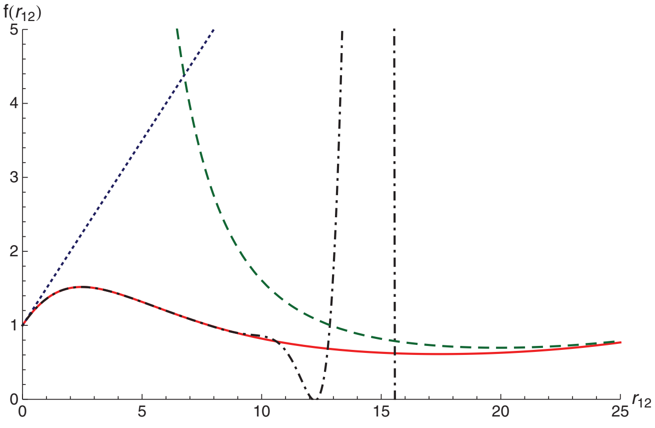

FIG. 5. The correlation factor $f(r)$ calculated for the helium atom by using the wave function (44) ($N = 2$) and $\alpha = 1.920904$. Red solid line is the result of the numerical propagation of the corresponding differential equation. Black dotted line is the variational solution with $f(r)$ expanded in the powers of r. Green dashed line is the leading term of the asymptotic expansion of $f(r)$ calculated for the relevant values of the parameters [see Eqs. (46) and (47)]. Blue dotted line $(1 + \frac{1}{2}r)$ is plotted for the comparison purposes.

E. The Kutzelnigg ansatz

In this section, we extend our approach by considering the following ansatz:

$$\Psi(r_1, r_2, r) = \Psi_0(r_1, r_2) f(r) + \chi(r_1, r_2, r), \tag{60}$$

where $\Psi_0(r_1, r_2)$ is a reference function (either a product of simple exponential functions or SCF orbitals) and the complementary function $\chi(r_1, r_2, r)$ is an ordinary expansion in a set of orbital products. This form of the wave function with $f(r)$ chosen as $1 + \frac{1}{2}r$ was used by Kutzelnigg in his work on the R12 theory.[36] To simplify derivations, we assume that the complementary wave function $\chi(r_1, r_2, r)$ is restricted to the following form:

$$\chi(r_1, r_2, r) = e^{-\alpha(r_1+r_2)} \sum_{kl}^{M} d_{kl}\, r_1^k r_2^l. \tag{61}$$

The basis set used in expansion (61) is incomplete due to lack of angular functions. Including them (via even powers of r) is straightforward and we shall show later that it will not affect the asymptotic behavior of $f(r)$. To avoid technical complications, we make the choice $\Psi_0(r_1, r_2) = e^{-\alpha(r_1+r_2)}$. The main result of this section can be formulated as follows.

Theorem. *If the wave function for the helium like ions has the form*

$$\Psi(r_1, r_2, r) = e^{-\alpha(r_1+r_2)} f(r) + e^{-\alpha(r_1+r_2)} \sum_{kl}^{M} d_{kl}\, r_1^k r_2^l, \tag{62}$$

then the optimal correlation factor $f(r)$ behaves at large r as $r^\rho e^{Br}$, where ρ and B are given by Eqs. (18) and (46), i.e., are the same as in the case of the wave function of Eq. (1).

To prove this theorem, we have to analyze a differential equation for $f(r)$. Such an equation is obtained by inserting Eq. (60) into the Rayleigh-Ritz functional, evaluating its functional derivative with respect to $f(r)$, and equating this derivative to zero. The resulting equation reads

$$\int_0^\infty \int_{|r_1-r|}^{r_1+r} r_1 r_2\, e^{-\alpha(r_1+r_2)} (\hat{H} - E) e^{-\alpha(r_1+r_2)} f(r) dr_2 dr_1$$
$$= -\int_0^\infty \int_{|r_1-r|}^{r_1+r} r_1 r_2\, e^{-\alpha(r_1+r_2)} (\hat{H} - E) \chi(r_1, r_2) dr_2 dr_1. \tag{63}$$

We assume here that the linear coefficients d_{kl} on the rhs are fixed and have already been optimized by solving appropriate algebraic equations involving the optimal $f(r)$.

The homogeneous, left-hand side of the above equation is the same as in Eq. (7), except for an additional factor of $-e^{-2\alpha r}/(48\alpha^3)$. The inhomogeneity on the rhs, which we will further denote by $G(r)$, can be easily expressed through the combinations of auxiliary integrals $I_{mn}(2\alpha, 2\alpha) \equiv I_{mn}$ evaluated in Appendix A. The result reads

$$\begin{aligned}G(r) = \sum_{kl}^{M} d_{kl}\bigg[&\left(\alpha^2 + E - \frac{1}{r}\right) I_{k+1,l+1}\\ &- \alpha(k+1)I_{k,l+1} - \alpha(l+1)I_{k+1,l}\\ &+ \frac{1}{2}k(k+1)I_{k-1,l+1} + \frac{1}{2}l(l+1)I_{k+1,l-1}\\ &+ Z(I_{k,l+1} + I_{k+1,l})\bigg]. \qquad (64)\end{aligned}$$

According to Eq. (A8) from Appendix A each of the integrals I_{mn} appearing in the equation above is a finite order polynomial in r multiplied by the exponential function $e^{-2\alpha r}$. Therefore, the inhomogeneity $G(r)$ is also a polynomial [of the $(2M + 3)$th order] times $e^{-2\alpha r}$. Substituting this form of $G(r)$ into Eq. (63), using Eq. (7) to represent the homogeneous part of Eq. (63), and canceling the exponential factors, we find the following differential equation for $f(r)$:

$$\begin{aligned}&[-3 + 3(4\alpha Z - 2\alpha - 3\alpha^2 + E)r\\ &\quad + 2\alpha(12\alpha Z - 2\alpha - 9\alpha^2 + 3E)r^2 + 4\alpha^2(\alpha^2 + E)r^3]f(r)\\ &\quad + [6 + 12\alpha r + 4\alpha^2 r^2 - 8\alpha^3 r^3]f'(r)\\ &\quad + r[3 + 6\alpha r + 4\alpha^2 r^2]f''(r) = -48\alpha^3 \sum_{k=0}^{2M+3} g_k\, r^k, \qquad (65)\end{aligned}$$

where the coefficients g_k can be easily expressed through d_{kl} and the C_{mn} coefficients of Appendix A.

It is known that the general solution of an inhomogeneous differential equation is given by a linear combination of the solutions of the homogeneous problem plus any particular solution. To find this particular solution, denoted by $f_S(r)$, we try a finite order polynomial as an educated guess,

$$f_S(r) = \sum_{k=0}^{2M+3} h_k\, r^k. \qquad (66)$$

Equations determining the coefficients h_k are found by inserting the above ansatz into the differential equation (65) and gathering the factors multiplying the same powers of r. The first three of these equations are

$$\begin{aligned}&-h_0 + 2h_1 + 16\alpha^3 g_0 = 0,\\ &3h_0(-2\alpha - 3\alpha^2 + E + 4\alpha Z)\\ &\quad + h_1(4\alpha - 1) + 6h_2 + 16\alpha^3 g_1 = 0, \qquad (67)\\ &\alpha h_0(-4\alpha - 18\alpha^2 + 6E + 24\alpha Z)\\ &\quad + h_1(-6\alpha - 5\alpha^2 + 3E + 12\alpha Z)\\ &\quad + 3h_2(12\alpha - 1) + 36h_3 + 48\alpha^3 g_2 = 0,\end{aligned}$$

and the general form is

$$\begin{aligned}&4\alpha^2(\alpha^2+E)h_n - 2\alpha[2\alpha + (13+4n)\alpha^2 - 3E - 12\alpha Z]h_{n+1}\\ &\quad + [-6\alpha + \alpha^2(2n+1)(2n+7) + 3E + 12\alpha Z]h_{n+2}\\ &\quad + [-3 + 6\alpha(n+4)(n+3)]h_{n+3}\\ &\quad + 3(n+4)(n+5)h_{n+4} + 48\alpha^3 g_n = 0. \qquad (68)\end{aligned}$$

The number of equations is the same as the number of coefficients and the determinant of the system of equations does not vanish. Having found the special solution $f_S(r)$, we can write the general solution of Eq. (65),

$$f(r) = c_1 f_1(r) + c_2 f_2(r) + f_S(r), \qquad (69)$$

where $f_1(r)$ and $f_2(r)$ are the solutions of the homogeneous problem behaving asymptotically as, $e^{(\alpha-\sqrt{-E})r} r^{\rho}$ and $e^{(\alpha+\sqrt{-E})r} r^{\rho'}$, respectively, see the discussion around Eqs. (19)–(24) in Sec. II A.

We can fix the value of c_2 as equal to zero, otherwise the wave function would not be normalizable. Thus, the long-range behavior of $f(r)$ in the present case reads:

$$f(r) \sim c_1 e^{(\alpha-\sqrt{-E})r} r^{\rho} + f_S(r), \qquad (70)$$

where c_1 can be fixed by normalization. Since the particular solution is characterized by a polynomial growth and the chosen solution of the homogeneous problem grows exponentially, the leading term of the asymptotic expansion remains exponential. In other words, for a sufficiently large r the behavior of $f(r)$ is always dominated by the exponential growth of the solution to the homogeneous problem. This formally completes the proof of the theorem stated at the beginning of this section.

It is easy to extend the above theorem by including higher angular momentum functions in the one-electron basis set. One can show that this is equivalent to taking the following form of the complementary wave function

$$\begin{aligned}\chi(r_1, r_2, r) = e^{-\alpha(r_1+r_2)} \sum_{kl} d_{kl}^{(0)}\, r_1^k r_2^l + r^2 e^{-\alpha(r_1+r_2)} \sum_{kl} d_{kl}^{(1)}\, r_1^k r_2^l\\ + r^4 e^{-\alpha(r_1+r_2)} \sum_{kl} d_{kl}^{(2)}\, r_1^k r_2^l + \ldots \qquad (71)\end{aligned}$$

This extension does not change the main feature of the differential equation that was used in the proof. Namely, the solution of the homogeneous problem remains unchanged and the inhomogeneity is still a finite-order polynomial in r. Therefore, a special solution has the polynomial character and does not contribute to the leading term in the long-range asymptotics.

We also considered another variant of the Kutzelnigg ansatz,

$$\Psi(r_1, r_2, r) = e^{-\alpha(r_1+r_2)} f(r) + e^{-\beta(r_1+r_2)} \sum_{kl}^{M} d_{kl}\, r_1^k r_2^l, \qquad (72)$$

which differs from the wave function (62) by the choice of different exponent in the complementary part $\chi(r_1, r_2, r)$ of the wave function. This additional flexibility is not very effective in the calculations on the helium atom. We checked that the optimal value of β is very close to the adopted value of α

and the energy gain is insignificant. However, when passing to many-electron systems and using the expansion of pair functions similar to Eq. (72), the splitting of α and β corresponds to the use of more diffuse (or more tight) basis set functions in $\Psi(r_1, r_2, r)$ than in $\Psi_0(r_1, r_2)$. This is an important case and therefore the model (72) is worth considering. As before, the extension of (72) by including higher angular momentum functions is simple, so we proceed only with s-type functions in the basis.

By repeating the derivation in the previous model, Eqs. (63)–(65), we find that the differential equation for $f(r)$ is the same as Eq. (65), except that the inhomogeneity in Eq. (65) is now given by the function

$$\widetilde{G}(r) = -48\alpha^3\, e^{-2(\beta-\alpha)r} \sum_{t=0}^{2M+3} \widetilde{g}_k\, r^k, \tag{73}$$

where $\widetilde{g}_k$ are defined in the same way as the g_k coefficients in Eq. (65). The solution of the homogeneous problem is the same as in Sec. II A. We also found that with appropriate choice of $\widetilde{h}_k$, the function

$$\widetilde{f_S}(r) = e^{-2(\beta-\alpha)r} \sum_{k=0}^{2M+3} \widetilde{h}_k\, r^k \tag{74}$$

is a particular solution of the full equation containing the inhomogeneity $\widetilde{G}(r)$. We can thus use the same arguments as previously and infer that

$$f(r) \sim c_1 e^{(\alpha-\sqrt{-E})r} r^\rho + e^{-2(\beta-\alpha)r} \sum_{k=0}^{2M+3} \widetilde{h}_k\, r^k, \tag{75}$$

asymptotically for large r. The dominant term of this formula depends on the relation between α and β. In particular, the large-r the asymptotics of $f(r)$ is given by

$$f(r) \sim r^\rho\, e^{(\alpha-\sqrt{-E})r} \quad \text{for} \quad \beta > \beta_c, \tag{76}$$

$$f(r) \sim r^{2M+3}\, e^{2(\alpha-\beta)r} \quad \text{for} \quad \beta < \beta_c, \tag{77}$$

where β_c is the critical value of β equal to

$$\beta_c = \frac{1}{2}(\alpha + \sqrt{-E}). \tag{78}$$

Thus, independent of the choice of β, we find an exponential growth of $f(r)$ at large r.

III. DISCUSSION AND CONCLUSIONS

A. The "range-separated" model of the correlation factor

The analytic results presented in Sec. II can be put into practical use only if a simple analytical form of the correlation factor can be found that mimics, to a good approximation, the exact behavior of $f(r)$ both at small and at large interelectronic distances r. This goal is far from being straightforward. This is mainly due to considerable change in the shape of the correlation factor when the function Ψ_0 is modified. For the simplest possible Ψ_0 taken as the product of 1s orbitals, the correlation factor is a monotonically growing function, while for Ψ_0 taken as an SCF determinant, $f(r)$ exhibits a maximum and minimum before the onset of the monotonic exponential growth. Knowing the behavior of the correlation factor at small and large r, we can propose a "range-separated" form with a Gaussian switching

$$f(r) = \left(1 + \frac{1}{2}r\right) e^{-\mu r^2} + c\, r^\rho\, e^{Br}\, S_n(\mu r^2), \tag{79}$$

where

$$S_n(x) = 1 - e^{-x} \sum_{l=0}^{n} \frac{x^l}{l!} \tag{80}$$

serves as the "switching function" that interpolates smoothly between the two regimes and the switching is controlled by adjustable parameters c and μ. To eliminate the singularity appearing when $\rho < 0$, we take as n the smallest integer satisfying $2n + \rho \geq 0$. For positive ρ, we set $n = 0$. This form of $f(r)$ is slightly reminiscent of the error-function based range-separation of the Coulomb interaction in the density functional theory.[71] We can increase somewhat the flexibility of this representation by using the Ten-no's factor at short range,

$$f(r) = \frac{1 + 2\gamma - e^{-\gamma r}}{2\gamma}\, e^{-\mu r^2} + c\, r^\rho\, e^{Br}\, S_n(\mu r^2). \tag{81}$$

We found that, the analytical form (81) is very flexible. By means of the optimization of the adjustable parameters, we are able to obtain a very good analytic fit for each correlation factor discussed in the paper.

When the correlation factor of the form (81) is used in the calculations, new classes of two-electron integrals arise that were not considered in the literature so far. In these integrals, the factors r^ρ, e^{-ar}, and e^{-ar^2} are present collectively. For the atomic calculations, we managed to express these integrals in terms of the incomplete Gamma and error functions, both in the Slater and Gaussian one-electron basis, and implement them efficiently. These integrals become substantially more difficult when one passes to the many-center molecular systems. The work on evaluating them is in progress in our laboratory.

B. Results of exemplary calculations

To check the effectiveness of the "range-separated" representation of Eqs. (79) and (81), we performed variational calculations with the wave function of the form of Eqs. (1) and (62). The values of the parameters B and ρ were fixed according to Eqs. (46) and (18). The exponent α was set equal to 1.84833. The parameters γ, μ, and c were obtained by a least square fit to the exact correlation factor in Eq. (1), obtained from the numerical solution of Eq. (8). We found that for the helium atom $\gamma = 0.209587$, $\mu = 0.448695$, and $c = 1.170940$ are optimal when Eq. (81) is used, while for Eq. (79) the values $\mu = 0.861347$ and $c = 1.169033$ are appropriate.

The results are summarized in Table II. An inspection of this table shows that accounting for the correct large-r behavior of $f(r)$ via simple formulas of Eqs. (79) and (81) improves significantly the energies obtained with the standard R12 or F12 correlation factors. As expected, the improvement is smaller when the exponential factor with optimized γ is

TABLE II. Ground-state energies of the helium atom obtained with approximate wave functions of Eqs. (1) and (62). Results obtained with the linear, $1 + r/2$, and exponential, $(1 + 2\gamma - e^{-\gamma r})/(2\gamma)$, correlation factors are denoted by R12 and F12, respectively. The parameter $\gamma = 0.2$ is close to optimal. Equations (79) and (81) are evaluated with $n = 0$. The orbital exponent α was always set equal to 1.84833.

$f(r)$	Wave function of Eq. (1)	Wave of function Eq. (62)
R12	– 2.887447	– 2.903014
F12 ($\gamma = 0.5$)	– 2.886746	– 2.902976
F12 ($\gamma = 1.0$)	– 2.874472	– 2.900928
F12 ($\gamma = 0.2$)	– 2.890349	– 2.903277
Eq. (79)	– 2.890886	– 2.903266
Eq. (81)	– 2.891048	– 2.903325
Limit	– 2.891254[a]	– 2.903512[b]

[a] Obtained by numerical integration of differential equation.

[b] Obtained by expanding $f(r)$ in powers of r (saturated results, all digits shown are correct).

used. Note, however, that the optimal value of γ, equal to 0.2, is in this case much smaller than the value recommended in standard F12 calculations.[75]

It can be seen that with the correlation factor of the form (81) used in the wave function of Eq. (1), we recover about 70% of the correlation energy, so that the expansion in a set of excited state determinants is required only for the remaining 30%. Standard R12 approximation is worse in this respect, recovering about 60% of the correlation energy.

When the wave function of the form of Eq. (62) is used in the calculations, the obtained energy differences are much smaller but one can see that including the correct asymptotics of $f(r)$ always improves the results. It should be pointed out that in this case the parameters of the correlation factors of Eqs. (79) and (81) were optimized for the wave function of Eq. (1). Nevertheless, the difference between the energy obtained with the approximate correlation factor of Eq. (81) and the fully optimal one, equal to 0.18 milihartree, is smaller than the corresponding difference remaining when using the wave function of Eq. (1). It may also be noted that the energy obtained with the optimal wave function of Eq. (62), i.e., with orbitals of *s*-type symmetry only, is slightly better than the energy from the full CI calculations in the saturated *spdf* basis set.[72–74] With the linear correlation factor the *spd* limit would be reached with this wave function.

We also performed calculations with Ten-no's exponential correlation factor and several values of γ which are usually recommended in the literature with $\gamma = 1.0$ being the most common choice.[75,76] Other values, $\gamma = 0.5$ and $\gamma = 1.5$ were also employed.[77–79] The results are shown in Table II. On can see that all these choices of γ give results worse than the "range-separated" correlation factor of Eq. (81). However, when the exponential correlation factor with optimal γ is used in the wave function of Eq. (62), the energy is slightly better than the one obtained with the asymptotically corrected linear correlation factor of Eq. (79). This is the manifestation of the superiority of the Ten-no's factor over the linear one at intermediate interelectronic distances.

C. Summary and conclusions

In this work, we have considered the problem of an optimal form of the correlation factor $f(r)$ for explicitly correlated wave functions, specifically, its asymptotic behavior at large interelectronic distances r. We employed the helium atom and helium-like ions as model systems and studied several approximate forms of the wave function. For the simplest case of the wave function of the form $e^{-\alpha(r_1+r_2)} f(r)$, the optimal correlation factor is an exponentially growing function with no extremal points at short range. On the other hand, for the case of an SCF determinant multiplied by the correlation factor, $f(r)$ possesses a single maximum in a small r regime and a minimum at medium r distances. However, in both cases, the asymptotic form of the correlation factor is $r^\rho e^{Br}$, with $B > 0$, so that at large interelectronic distances $f(r)$ diverges exponentially. While the presence of a maximum in the correlation factor for the SCF case has been observed in the study of Tew and Klopper,[64] neither the presence of the minimum nor the large-r divergence of $f(r)$ have been noticed.

We presented a method to derive a well-defined differential equation for $f(r)$ that can be solved analytically in the large-r regime or alternatively integrated numerically with arbitrary precision using well-developed propagation techniques. The exact analytic information about its solution gives us an opportunity to design new functional form for the correlation factor. We proposed a "range-separated" model where the short- and long-range regimes are approximated by different formulas and sewed together by using a switching function. Simple exemplary calculations with the new form of the correlation factor show that it performs significantly better than the correlation factors used in R12 or F12 methods.

The method proposed in this paper can be a subject to several extensions. First of all, it can be applied to a two-center system to reveal the possible dependence of the correlation factor on the internuclear distance. The second extension goes toward the three-electron atomic systems, such as the lithium atom. This extension may shed some light on the problem of "explicit correlation of triples" considered recently in the literature[80,81]

To apply the proposed form of the correlation factor in calculations for molecular systems, difficulties concerning the evaluation of the new integrals and application of the RI approximations must be addressed. The work in this direction is in progress in our laboratory. We hope that the proposed models of $f(r)$ will find applications in explicitly correlated atomic and molecular calculations and will help to increase the accuracy of these calculations.

ACKNOWLEDGMENTS

This work was supported by the NCN Grant No. NN204182840. M.L. thanks the Polish Ministry of Science and Higher Education for the support through the project "Diamentowy Grant" No. DI2011 012041. R.M. thanks the Foundation for Polish Science for support within the MISTRZ programme. Part of this work was done while R.M. was visiting the Kavli Institute for Theoretical Physics, University of

California at Santa Barbara and was supported by the NSF Grant No. PHY11-25915.

APPENDIX A: EVALUATION OF AUXILIARY INTEGRALS

In this Appendix, we give expressions for the integrals,

$$I_{mn}(\alpha,\beta,r)=\int_0^\infty\int_{|r_1-r|}^{r_1+r}e^{-\alpha r_1-\beta r_2}r_1^m r_2^n dr_2 dr_1, \tag{A1}$$

which appear in the derivation of differential equations for $f(r)$. We will assume that m and n are non-negative integers and that $\alpha+\beta>0$. The closed form expressions for the integrals (A1) can be obtained most easily by the change of variables $\xi=(r_1+r_2)/r$, $\eta=(r_1-r_2)/r$ and the appropriate change of integration range to $\xi\in[1,+\infty]$ and $\eta\in[-1,+1]$. The absolute value of the Jacobian is $|J|=r^2/2$. The integral (A1) can now be written as

$$I_{mn}(\alpha,\beta,r)=\sum_{l=0}^{m}\sum_{k=0}^{n}\binom{m}{l}\binom{n}{k}(-1)^{n-k}J_{k+l,m+n-l-k}(\alpha,\beta,r), \tag{A2}$$

where

$$J_{kl}(\alpha,\beta,r)=2\left(\frac{r}{2}\right)^{k+l+2}A_k(p)\,B_l(q), \tag{A3}$$

$A_k(p)$ and $B_k(q)$ being the well-known integrals,

$$A_k(p)=\int_1^\infty \xi^k e^{-p\xi}d\xi=\frac{k!}{p^{k+1}}e^{-p}\sum_{j=0}^{k}\frac{p^j}{j!}, \tag{A4}$$

$$\begin{aligned}B_l(q)&=\int_{-1}^{1}\eta^l e^{-q\eta}d\eta\\&=\frac{l!}{q^{l+1}}\left[e^q\sum_{j=0}^{l}\frac{(-1)^j q^j}{j!}-e^{-q}\sum_{j=0}^{l}\frac{q^j}{j!}\right]\end{aligned} \tag{A5}$$

computed at $p=r(\alpha+\beta)/2$ and $q=r(\alpha-\beta)/2$. When $\alpha=\beta$, i.e., $q=0$, then

$$B_l(0)=\frac{1}{l+1}[1+(-1)^l]. \tag{A6}$$

In Sec. II D, we need information about the large r behavior of the integrals $I_{mn}(\alpha,\alpha,r)$. Using Eq. (A3), we find

$$\begin{aligned}J_{kl}(\alpha,\alpha,r)=&\frac{e^{-\alpha r}}{\alpha}\left(\frac{r}{2}\right)^{k+l+1}\frac{1+(-1)^l}{1+l}\\&\times\left[1+\frac{k}{\alpha r}+\mathcal{O}\left(\frac{1}{r^2}\right)\right].\end{aligned} \tag{A7}$$

Inserting this result into Eq. (A2) and rearranging summation order, we arrive at

$$I_{mn}(\alpha,\alpha,r)=\frac{e^{-\alpha r}}{\alpha}r^{m+n+1}\left[C_{mn}+\frac{D_{mn}}{2\alpha r}+\mathcal{O}\left(\frac{1}{r^2}\right)\right], \tag{A8}$$

where

$$C_{mn}=\frac{1}{2^{m+n+1}}\sum_{l=0}^{m}\sum_{k=0}^{n}\binom{m}{l}\binom{n}{k}\frac{(-1)^k+(-1)^l}{k+l+1}, \tag{A9}$$

and

$$D_{mn}=\frac{1}{2^{m+n}}\sum_{l=0}^{m}\sum_{k=0}^{n}\binom{m}{l}\binom{n}{k}\frac{(-1)^k+(-1)^l}{k+l+1}(m-l+n-k). \tag{A10}$$

Using the formula[82]

$$\sum_{k=0}^{n}\binom{n}{k}\frac{(-1)^k}{k+l+1}=\frac{n!\,l!}{(n+l+1)!}, \tag{A11}$$

the summations in Eq. (A9) can be carried out and one obtains a simple expression for C_{mn},

$$C_{mn}=\frac{n!\,m!}{(n+m+1)!}. \tag{A12}$$

The corresponding expression for D_{mn} can be obtained from that for C_{mn}. After a few simple manipulations, one finds that

$$D_{mn}=2(m+n+1)C_{mn}-\delta_{m0}-\delta_{n0}, \tag{A13}$$

where δ_{ij} is the Kronecker symbol.

APPENDIX B: PROOF OF EQ. (55)

To derive Eq. (55), we have to extract terms proportional to r^{4N+2} that appear in the integrals M_1 and M_2. To do so, we need an explicit expression for the remainder $\mathcal{R}_{4N+2}$ in Eq. (55). Representing M_1 in terms of the I_{mn} integrals and invoking the asymptotic relation (A8), one obtains

$$\begin{aligned}\mathcal{R}_{4N+2}=&f(r)[2\alpha(N+1)I_{2N,2N+1}\\&-2ZI_{2N,2N+1}+r^{-1}I_{2N+1,2N+1}]\\&+r^{-1}f'(r)[(N+2)I_{2N+1,2N+1}+Nr^2I_{2N-1,2N+1}\\&-NI_{2N-1,2N+3}]+\mathcal{R}_{4N+1}.\end{aligned} \tag{B1}$$

We expand now the I_{mn} integrals in Eqs. (55) and (B1) with the help of Eq. (A8) and after some rearrangements and simplifications, we arrive the following formula for M_1:

$$M_1=r^{4N+2}\frac{e^{-2\alpha r}}{2\alpha}[r\,\Xi_{4N+3}+\Omega_{4N+2}+\mathcal{O}(r^{-1})], \tag{B2}$$

where

$$\Xi_{4N+3}=-[f(r)(\alpha^2+E)-2\alpha f'(r)+f''(r)]C_{2N+1,2N+1}, \tag{B3}$$

cf. Eqs. (52) and (53), and

$$\begin{aligned}\Omega_{4N+2}=f(r)\Big[&-\frac{1}{2}(\alpha+\frac{E}{2\alpha})D_{2N+1,2N+1}\\&+2(\alpha N+\alpha-Z)C_{2N,2N+1}+C_{2N+1,2N+1}\Big]\end{aligned}$$

$$
\begin{aligned}
&- f'(r)\Big[(N+2)C_{2N+1,2N+1} \\
&- \frac{1}{4}D_{2N+2,2N+1} + NC_{2N-1,2N+1} \\
&- NC_{2N-1,2N+3} - \frac{1}{4}D_{2N,2N+1} + \frac{1}{4}D_{2N,2N+3}\Big] \\
&- \frac{1}{4\alpha}D_{2N+1,2N+1}f''(r). \qquad \text{(B4)}
\end{aligned}
$$

The expression for Ω_{4N+2} can be simplified using Eq. (A13) and the following two identities holding for every $N \geq 0$:

$$
\begin{aligned}
&2(N+1)C_{2N,2N+1} - \frac{1}{2}(4N+3)C_{2N+1,2N+1} \\
&\quad = \frac{1}{2}(2N+3)C_{2N,2N+1}, \qquad \text{(B5)}
\end{aligned}
$$

$$
\begin{aligned}
&NC_{2N-1,2N+1} - NC_{2N-1,2N+3} - (2N+1)C_{2N,2N+1} \\
&\quad + (2N+2)C_{2N,2N+3} = 0. \qquad \text{(B6)}
\end{aligned}
$$

The result of these simplifications is

$$
\begin{aligned}
\Omega_{4N+2} = f(r)\Big[&\frac{\alpha}{2}(2N+3)C_{2N,2N+1} - 2ZC_{2N,2N+1} \\
&+ C_{2N+1,2N+1} - \frac{E}{2\alpha}(4N+3)C_{2N+1,2N+1}\Big] \\
&- f'(r)C_{2N+1,2N+1} - \frac{4N+3}{2\alpha}C_{2N+1,2N+1}f''(r). \qquad \text{(B7)}
\end{aligned}
$$

We still need to determine the last required ingredient — the terms proportional to r^{4N+2} that are in contained M_2. Expressing M_2 in terms of I_{mn} integrals, we find

$$
\begin{aligned}
M_2 = &- f(r)(\alpha^2 + E)I_{2N+1,2N} + \frac{1}{2}\alpha\, r^{-1} \\
&\times f'(r)[I_{2N+2,2N} + r^2 I_{2N,2N} + r^2 I_{2N+1,2N-1} \\
&+ I_{2N+1,2N+1} - I_{2N,2N+2} - I_{2N+3,2N-1}] \\
&- I_{2N+1,2N}f''(r) + \mathcal{R}_{4N+1}. \qquad \text{(B8)}
\end{aligned}
$$

Expansion of every I_{mn} integral according to Eq. (A8) gives

$$
M_2 = r^{4N+2}\,\frac{e^{-2\alpha r}}{2\alpha}\,[\,\Lambda_{4N+2} + \mathcal{O}(r^{-1})\,], \qquad \text{(B9)}
$$

where

$$
\Lambda_{4N+3} = -C_{2N+1,2N}[(\alpha^2 + E)f(r) - 2\alpha f'(r) + f''(r)]. \qquad \text{(B10)}
$$

To derive Eq. (B10), we used the following relation holding for every $N \geq 0$:

$$
\begin{aligned}
&C_{2N,2N} + C_{2N+1,2N-1} + C_{2N+1,2N+1} - C_{2N+3,2N-1} \\
&\quad = 4C_{2N+1,2N}. \qquad \text{(B11)}
\end{aligned}
$$

We now have all elements needed to construct the two leading terms of the rhs of Eq. (48). Using Eqs. (B2) and (B9), one finds that the rhs of Eq. (48) can be written as

$$
\begin{aligned}
c_N^3\, r^{4N+2}\,\frac{e^{-2\alpha r}}{2\alpha}[&c_N\,(r\,\Xi_{4N+3} + \Omega_{4N+2}) \\
&+ 4c_{N-1}\,\Lambda_{4N+2} + \mathcal{O}(r^{-1})], \qquad \text{(B12)}
\end{aligned}
$$

where Ξ_{4N+3}, Ω_{4N+2} and Λ_{4N+2} are given by Eqs. (B3), (B7), and (B10), respectively, and c_N and c_{N-1} are defined through Eq. (45). The factor of 4 in front of c_{N-1} is a result of the symmetry discussed in Eqs. (49) and (50). By neglecting the terms of the order lower than r^{4N+2} and equating the remaining ones to zero, we obtain the required differential equation for the function that determines the large-r asymptotic behavior of $f(r)$,

$$
r\,\Xi_{4N+3} + \Omega_{4N+2} + 4b_N\,\Lambda_{4N+2} = 0, \qquad \text{(B13)}
$$

where $b_N = c_{N-1}/c_N$. Inserting into Eq. (B13) the explicit expressions for Ξ_{4N+3}, Ω_{4N+2}, and Λ_{4N+2}, given by Eqs. (B3), (B7), and (B10), dividing by $C_{2N+1,\,2N+1}$ and using the trivial identity,

$$
\frac{C_{2N,2N+1}}{C_{2N+1,2N+1}} = \frac{4N+3}{2N+1}, \qquad \text{(B14)}
$$

one arrives at Eq. (55).

[1] C. Hättig, W. Klopper, A. Köhn, and D. P. Tew, Chem. Rev. **112**, 4 (2012).

[2] L. Kong, F. A. Bischoff, and E. F. Valeev, Chem. Rev. **112**, 75 (2012).

[3] T. Kato, Commun. Pure Appl. Math. **10**, 151 (1957).

[4] R. T. Pack and W. Byers Brown, J. Chem. Phys. **45**, 556 (1966).

[5] S. Furnais, M. Hoffmann-Ostenhof, T. Hoffmann-Ostenhof, and T. Ø. Sørensen, Commun. Math. Phys. **255**, 183 (2005).

[6] M. Hoffmann-Ostenhof, T. Hoffmann-Ostenhof, and H. Stremnitzer, Phys. Rev. Lett. **68**, 3857 (1992).

[7] K. Szalewicz and B. Jeziorski, Mol. Phys. **108**, 3091 (2010).

[8] S. Ten-no, Theor. Chem. Acc. **131**, 1070 (2012).

[9] R. Bukowski, B. Jeziorski, and K. Szalewicz, in *Explicitly Correlated Functions in Chemistry and Physics: Theory and Applications*, edited by J. Rychlewski (Kluwer, Dordrecht, 2003), p. 185.

[10] J. Rychlewski, and J. Komasa, in *Explicitly Correlated Functions in Chemistry and Physics: Theory and Applications*, edited by J. Rychlewski (Kluwer, Dordrecht, 2003), p. 91.

[11] S. Bubin, M. Pavanelo, W. C. Tung, K. L. Sharkley, and L. Adamowicz, Chem. Rev. **113**, 36 (2013).

[12] J. C. Slater, Phys. Rev. **31**, 333 (1928).

[13] E. A. Hylleraas, Z. Phys. **54**, 347 (1929).

[14] E. A. Hylleraas, Z. Phys. **48**, 469 (1928).

[15] R. Jastrow, Phys. Rev. **98**, 1479 (1955).

[16] A. Lüchow and J. B. Anderson, Annu. Rev. Phys. Chem. **51**, 501 (2000).

[17] W. M. C. Foulkes, L. Mitas, R. J. Needs, and G. Rajagopal, Rev. Mod. Phys. **73**, 33 (2001).

[18] S. A. Kucharski and R. J. Bartlett, Adv. Quantum Chem. **18**, 281 (1986).

[19] R. J. Bartlett and M. Musiał, Rev. Mod. Phys. **79**, 291 (2007).

[20] F. W. Byron and C. J. Joachain, Phys. Rev. **146**, 1 (1966).

[21] K. C. Pan and H. F. King, J. Chem. Phys. **53**, 4397 (1970).

[22] K. C. Pan and H. F. King, J. Chem. Phys. **56**, 4667 (1972).

[23] G. Chałasiński, B. Jeziorski, J. Andzelm, and K. Szalewicz, Mol. Phys. **33**, 971 (1977).

[24] K. Szalewicz and B. Jeziorski, Mol. Phys. **38**, 191 (1979).

[25] K. Szalewicz, B. Jeziorski, H. J. Monkhorst, and J. G. Zabolitzky, Chem. Phys. Lett. **91**, 169 (1982).

[26] K. Szalewicz, B. Jeziorski, H. J. Monkhorst, and J. G. Zabolitzky, J. Chem. Phys. **79**, 5543 (1983).

[27] B. Jeziorski, K. Szalewicz, H. J. Monkhorst, and J. G. Zabolitzky, J. Chem. Phys. **81**, 368 (1984).

[28] L. Adamowicz and A. J. Sadlej, J. Chem. Phys. **67**, 4298 (1977).

[29] L. Adamowicz and A. J. Sadlej, J. Chem. Phys. **69**, 3992 (1978).

[30] L. Adamowicz, Int. J. Quantum Chem. **13**, 265 (1978).

[31] R. Bukowski, B. Jeziorski, and K. Szalewicz, J. Chem. Phys. **110**, 4165 (1999).
[32] M. Przybytek, B. Jeziorski, and K. Szalewicz, Int. J. Quantum Chem. **109**, 2872 (2009).
[33] K. Patkowski, W. Cencek, M. Jeziorska, B. Jeziorski, and K. Szalewicz, J. Phys. Chem. A **111**, 7611 (2007).
[34] K. B. Wenzel, J. G. Zabolitzky, K. Szalewicz, B. Jeziorski, and H. Monkhorst, J. Chem. Phys. **85**, 3964 (1986).
[35] R. Bukowski, B. Jeziorski, S. Rybak, and K. Szalewicz, J. Chem. Phys. **102**, 888 (1995).
[36] W. Kutzelnigg, Theor. Chim. Acta **68**, 445 (1985).
[37] W. Klopper and W. Kutzelnigg, Chem. Phys. Lett. **134**, 17 (1987).
[38] W. Kutzelnigg and W. Klopper, J. Chem. Phys. **94**, 1985 (1991).
[39] J. Noga, W. Kutzelnigg, and W. Klopper, Chem. Phys. Lett. **199**, 497 (1992).
[40] J. Noga and W. Kutzelnigg, J. Chem. Phys. **101**, 7738 (1994).
[41] W. Klopper, and J. Noga, in *Explicitly Correlated Functions in Chemistry and Physics: Theory and Applications*, edited by J. Rychlewski (Kluwer, Dordrecht, 2003), p. 149.
[42] W. Klopper and C. C. M. Samson, J. Chem. Phys. **116**, 6397 (2002).
[43] F. R. Manby, J. Chem. Phys. **119**, 4607 (2003).
[44] S. Ten-no, J. Chem. Phys. **121**, 117 (2004).
[45] S. Ten-no and F. R. Manby, J. Chem. Phys. **119**, 5358 (2003).
[46] E. F. Valeev, Chem. Phys. Lett. **395**, 190 (2004).
[47] E. F. Valeev and H. F. Schaefer, J. Chem. Phys. **113**, 3990 (2000).
[48] E. F. Valeev and C. L. Janssen, J. Chem. Phys. **121**, 1214 (2004).
[49] R. J. Gdanitz, Chem. Phys. Lett. **210**, 253 (1993).
[50] R. J. Gdanitz, Chem. Phys. Lett. **283**, 253 (1998).
[51] B. J. Persson and P. R. Taylor, J. Chem. Phys. **105**, 5915 (1996).
[52] B. J. Persson and P. R. Taylor, Theor. Chem. Acc. **97**, 240 (1997).
[53] P. Dahle and P. R. Taylor, Theor. Chem. Acc. **105**, 401 (2001).
[54] A. J. May, E. Valeev, R. Polly, and F. R. Manby, Phys. Chem. Chem. Phys. **7**, 2710 (2005).
[55] A. J. May and F. R. Manby, J. Chem. Phys. **121**, 4479 (2004).
[56] S. Ten-no, Chem. Phys. Lett. **398**, 56 (2004).
[57] T. Shiozaki, G. Knizia, and H.-J. Werner, J. Chem. Phys. **134**, 034113 (2011).
[58] T. Shiozaki and H.-J. Werner, J. Chem. Phys. **134**, 184104 (2011).
[59] S. Ten-no, Chem. Phys. Lett. **447**, 175 (2007).
[60] M. Torheyden and E. F. Valeev, J. Chem. Phys. **131**, 171103 (2009).
[61] T. Shiozaki and H.-J. Werner, J. Chem. Phys. **133**, 141103 (2010).
[62] S. Kedzuch, O. Demel, J. Pittner, S. ten-no, and J. Noga, Chem. Phys. Lett. **511**, 418 (2011).
[63] T. J. Martinez and S. Varganov, J. Chem. Phys. **132**, 054103 (2010).
[64] D. P. Tew and W. Klopper, J. Chem. Phys. **123**, 074101 (2005).
[65] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables* (Dover, New York, 1972).
[66] G. Pestka, J. Phys. A: Math. Theor. **41**, 235202 (2008).
[67] G. Arfken, *Mathematical Methods for Physicists*, 3rd ed. (Academic Press, Inc., London, UK, 1985).
[68] C. M. Bender and S. A. Orszag, *Advanced Mathematical Methods for Scientists and Engineers: Asymptotic Methods and Perturbation Theory* (Springer-Verlag, New York, USA, 1999).
[69] D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953).
[70] K. Szalewicz and H. J. Monkhorst, J. Chem. Phys. **75**, 5785 (1981).
[71] T. Leininger, H. Stoll, H.-J. Werner, and A. Savin, Chem. Phys. Lett. **275**, 151 (1997).
[72] D. P. Carrol, H. J. Silverstone, and R. M. Metzger, J. Chem. Phys. **71**, 4142 (1979).
[73] C. F. Bunge, Theor. Chim. Acta (Berlin) **16**, 126 (1970).
[74] A. Weiss, Phys. Rev. **122**, 1826 (1961).
[75] J. Noga, S. Kedžuch, J. Šimunek, and S. Ten-no, J. Chem. Phys. **128**, 174103 (2008).
[76] W. Skomorowski, F. Pawłowski, T. Korona, R. Moszynski, P. S. Żuchowski, and J. M. Hutson, J. Chem. Phys. **134**, 114109 (2011).
[77] G. Rauhut, G. Knizia, and H.-J. Werner, J. Chem. Phys. **130**, 054105 (2009).
[78] T. Shiozaki, M. Kamiya, S. Hirata, and E. F. Valeev, J. Chem. Phys. **130**, 054101 (2009).
[79] K. E. Yousaf and K. A. Peterson, J. Chem. Phys. **129**, 184108 (2008).
[80] A. Köhn, J. Chem. Phys. **130**, 131101 (2009).
[81] A. Köhn, J. Chem. Phys. **133**, 174118 (2010).
[82] R. Garrappa, Int. Math. Forum **2**, 725 (2007).