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ABSTRACT

The scaling function g of the scaled Schrödinger equation (SSE) is generalized to obtain accurate solutions of the Schrödinger equation (SE) with the free complement (FC) theory. The electron–nuclear and electron–electron scaling functions, g_{iA} and g_{ij}, respectively, are generalized. From the relations between SE and SSE at the inter-particle distances being zero and infinity, the scaling function must satisfy the collisional (or coalescent) condition and the asymptotic condition, respectively. Based on these conditions, general scaling functions are classified into "correct" (satisfying both conditions), "reasonable" (satisfying only collisional condition), and "approximate but still useful" (not satisfying collisional condition) classes. Several analytical scaling functions are listed for each class. Popular functions r_{iA} and r_{ij} belong to the reasonable class. The qualities of many electron–electron scaling functions are examined variationally for the helium atom using the FC theory. Although the complement functions of FC theory are produced generally from both the potential and kinetic operators in the Hamiltonian, those produced from the kinetic operator were shown to be less important than those produced from the potential operator. Hence, we used only the complement functions produced from the potential operator and showed that the correct-class g_{ij} functions gave most accurate results and the reasonable-class functions were less accurate. Among the examined correct and reasonable functions, the conventional function r_{ij} was worst in accuracy, although it was still very accurate. Thus, we have many potentially accurate "correct" scaling functions for use in FC theory to solve the SEs of atoms and molecules.

I. INTRODUCTION

Quantum mechanics describes the central principles that govern chemistry.[1] In particular, the non-relativistic Schrödinger equation (SE) and the relativistic Dirac equation (DE) represent the governing principle of chemistry. Therefore, to find a general method of solving these equations is a central problem in theoretical chemistry. SE for atoms and molecules is given by

$$(H - E)\,\psi = 0, \tag{1}$$

where the Hamiltonian H is written as

$$H = -\sum_i \frac{1}{2}\Delta_i - \sum_A \frac{1}{2}\Delta_A - \sum_{i,A} \frac{Z_A}{r_{iA}} + \sum_{i<j} \frac{1}{r_{ij}} + \sum_{A<B} \frac{Z_A Z_B}{R_{AB}}. \tag{2}$$

The first two terms represent the kinetic operators of electrons and nuclei, respectively, and the next three terms represent the Coulombic potentials among the electrons and nuclei. The indices i, j, and A, B represent electrons and nuclei, respectively. r_{iA}, r_{ij}, and R_{AB} denote the electron–nucleus (e–n), electron–electron (e–e), and nucleus–nucleus distances, respectively. Z_A denotes the nuclear charge of nucleus A. These Coulombic potentials are singular at r_0 where the two particles collide with each other.

The variational principle given by

$$\langle \delta\psi | H - E | \psi \rangle = 0 \tag{3}$$

is believed to be equivalent with SE, as understood from Eq. (1). This is true in general. However, when we want to solve SE using the variational principle, we encounter a difficulty. We explain this as follows: When we try to solve SE using the variational principle, the trial wave function must have the exact structure:[2,3] namely, it must include the exact wave function within its variational space. Because the exact wave function should be a functional of the Hamiltonian, as understood from SE given by Eq. (1), the trial function having the exact structure[2,3] is written, in general, as $\psi(H)$. We expand $\psi(H)$

formally with Taylor expansion, $\psi(H) = \left[c_0 + c_1 H + c_2 H^2 + \cdots\right]\phi_0$, where $\{c_i\}$ are expansion coefficients and ϕ_0 is some arbitrary initial function. When we insert this expression into Eq. (3), we have an integral expressed like $\langle\phi_0|H^m|\phi_0\rangle \quad m \geq 3$, which diverges to infinity for the existence of the Coulombic potentials in the Hamiltonian.[3,4] Thus, the variational equation breaks down and the equivalence between SE and variational principle breaks down.

To overcome this divergence difficulty, one of the authors introduced[3] in 2004 the scaled Schrödinger equation (SSE) given by

$$g(H - E)\,\psi = 0, \tag{4}$$

where g is a scaling function that eliminate the divergence difficulty.[3,4] g must be positive and must satisfy

$$\lim_{r \to r_0} gV = a, \tag{5}$$

with r_0 being the collisional point and a being a non-zero finite constant, to assure that SE and SSE have the same set of solutions. We have used many different g functions that are appropriate to the different systems. They are dependent on the coordinate system used and affect the efficiency of the calculations. A simple general choice was

$$g = \sum_{i,A} r_{iA} + \sum_{i<j} r_{ij}, \tag{6}$$

which is natural, considering the forms of the Coulombic potentials given by Eq. (2), because the g function works to cancel the diverging Coulombic potential at the collisional point r_0. An important consequence of introducing SSE is that the variational principle associated with SSE given by

$$\langle\delta\psi|g(H - E)|\psi\rangle = 0 \tag{7}$$

does not meet the divergence difficulty. Thus, SSE and the variational principle given by Eq. (7) become a useful combination of the principles for calculating the exact solutions of SE or SSE of atoms and molecules. As a result, we have proposed the free complement (FC) theory (first called free ICI theory) for solving SE for atoms and molecules.[3,4]

FC theory has been applied in two different ways. One is to use the variational principle when integral evaluations are possible. The FC variational theory straightforwardly gave the essentially exact solutions of SE. For example, we have applied it to (i) one electron H and H_2^+ in Born–Oppenheimer (BO), non-BO, non-relativistic, and relativistic equations and in different situations,[5,6] (ii) to the helium atom using different g functions,[7] and (iii) to hydrogen molecule,[8] Li, Be,[9] and C(sp^3),[10] obtaining the super-accurate results for all. However, integral evaluations were possible only for small atoms and molecules. When integral evaluations are not possible, we proposed to use the local SE (LSE) itself as a deterministic equation, in combination with the sampling-type methodology. We referred to this method as the FC-LSE method.[11] Because FC theory is a potentially exact theory, the constancy of the local energy is expected at high orders of FC theory.[12] Furthermore, since chemistry is local, we can utilize the inter-exchange theory[13] that helps to reduce the labors of antisymmetrizations that become heavy tasks in the calculations of large systems. Accurate results of the FC-LSE theory have been reported to the size of the molecules like formaldehyde.[4,13,14] In such calculations, we have utilized many established methods in the sampling-type methodologies.[15–18]

Recently, we proposed the FC s_{ij} theory based on the choice,[19]

$$g_{ij} = s_{ij}, \qquad s_{ij} = r_{ij}^2, \tag{8}$$

which makes *variational* calculations possible for general atoms and molecules, because the relation

$$\begin{aligned} s_{ij} &= (x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2 \\ &= r_i^2 + r_j^2 - 2x_i x_j - 2y_i y_j - 2z_i z_j \end{aligned} \tag{9}$$

guarantees that the wave functions of FC s_{ij} theory are written entirely with the products of one-electron functions alone. They are separable into one-electron terms when we integrate with the coordinates of electrons i and j. Then, the calculations of the FC s_{ij} theory can be performed using only one- and two-electron integrals like in most conventional quantum chemistry codes. We are testing its potentiality.

In this paper, we will propose general scaling functions g that are different from those we have utilized so far. From the comparison between SE and SSE, the general scaling functions must satisfy not only the condition given by Eq. (5) but also the condition given in Sec. II. The general scaling functions are classified according to whether they satisfy these two conditions. Test applications will be done for the helium atom using the variational principle for fixing the parameters included in the individual g functions. Accurate scaling functions introduced in this paper have high potentiality of giving more accurate wave functions than before, resulting in a faster convergence of FC theory to the exact solutions of SE. This is particularly important in the FC-LSE approach. Partial summaries of the present studies were given in the annual reports of the Computer Center of the Institute of Molecular Science, Okazaki.[20]

II. GENERAL SCALING FUNCTIONS AND LIMITING CONDITIONS

The scaling function g of SSE plays a central role for eliminating the divergence difficulty of the original variational equation (3) by giving a new variational formula given by Eq. (7).[3] It also describes the local interactions of the two colliding particles and, therefore, is related to the inter-particle distances and the natures of the particles like charges and spins. To give a wider freedom to the g function than the one given by Eq. (6), we generalize it as

$$g = \sum_{i,A} g_{iA}(r_{iA}) + \sum_{i<j} g_{ij}(r_{ij}) \tag{10}$$

and consider its general behaviors and properties. In Eq. (10), g_{iA} represents the e–n interaction and g_{ij} represents the e–e interaction. In FC theory, the scaling functions must work not only to prevent the divergence difficulty but also to describe the quantum physics of the inter-particle interactions. As a result, they accelerate the convergence rate of FC theory to the exact wave function. Thus, the functions g_{iA} and g_{ij} have, in some sense, the roles of complementing the concepts of the orbitals and geminals, respectively, considered for the e–n and e–e pair interactions. Therefore, by examining the scaling functions from a general point of view, we may be able to advance the accuracy of the theory. This is a motivation of the present study.

Let us consider the limiting conditions that the general scaling functions must satisfy. First, we consider the necessary condition at

the collisional region of the charged particles. Kato considered the physics in detail for the first time, as summarized in his famous study on the cusp conditions.[21] Kato's cusp conditions and the higher-order conditions studied by Rassolov and Chipman[22] and others[23,24] represent some of the few known exact explicit formulas that the exact wave function must satisfy. Kato's cusp condition is most important and describes the correct first derivatives of the wave function with respect to the inter-particle distances r_{iA} and r_{ij} in the collisional regions.

FC theory produces the exact wave function from approximate ones. Therefore, when we apply FC theory to some approximate function that does not satisfy the cusp condition, we obtain the wave function that satisfies the cusp condition. To obtain such a correct wave function, the dependences of the g_{iA} and g_{ij} functions at the collisional point r_0 must be proportional to r_{iA} and r_{ij}, respectively. In particular,

$$g_{iA} = r_{iA} + O(r_{iA}^2), \quad g_{ij} = r_{ij} + O(r_{ij}^2), \tag{11}$$

where $O(r^2)$ represents the higher order dependence on r. We refer to this condition as the *collisional* or *coalescent condition*. The g function that satisfies Eq. (5) also satisfies this condition. If the g function used in FC theory satisfies this condition, the resultant wave function is guaranteed to satisfy the e–n and e–e cusp conditions, independent of the quality of the initial function. For example, this is true even when the initial function is written using only Gaussian functions. The g function given by Eq. (6) satisfies this condition for the e–n and e–e collisional regions. However, the s_{ij} function given by Eq. (8) does not satisfy this condition at the e–e collisional region; hence, this function is approximate. Note that the FC wave function satisfies not only the Kato's cusp condition but also the higher-order ones[24] because it includes higher-order complement functions that include higher-order terms of g_{iA} and g_{ij}.

Next, we consider the necessary condition when the inter-particle distance becomes large enough and so the collision would never occur. In such a situation, the g function becomes unnecessary and SSE should reduce to the original SE, namely,

$$\lim_{r_{iA}\to\infty} g_{iA}(r_{iA}) = c, \quad \lim_{r_{ij}\to\infty} g_{ij}(r_{ij}) = c, \tag{12}$$

where c is a positive finite constant like unity. We refer to this condition as the *asymptotic condition*. This condition has not received much attention before but is important as will be shown below.

Now, we refer to the g functions that satisfy both collisional and asymptotic conditions as "*correct*" functions. Between the collisional and asymptotic conditions, the former is more important energetically than the latter. Therefore, we refer to the g functions that satisfy only the collisional condition as "*reasonable*" g functions. When the g function is composed of the functions like the s_{ij} function given by Eq. (8), it does not satisfy the collisional condition. Therefore, when the initial wave function of FC theory is non-correlated, the resultant wave function does not satisfy the Kato's e–e cusp condition. Therefore, we refer to such functions as "*approximate*" g functions. Many examples of the g functions belonging to each class will be shown in Sec. III.

Here, we note that the distinction between the "correct" and "reasonable" functions is based on the introduction of SSE, which gives a clear reasoning for the asymptotic condition. Furthermore, it is remarkable that the popular function r_{ij} given by Eq. (6) belongs to the "reasonable" class, not to the "correct" class. Thus, the present theory suggests the existence of the g_{ij} functions that are more accurate than the popular function r_{ij} in the correct class of the functions. These points will be demonstrated in Sec. IV.

III. FUNCTIONAL FORMS OF THE SCALING FUNCTIONS

Here, we list many examples of correct, reasonable, and approximate scaling functions. For brevity, we collectively refer to the g_{iA} and g_{ij} functions as g_{pq} functions.

A. Correct scaling function

The following five functions are studied in this paper as correct scaling functions that satisfy both collisional and asymptotic conditions:

$$g_{pq} = 1 - \exp(-\gamma r_{pq}), \tag{13a}$$

$$g_{pq} = r_{pq}/(r_{pq} + a), \tag{13b}$$

$$g_{pq} = \mathrm{Ei}(-\gamma_1 r_{pq} - \gamma_2) - \mathrm{Ei}(-\gamma_2), \tag{13c}$$

$$g_{pq} = \arctan(\gamma r_{pq}), \tag{13d}$$

$$g_{pq} = \tanh(\gamma r_{pq}). \tag{13e}$$

These functions were listed from the mathematical handbooks from the knowledge of the two limiting conditions given by Eqs. (11) and (12). The Ei function of Eq. (13c) is given by $\mathrm{Ei}(x) = -\int_{-x}^{\infty} \mathrm{e}^{-t}/t\, dt$. The parameters γ, a, and b are normally positive and depend on the nuclear charge for the e–n case and on the singlet and triplet couplings for the e–e case. Furthermore, in the case of g_{iA}, the parameter γ of Eq. (13a), for example, may become negative to some extent when it works to reduce the orbital exponent to improve the wave function. Figure 1 illustrate the plots of some of these

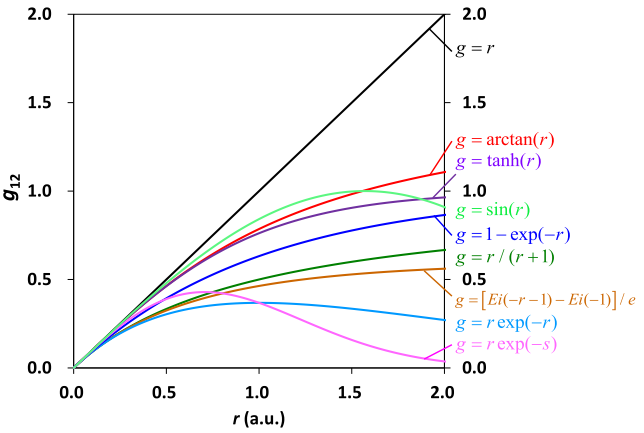

FIG. 1. Schematic plots of some of the functions used in this paper as the scaling functions of the scaled Schrödinger equation.

functions against r. All the above functions are proportional to r near $r = 0$ [Eq. (11), collisional condition] and approach unity or some constants as r increases [Eq. (12), asymptotic condition].

The functions of Eqs. (13a), (13b), and (13d) were used by Nooijen and Bartlett in the study of the transformed Hamiltonian.[25] The function (13b) was previously considered by one of the authors[3] as a candidate of the g_{ij} function. The Ei function was examined by Davis and Maslen[26] for the accurate calculations of atoms. In addition, it was used efficiently by us in the highly accurate FC calculations of the helium atom.[7] Hirata and others demonstrated some of these functions to be very useful in the study of the explicitly correlated second-order many-body perturbation theory.[27,28] They efficiently calculated the integrals including these geminals using the Monte Carlo method[29] with the Metropolis algorithm.[15,16] A Slater-type geminal, $\exp(-\gamma r_{ij})$, was studied by Ten-no[30–33] in the scope of the R12, F12 theory[34–38] instead of the Gaussian-type geminal $\exp(-\gamma r_{ij}^2)$ introduced by Boys[39] and Singer.[40] Some of the functions listed above, particularly those like Eq. (13b), have been used as Jastrow factors[41] in quantum and variational Monte Carlo studies,[13,14] giving accurate results.[42–44] Bouabca, Braïda, and Caffarel[45] introduced the multi-Jastrow functions to efficiently describe the local correlations of different physics. Braïda *et al.*[46] proposed a quantum Monte Carlo method with the Jastrow-valence bond functions and applied it successfully to the V state of ethylene.[47] However, many of these wave functions could not become exact because, as shown by Fillippi and Umrigar,[43] the wave function constructed using a nonsymmetrical Jastrow factor yields a wave function that is not an eigenstate of the spin-squared operator S^2; alternatively, the use of a symmetric Jastrow factor violates the e–e cusp conditions for either parallel or antiparallel spins. This is different from the potentially exact wave functions produced by the present FC theory.

It would be interesting to discuss the connection and distinction between the scaling function g of the present paper and the correlation factors reported in the past as cited above. The scaling function of this paper was defined when SSE was introduced in 2004. It has a clear origin of eliminating the divergence difficulty of the variational equation originating from SE. Its physics is closely related to the inter-particle collisions among electrons and nuclei in atoms and molecules. On the other hand, the correlation factors reported in the past were defined like the *variational functions* related to r_{ij} and their physics were different case by case. For example, in the R12 and/or F12 theories, they were related to describing well the cusp condition and so may have a similar origin. However, the FC theory based on SSE has been formulated along the potentially exact formalism to reach the exact solutions at a limit.

It is interesting to compare these functions in the power series expansion forms as

$$1 - \exp(-r) = r - \frac{1}{2}r^2 + \frac{1}{6}r^3 - \frac{1}{24}r^4 + \frac{1}{120}r^5 + O(r^6), \tag{14a}$$

$$\frac{r}{r+1} = r - r^2 + r^3 - r^4 + r^5 + O(r^6), \tag{14b}$$

$$\mathrm{Ei}(-\mathrm{e}r - 1) - \mathrm{Ei}(-1) = r - \mathrm{e}r^2 + \frac{5}{6}\mathrm{e}^2 r^3 - \frac{2}{3}\mathrm{e}^3 r^4 + \frac{13}{24}\mathrm{e}^4 r^5 + O(r^6), \tag{14c}$$

$$\arctan(r) = r - \frac{1}{3}r^3 + \frac{1}{5}r^5 + O(r^6), \tag{14d}$$

$$\tanh(r) = r - \frac{1}{3}r^3 + \frac{2}{15}r^5 + O(r^6), \tag{14e}$$

where e in Eq. (14c) is Napier's constant (e = 2.718 281 828). The first three functions include all powers of r, whereas the latter two include only the odd powers of r.

Because atoms and molecules are complex many-particle systems, g functions of different curvatures may be necessary to describe real systems. Therefore, the scaling function composed of multiple g functions would be useful to describe many-electron systems. In this paper, we consider the following multiple functions:

$$g_{pq} = \sum_k c_k[1 - \exp(-\gamma_k r_{pq})], \tag{15a}$$

$$g_{pq} = c_1 \cdot [1 - \exp(-\gamma_1 r_{pq})] + c_2 \cdot \arctan(-\gamma_2 r_{pq}), \tag{15b}$$

$$g_{pq} = c_1 r_{pq}/(r_{pq} + a) + c_2[1 - \exp(-\gamma r_{pq})], \tag{15c}$$

$$g_{pq} = c_1 r_{pq}/(r_{pq} + a) + c_2 \arctan(\gamma r_{pq}), \tag{15d}$$

$$g_{pq} = c_1 r_{pq}/(r_{pq} + a_1) + c_2 r_{pq}/(r_{pq} + a_2), \tag{15e}$$

$$g_{pq} = c_1[Ei(-\gamma_1 r_{pq} - \gamma_2) - Ei(-\gamma_2)] + c_2 r_{pq}/(r_{pq} + a). \tag{15f}$$

Here, we combined these different functions for not increasing the size of the calculations: single g_{pq} functions were replaced with linear combinations of multiple g_{pq} functions to describe complicated r_{pq} dependences. Although using these multiple g_{pq} functions independently will increase the accuracy of the results, it will also increase the sizes of the calculations. Such calculations will be reported separately.

B. Reasonable scaling function

We examine here the following reasonable scaling functions that satisfy the collisional condition but do not satisfy the asymptotic condition:

$$g_{pq} = r_{pq}, \tag{16a}$$

$$g_{pq} = r_{pq} \exp(-\gamma r_{pq}), \tag{16b}$$

$$g_{pq} = r_{pq} \exp(-\gamma s_{pq}), \tag{16c}$$

$$g_{pq} = \sin(\gamma r_{pq}). \tag{16d}$$

In our earlier papers,[3] the two-electron function r_{ij}, which is shown in Fig. 1 in black, was used. However, this function approaches plus infinity as r_{ij} increases without satisfying the asymptotic condition. Other g_{pq} functions of Eq. (16) do not approach infinity as r_{pq} increases. The second and third functions reach some maxima and

then converge to zero as r_{pq} increases (see the light-blue and purple-red curves in Fig. 1). We also try to use the sine function, assuming that the important region is covered within the region $0 < \gamma r < \pi/2$ (see the light green curve in Fig. 1).

These reasonable functions are written in power series expansions as

$$r\exp(-r) = r - r^2 + \frac{1}{2}r^3 - \frac{1}{3!}r^4 + \frac{1}{4!}r^5 + O(r^6), \tag{17a}$$

$$r\exp(-s) = r - r^3 + \frac{1}{2}r^5 + O(r^6), \tag{17b}$$

$$\sin(r) = r - \frac{1}{3!}r^3 + \frac{1}{5!}r^5 + O(r^6). \tag{17c}$$

The leading term is r as in Eq. (14) for the correct functions. Since these functions satisfy the collisional condition, they can lead to the wave functions that satisfy the e–n and e–e cusp conditions. This is clearly seen by comparing Eq. (17) to Eq. (11).

The multiple functions composed of different-class scaling functions would be effective to describe complicated behaviors of the wave functions of the many-electron system. As a trial, we will use the g function within the reasonable functions,

$$g_{pq} = c_1 \cdot r_{pq} + c_2 \cdot \sin(\gamma r_{pq}), \tag{18a}$$

and the g functions of the correct and reasonable classes like

$$g_{pq} = c_1 \cdot [1 - \exp(-\gamma_1 r_{pq})] + c_2 \cdot \sin(\gamma_2 r_{pq}), \tag{18b}$$

$$g_{pq} = c_1 \cdot \arctan(-\gamma_1 r_{pq}) + c_2\ \sin(\gamma_2 r_{pq}). \tag{18c}$$

We will test the quality of these multiple functions in Sec. IV.

C. Approximate but useful scaling functions

Here, we introduce some g_{ij} functions that are "*approximate*" but useful. They are defined by using the function s_{pq} $(=r_{pq}^2)$ in place of r_{pq}. For the one-electron case, this corresponds to using the Gaussian function instead of the Slater function. The main reason is the easier integrability of the Gaussian function than the Slater function.[39,40,48] This is particularly so for the case of $s_{pq} = s_{ij}$. The approximate functions examined in this paper are

$$g_{pq} = s_{pq}, \tag{19a}$$

$$g_{pq} = s_{pq}\exp(-\gamma s_{pq}), \tag{19b}$$

$$g_{pq} = \sin(-\gamma s_{pq}), \tag{19c}$$

$$g_{pq} = 1 - \exp(-\gamma s_{pq}), \tag{19d}$$

$$g_{pq} = s_{pq}/(s_{pq} + a), \tag{19e}$$

$$g_{pq} = \arctan(-\gamma s_{pq}). \tag{19f}$$

Although the functions given by Eqs. (19a)–(19c) do not satisfy both the collisional and asymptotic conditions, the other functions below satisfy the asymptotic condition. We will see that this feature of the functions given by Eqs. (19d)–(19f) causes them to be accurate in the actual applications to the helium atom. The function given by Eq. (19d) is close to the Gaussian function $\exp(-\gamma s_{ij})$, whose integrability was noted by Boys[39] and Singer.[40]

We have examined the following multiple combinations of the approximate functions:

$$g_{pq} = \sum_k c_k[1 - \exp(-\gamma_k s_{pq})], \tag{20a}$$

$$g_{pq} = c_1[1 - \exp(-\gamma_1 s_{pq})] + c_{at}\ \arctan(-\gamma_2 s_{pq}), \tag{20b}$$

$$g_{pq} = \sum_{k=1}^{3} c_k s_{pq}\ \exp(-\gamma_k s_{pq}), \tag{20c}$$

$$g_{pq} = \sum_{k=1}^{3} c_k {s_{pq}}^k\ \exp(-\gamma s_{pq}), \tag{20d}$$

$$g_{pq} = c_1 s_{pq} + c_2\ \sin(\gamma s_{pq}). \tag{20e}$$

For the e–e g_{ij} functions, although they do not satisfy the e–e cusp condition, the variational usage of these functions may give encouraging results, even in comparison with the original function r_{ij}, when they satisfy the asymptotic condition. In addition, some of the approximate g_{ij} functions have practical merits in the integrability like the function s_{ij} used in the FC- s_{ij} theory.[19]

IV. APPLICATION TO HELIUM ATOM USING VARIATIONAL PRINCIPLE

Helium, a two-electron atom, is a special system lying between one- and many- (more-than-three) electron systems. This is the atom for which Hylleraas[49] performed historical calculations, including the function r_{12} explicitly in the wave function. We examine here the general e–e scaling functions listed in Sec. III, fixing the e–n scaling function to the simplest reasonable function r_{iA}. For helium, all the analytical integrals involving the general scaling functions are calculated analytically using the mathematical software MAPLE.[50] In contrast to the simple scaling function r_{ij} given by Eq. (6), the general scaling functions listed above include the parameters such as γ and a, which were energetically optimized using the variational principle at each order (their values are given in the footnotes of Table II). The results obtained here will be useful in the studies of larger atoms and molecules, since these parameters should be transferable depending only on the nuclear charge, spin-multiplicity, etc., that are intrinsic to the colliding two particles.

A. Formation of the complement functions of FC theory

FC calculations were performed using a simple initial function $\psi_0 = (1s)^2\alpha\beta$ with $1s = N\exp(-\alpha r_{iA})$. Starting from this initial function, we performed the simplest ICI (SICI) recursion calculations based on SSE to some order n as given by

$$\psi_n = [1 + C_n g(H - E_{n-1})]\,\psi_{n-1}, \tag{21}$$

where the Hamiltonian with the fixed nucleus is written as

$$H = -\frac{1}{2}\frac{\partial^2}{\partial {r_1}^2} - \frac{1}{r_1}\frac{\partial}{\partial r_1} - \frac{1}{2}\frac{\partial^2}{\partial {r_2}^2} - \frac{1}{r_2}\frac{\partial}{\partial r_2} - \frac{\partial^2}{\partial {r_{12}}^2} - \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}} - \frac{1}{2}\frac{({r_1}^2 + {r_{12}}^2 - {r_2}^2)}{r_1 r_{12}}\frac{\partial^2}{\partial r_1 \partial r_{12}} - \frac{1}{2}\frac{({r_2}^2 + {r_{12}}^2 - {r_1}^2)}{r_2 r_{12}}\frac{\partial^2}{\partial r_2 \partial r_{12}} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}. \quad (22)$$

The first two lines give the kinetic operator and the last line is the potential operator with the nuclear charge Z being 2. Then, we expand all the functions of ψ_n into independent analytical functions and remove all the diverging functions. Then, all the remaining analytical functions $\{\phi_I\}$, which are referred to as the complement functions (cfns), are given independent coefficients $\{c_I\}$, and the SICI formula is finally rewritten as

$$\psi_n = \sum_{I=0}^{M} c_I \phi_I. \quad (23)$$

This algorithm is easily formulated with the mathematical software MAPLE.[50] The FC wave function is a sum of the independent analytical functions given by the SICI formula. At large n, the function ψ_n is potentially exact; thus, when we determine the coefficients $\{c_I\}$ using the variational principle or some other principle, such as the LSE method, which is equivalent to SE, we can obtain essentially exact solutions of SE.

For the initial function composed of the Slater functions alone, the cfns arising from the scaling functions r_{iA} and r_{ij} given by Eq. (6) come only from the potential operators of the Hamiltonian: those arising from the kinetic operator are the same as those arising from the potential operator. (Note that with the Gaussian functions, we obtain different results.) However, when we use the general scaling functions given in Sec. III, the cfns are produced also from the kinetic operator from $n = 2$. Therefore, we examine here the following two ways of calculations: one is to use the cfns produced from the potential functions alone, and the other is to use the cfns produced from both kinetic and potential operators. We refer to these two methods as the p-alone method and p + k method, respectively.

With the p-alone method, we use only the potential operator of the Hamiltonian, and therefore, the cfns are expressed, in general, in a simple form as

$$\phi_I = (1 + P_{12})\left[{r_1}^{a_I} {r_2}^{b_I} {g_{12}}^{c_I} e^{-\alpha r_1} e^{-\alpha r_2}\right], \quad (24)$$

where a_I, b_I, c_I are non-negative integer, since if negative, it is a diverging function. It is important to note again that this result is the same as using the g function of the form $g = r_1 + r_2 + r_{12}$ and replacing r_{12} with g_{12} when the initial function is composed of the Slater functions alone. On the other hand, with the p + k method, we consider further the cfns that are produced through the kinetic operator in the Hamiltonian. Since we handle many different g_{12} functions, we do not initially use their explicit forms in the formulation so that the cfns are written in the form

$$\phi_I = (1 + P_{12}) {r_1}^{a_I} {r_2}^{b_I} {r_{12}}^{c_I} {g_{12}}^{d_I^{(0)}} \left[\partial g_{12}/\partial r_{12}\right]^{d_I^{(1)}} \times \left[\partial^2 g_{12}/\partial {r_{12}}^2\right]^{d_I^{(2)}} \ldots e^{-\alpha r_1} e^{-\alpha r_2}, \quad (25)$$

where the dots indicate higher derivatives of the g_{12} function. These derivative terms arise from the expressions of the kinetic operator in Eq. (22). Again, a_I, b_I, c_I are non-negative integers from the same reason as above. When the explicit from of the g_{12} function is given, we put it in Eq. (25) and eliminate if the cfn is diverging. Furthermore, we eliminate the redundant functions, where we keep the functions arising from the p-alone method and arising from the lower-order derivatives of the g_{12} function.

Table I shows the results of the FC calculations using the p-alone and p + k methods for the four correct g_{ij} functions

TABLE I. Free-complement variational calculations of the helium atom using the p-alone and p + k methods with some correct and reasonable e–e scaling functions g_{12}. n and M are the order and dimension, respectively, and ΔE is the energy in kcal/mol relative to the exact energy −2.903 724 377 a.u. The nonlinear parameters in ψ_0 and in the e–e scaling functions were optimized for the p-alone method and are given in the footnotes of Table II. Values of ΔE smaller than 1 kcal/mol are shown in boldface.

g_{12}		Method of cf generation	$n = 1$		$n = 2$		$n = 3$		$n = 4$	
			M	ΔE (kcal/mol)	M	ΔE (kcal/mol)	M	ΔE (kcal/mol)	M	ΔE (kcal/mol)
	Correct									
G_1	$Ei(-\gamma_{12}^{(1)} r_{12} - \gamma_{12}^{(2)}) - Ei(-\gamma_{12}^{(2)})$	p-alone	3	7.7073	7	**0.1199**	13	**0.017 4**	22	**0.001 31**
		p + k	4	7.7073	17	**0.1117**	70	**0.003 04**		
G_2	$r_{12}/(r_{12} + a_{12})$	p-alone	3	7.7106	7	**0.1278**	13	**0.022 1**	22	**0.001 99**
		p + k	3	7.7106	10	**0.1135**	25	**0.003 27**		
G_3	$\arctan(\gamma_{12} r_{12})$	p-alone	3	7.7806	7	**0.1741**	13	**0.025 2**	22	**0.003 78**
		p + k	4	7.7743	19	**0.1111**	97	**0.002 56**		
G_4	$1 - \exp(-\gamma_{12} r_{12})$	p-alone	3	7.7180	7	**0.1361**	13	**0.026 0**	22	**0.002 88**
		p + k	4	7.7179	13	**0.1127**	34	**0.003 19**		
	Reasonable									
G_6	$r_{12} \exp(-\gamma_{12} r_{12})$	p-alone	3	7.7221	7	**0.1403**	13	**0.028 4**	22	**0.003 34**
		p + k	4	7.7221	13	**0.1128**	33	**0.003 39**		
G_8	$\sin(\gamma_{12} r_{12})$	p-alone	3	7.7989	7	**0.1802**	13	**0.037 8**	22	**0.005 47**
		p + k	4	7.7903	15	**0.1123**	47	**0.003 68**		
G_9	r_{12}	p-alone, p + k	3	7.8388	7	**0.1873**	13	**0.052 7**		

and for the three reasonable g_{ij} functions. (The designation numbers G_1, G_2, etc., are the ones borrowed from Table II used later.) M is the number of the cfns for the different order and method, and ΔE is the difference in kcal/mol unit between the calculated energy and the known exact energy[7]—2.903 724 377 a.u. The parameters in the scaling functions were optimized for the p-alone method and the same values were used for the p + k method. At n = 1, the two methods give almost the same results, but from $n \geq 2$, the results are different. When we compare the results at the same order, the p + k method always gives better results than the p-alone method because the latter includes the cfns not only from the potential operator but also from the kinetic one. However, when we compare the n = 2 result of the p + k method to the n = 3 result of the p-alone method, the latter is always better even when the dimension M of n = 3 of the p-alone method is smaller than that of n = 2 of the p + k method. This trend is also seen when we compare the n = 3 result of the p + k method to the n = 4 result of the p-alone method, except for the cases of the g_{12} functions of $\arctan(\gamma_{12}r_{12})$ and $\sin(\gamma_{12}r_{12})$: in the latter two cases, the numbers of the cfns M at n = 3 of the p + k method are much larger (97 and 47, respectively) than those (22 for both) of the p-alone method. This result implies that when we compare the efficiencies of the p-alone method and the p + k method from the number of the cfns used, the p-alone method is more efficient than the p + k method. This result agrees with our experiences that the cfns produced from the kinetic operators are generally less efficient than those generated from the potential operator. In other words, this suggests that rather than using the cfns produced from the kinetic operator, it is better to go higher orders using those produced from the potential operator. These facts might be attributed to the origin of the scaling g function in the SSE. In particular, it was introduced to eliminate the singularity difficulty caused by the Coulombic potential operators in the Hamiltonian.

Figure 2 shows more clearly the efficiency difference between the p-alone method and the p + k method against the number M of the cfns, which represents the actual labors of the calculations. The vertical axis represents the accuracy of the results in the form of $\log_{10}(\Delta E)$, and the horizontal axis shows the number of the cfns. The straight line in this figure corresponds to the p-alone method and the dotted line corresponds to the p + k method. First, we note that in all the panels of Fig. 2, the straight line is more vertical than the dotted line, showing that the p-alone method is more efficient than the p + k method for all the scaling functions examined here. This comes from the fact that the cfns produced by the potential operator of the Hamiltonian are more efficient than those produced from the kinetic operator. When we compare in Table I the n = 4 results of the p-alone method due to 22 cfns to the n = 3 results of the p + k method, the ΔE values are all 0.001–0.006 kcal/mol, but the p + k method uses from 25 to 97 cfns that are larger than 22.

Thus, from the efficiency point of view on energy, the p-alone method is recommended. Furthermore, when we use the p-alone method, the number of the cfns at order n is the same for any scaling functions so that we can compare the qualities of different scaling functions from only the ΔE values on the basis of the same number of the cfns. This is not possible with the p + k method. Hence, in the calculations below, we use the p-alone method and examine the qualities of different scaling functions in more detail. We note, however, that for other properties different from energy, the efficiency difference between the p + k and p-alone methods is not known yet. This subject will be investigated for general scaling functions.

B. Examination of the e–e scaling functions listed in Sec. III

We examine here the accuracy of many e–e scaling functions g_{12} listed in Sec. III. We performed extensive FC variational calculations of the He atom using many e–e scaling functions listed in Sec. III with the p-alone method, and the results are summarized in Table II. The left half of Table II deals with the *single* g_{12} functions, while the right half deals with the *multiple* g_{12} functions. In the first two columns, the designation number and the explicit formula of each g_{12} function are given for the groups of the correct (G_1 to G_5 and G_{16} to G_{21}), reasonable (G_6 to G_9 and G_{22} to G_{24}), and approximate (G_{10} to G_{15} and G_{25} to G_{29}) functions. The calculated energy is then given by the energy difference ΔE in kcal/mol from the exact energy[7]—2.903 724 377 au for the calculations of different orders (n = 1, 2, 3, and 4) with the dimensions (the number of cfns) of M = 3, 7, 13, and 22, respectively. We note that the dimensions M are very small, demonstrating the efficiency of FC theory. The optimized values of the variational parameters, such as α and γ, are summarized in the footnotes of Table II. It is very important to note that the ordering of the g_{12} functions within each class in Table II is based on the accuracy of the calculated result obtained at the third-order calculations (n = 3).

First, let us see the ordinary function, G_9, r_{12}, given by Eq. (6). This function was listed last of the "reasonable" functions. Among the correct and reasonable functions, the function r_{12} gave the worst result at all orders n of the FC calculations. This is attributed to the incorrect asymptotic behavior (i.e., it approaches infinity as r_{12} increases). However, we must note that the result of the r_{12} function is still very accurate. Rather, the present result implies that even more accurate scaling functions exist in the correct and reasonable classes of functions.

The scaling functions G_1 to G_5 belong to the "correct" class. The average values of ΔE are given at the bottom of each class. At n = 1, the ΔE values were ~7.7 kcal/mol for all the functions. At n = 2, 3, and 4, the ΔE values are rapidly improved as 0.147, 0.0244, and 0.002 96 kcal/mol, respectively. An order-of-magnitude improvement was achieved by increasing the order n by unity. The chemical accuracy was obtained from order 2. These results of FC theory are satisfactory, considering the very small dimensions of M, 7, 13, and 22. The best result at order 3 was obtained with the Ei function (G_1). (We note again that the ordering G_1, G_2, etc., of g_{12} functions is due to the accuracy at order 3.) Then, the order of the functions at n = 3 was $r_{12}/(r_{12}+a)$, $\arctan(\gamma r_{12})$, the well-known function, $1-\exp(-\gamma r_{12})$, and $\tanh(\gamma r_{12})$. The functions $\arctan(\gamma r_{12})$ and $\tanh(\gamma r_{12})$ worked very similarly at lower orders but differently at higher orders, as expected from the small difference in their power series expansion forms given by Eqs. (14d) and (14e), respectively. The rather poor behaviors of these trigonometric functions as the correct function are attributed to the absence of the quadratic term, $-r_{12}^2$, in Eqs. (14d) and (14e), which is the origin of their poor ability of describing higher-order cusp conditions as discussed by Klopper *et al.*[32] and Grüneis *et al.*[28] and as shown by Rassolov and Chipman[22] and Kurokawa *et al.*[24]

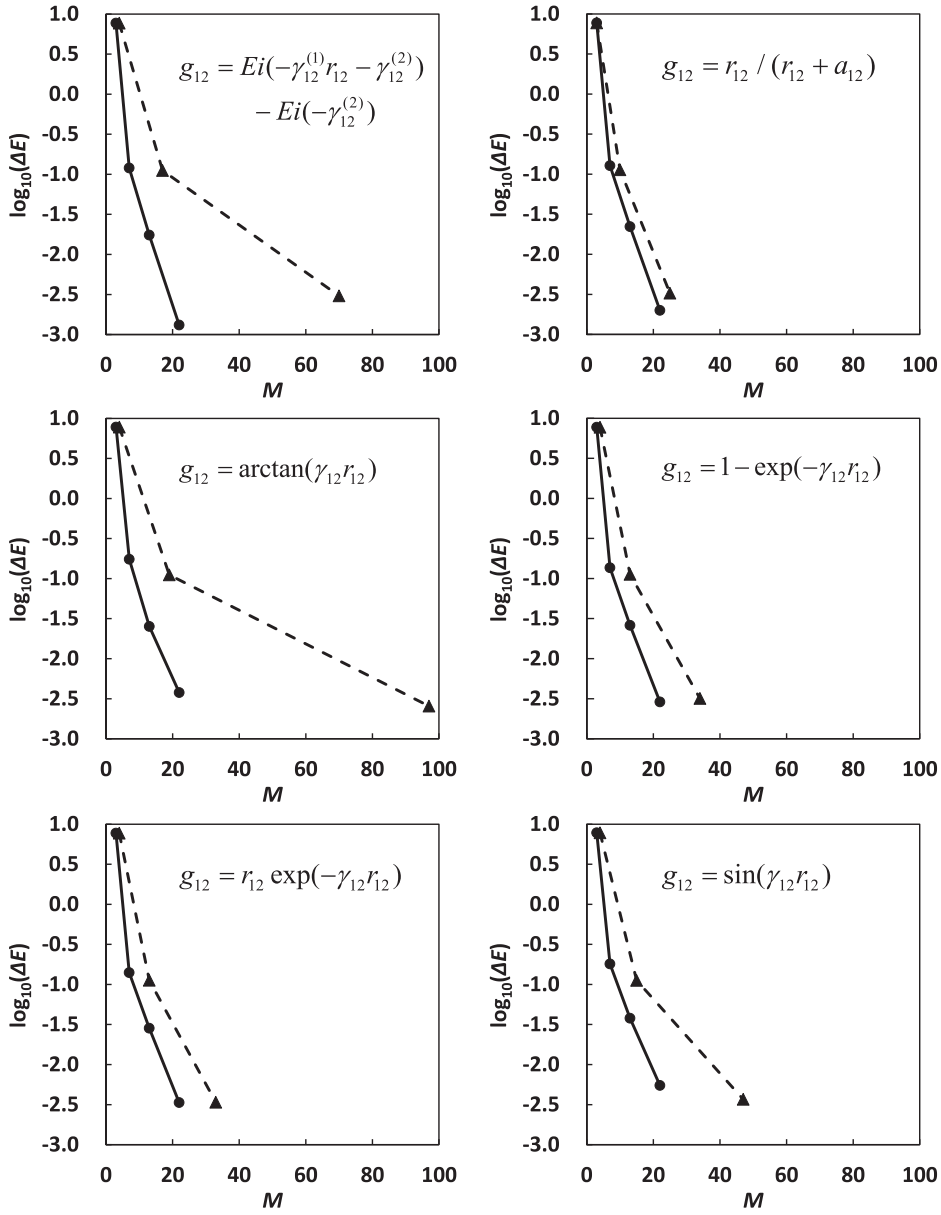

FIG. 2. Plots of ΔE in kcal/mol against the number M of the complement functions in the p-alone (normal lines) and p + k (dot lines) method of the free-complement variational calculations using the scaling functions given in Table I.

The functions G_6 to G_9 belong to the "reasonable" class of scaling functions. Unlike the correct functions, these functions do not satisfy the asymptotic condition. Although the reasonable g_{12} functions are less effective than the correct ones, as seen from the average values, they are still very accurate. The function G_6, $r_{12} \exp(-\gamma r_{12})$, certainly works better than some of the correct functions. These reasonable g_{12} functions also show an order-of-magnitude improvement in ΔE upon increasing the order n by unity. This indicates that satisfying the collisional condition is more important energetically than satisfying the asymptotic condition. While the collisional region is small, it is important energetically because both the e–n attractive and e–e repulsive energies are very large and balanced with the kinetic energy. The constancy of the local energy is a result of a balanced cancellation of the two large energetic components.

The functions G_{10} to G_{15} belong to the "approximate but still useful" class of scaling functions that are composed of the function s_{12}. These functions are approximate, since they do not satisfy the e–e cusp condition. The original single s_{12} function (G_{15}) gave the ΔE values at n = 2– 4 from 4.5 to 1.5 kcal/mol, much worse than the functions of the above two classes. It does not satisfy both the collisional condition and the asymptotic condition. However, when we use the scaling functions G_{10} $s_{12}/(s_{12} + a)$, G_{11} $\arctan(\gamma s_{12})$, and G_{12} $1 - \exp(-\gamma s_{12})$, we could obtain the chemical accuracy at orders

TABLE II. Free-complement variational energies of the helium atom using different e–e scaling functions g_{12} (G_1 to G_{29}) of the scaled Schrödinger equation. The energy is shown as the difference ΔE in kcal/mol from the exact energy, −2.903 724 377 a.u. Values of ΔE smaller than 1 kcal/mol are shown in boldface. n is the order of the free-complement calculations, and M is the dimension of the complement functions. The optimized values of the parameters are given in the footnotes.

		ΔE (kcal/mol)						ΔE (kcal/mol)			
	g_{12}	$n=1$ $M=3$	$n=2$ $M=7$	$n=3$ $M=13$	$n=4$ $M=22$		g_{12}	$n=1$ $M=3$	$n=2$ $M=7$	$n=3$ $M=13$	$n=4$ $M=22$
Single function						**Multiple function**					
Correct						**Correct**					
G_1	$Ei(-\gamma_1 r_{12}-\gamma_2)-Ei(-\gamma_2)$[a]	7.7073	**0.1199**	**0.0174**	**0.001 31**	G_{16}	$c_1[1-\exp(-\gamma_1 r_{12})]+c_2\arctan(\gamma_2 r_{12})$[b]	7.6751	**0.1139**	**0.0125**	**0.001 82**
G_2	$r_{12}/(r_{12}+a)$[c]	7.7106	**0.1278**	**0.0221**	**0.001 99**	G_{17}	$\sum_{k=1}^{3} c_k[1-\exp(-\gamma_k r_{12})]$[d]	7.6907	**0.1141**	**0.0137**	**0.001 43**
G_3	$\arctan(\gamma r_{12})$[e]	7.7806	**0.1741**	**0.0252**	**0.003 78**	G_{18}	$c_1 r_{12}/(r_{12}+a)+c_2[1-\exp(-\gamma r_{12})]$[f]	7.6624	**0.1143**	**0.0139**	**0.001 48**
G_4	$1-\exp(-\gamma r_{12})$[g]	7.7180	**0.1361**	**0.0260**	**0.002 88**	G_{19}	$c_1 r_{12}/(r_{12}+a)+c_2\arctan(\gamma r_{12})$[h]	7.6622	**0.1146**	**0.0139**	**0.001 50**
G_5	$\tanh(\gamma r_{12})$[i]	7.7888	**0.1775**	**0.0314**	**0.004 83**	G_{20}	$c_1 r_{12}/(r_{12}+a_1)+c_2 r_{12}/(r_{12}+a_2)$[j]	7.7106	**0.1140**	**0.0140**	**0.001 34**
	Average	7.7411	**0.1471**	**0.0244**	**0.002 96**	G_{21}	$c_1[Ei(-\gamma_1 r_{12}-\gamma_2)-Ei(-\gamma_2)]+c_2 r_{12}/(r_{12}+a)$[k]	7.6629	**0.1137**	**0.0149**	**0.001 31**
							Average	7.6773	**0.1141**	**0.0138**	**0.001 48**
Reasonable						**Reasonable**					
G_6	$r_{12}\exp(-\gamma r_{12})$[l]	7.7221	**0.1403**	**0.0284**	**0.003 34**	G_{22}	$c_1\arctan(\gamma_1 r_{12})+c_2\sin(\gamma_2 r_{12})$[m]	7.6841	**0.1270**	**0.0146**	**0.002 32**
G_7	$r_{12}\exp(-\gamma s_{12})$[n]	7.7970	**0.1798**	**0.0368**	**0.005 38**	G_{23}	$c_1[1-\exp(-\gamma_1 r_{12})]+c_2\sin(\gamma_2 r_{12})$[o]	7.6673	**0.1147**	**0.0202**	**0.002 35**
G_8	$\sin(\gamma r_{12})$[p]	7.7989	**0.1802**	**0.0378**	**0.005 47**	G_{24}	$c_1 r_{12}+c_2\sin(\gamma r_{12})$[q]	7.7110	**0.1264**	**0.0266**	**0.003 57**
G_9	r_{12}[r]	7.8388	**0.1873**	**0.0527**	**0.006 55**		Average	7.6875	**0.1227**	**0.0205**	**0.002 75**
	Average	7.7892	**0.1719**	**0.0389**	**0.005 19**						
Approximate						**Approximate**					
G_{10}	$s_{12}/(s_{12}+a)$[s]	9.6750	1.1592	**0.2140**	**0.173 4**	G_{25}	$\sum_{k=1}^{3} c_k[1-\exp(-\gamma_k s_{12})]$[t]	7.7865	**0.1613**	**0.0416**	**0.023 7**
G_{11}	$\arctan(\gamma s_{12})$[u]	11.2776	2.1144	**0.4298**	**0.381 3**	G_{26}	$c_1[1-\exp(-\gamma_1 s_{12})]+c_2\arctan(\gamma_2 s_{12})$[v]	8.0484	**0.3606**	**0.0905**	**0.069 3**
G_{12}	$1-\exp(-\gamma s_{12})$[w]	10.8264	1.8828	**0.6285**	**0.469 9**	G_{27}	$\sum_{k=1}^{3} c_k s_{12}\exp(-\gamma_k s_{12})$[x]	7.8972	**0.3090**	**0.1281**	**0.059 5**
G_{13}	$s_{12}\exp(-\gamma s_{12})$[y]	11.7389	2.4179	1.0657	**0.712 0**	G_{28}	$\sum_{k=1}^{3} c_k {s_{12}}^k\exp(-\gamma s_{12})$[z]	9.3570	1.0429	**0.4778**	**0.308 6**
G_{14}	$\sin(\gamma s_{12})$[aa]	13.3194	3.9403	1.8866	1.221 9	G_{29}	$c_1 s_{12}+c_2\sin(\gamma s_{12})$[bb]	12.1132	3.0655	1.5984	1.163 0
G_{15}	s_{12}[cc]	13.4830	4.5232	2.0568	1.488 1						

[a] $(\alpha, \gamma_1, \gamma_2)$ = (1.747, 0.0227, 0.138), (1.795, 0.001 89, 0.003 01), (1.816, 0.001 21, 0.000 238), (1.820, 0.0154, 0.002 00) for n = 1–4.
[b] $(\alpha, \gamma_1, \gamma_2, c_1, c_2)$ = (1.748, 0.298, 0.485, 1.0000, −0.3524), (1.808, 0.143, 0.245, 1.0000, −0.3678), (1.818, 0.109, 1.533, 1.0000, 0.4598), (1.851, 0.320, 0.316, 1.0000, −0.5819) for n = 1–4.
[c] (α, a) = (1.749, 11.675), (1.794, 5.331), (1.816, 2.509), (1.852, 2.313) for n = 1–4.
[d] $(\alpha, \gamma_1, \gamma_2, \gamma_3, c_1, c_2, c_3)$ = (1.747, 0.633, 0.0499, 0.0503, 1.0000, 17.5631, 8.2031), (1.806, 1.469, 0.0776, 0.0349, 1.0000, 15.1368, 41.2079), (1.830, 2.365, 0.713, 0.009 36, 1.0000, 1.2337, 26.3945), (1.850, 2.626, 0.631, 0.001 80, 1.0000, 2.5577, 133.9256) for n = 1–4.
[e] (α, γ) = (1.765, 0.212), (1.800, 0.237), (1.798, 0.482), (1.897, 0.418) for n = 1–4.
[f] $(\alpha, a, \gamma, c_1, c_2)$ = (1.753, 0.872, 0.0223, 1.0000, 70.7467), (1.805, 1.509, 0.0332, 1.0000, 21.570), (1.832, 0.658, 0.004 40, 1.0000, 17.0786), (1.898, 0.720, 0.0152, 1.0000, 15.0171) for n = 1–4.
[g] (α, γ) = (1.752, 0.146), (1.795, 0.238), (1.823, 0.378), (1.912, 0.332) for n = 1–4.
[h] $(\alpha, a, \gamma, c_1, c_2)$ = (1.753, 0.970, 0.0530, 1.0000, 24.5197), (1.805, 1.311, 0.0720, 1.0000, 11.723), (1.832, 0.663, 0.0129, 1.0000, 5.7236), (1.845, 1.033, 0.008 51, 1.0000, 3.7178) for n = 1–4.
[i] (α, γ) = (1.772, 0.188), (1.804, 0.183), (1.823, 0.307), (1.965, 0.230) for n = 1–4.
[j] $(\alpha, a_1, a_2, c_1, c_2)$ = (1.749, 11.675, 11.675, 1.0000, 1.0000), (1.806, 175.343, 1.689, 1.0000, 0.010 26), (1.831, 71.787, 0.627, 1.0000, 0.1673), (1.805, 6.234, 0.525, 1.0000, 1.0915) for n = 1–4, where $a^{(1)}$ and $a^{(2)}$ were optimized with the same value for n = 1.
[k] $(\alpha, \gamma_1, \gamma_2, a, c_1, c_2)$ = (1.754, 0.0393, 0.226, 9.664, 1.0000, −1.3101), (1.808, 0.0395, 0.227, 9.668, 1.0000, −1.3089), (1.838, 0.0317, 0.0610, 5.346, 1.0000, −2.0701), (1.821, 0.0136, 0.001 72, 1.157, 1.0000, 0.002 731) for n = 1–4.
[l] (α, γ) = (1.753, 0.0671), (1.796, 0.0961), (1.831, 0.135), (1.940, 0.112) for n = 1–4.
[m] $(\alpha, \gamma_1, \gamma_2, c_1, c_2)$ = (1.755, 0.523, 0.880, 1.0000, −0.1717), (1.813, 0.392, 0.557, 1.0000, −0.3642), (1.820, 0.810, 0.824, 1.0000, −0.074 76), (1.856, 0.711, 0.845, 1.0000, −0.042 12) for n = 1–4.
[n] (α, γ) = (1.779, 0.008 92), (1.806, 0.007 52), (1.847, 0.0152), (1.995, 0.008 40) for n = 1–4.
[o] $(\alpha, \gamma_1, \gamma_2, c_1, c_2)$ = (1.755, 0.249, 0.595, 1.0000, −0.096 74), (1.811, 0.141, 0.324, 1.0000, −0.2361), (1.842, 0.283, 0.282, 1.0000, −0.4078), (1.933, 0.332, 0.307, 1.0000, −0.2104) for n = 1–4.
[p] (α, γ) = (1.781, 0.223), (1.807, 0.203), (1.851, 0.282), (1.999, 0.210) for n = 1–4.
[q] $(\alpha, \gamma, c_1, c2)$ = (1.768, 1.462, 0.085 20), (1.812, 1.821, 0.058 14), (1.847, 0.850, 0.5134), (2.002, 0.910, 0.2272) for n = 1–4.
[r] α = 1.814, 1.815, 1.905, 2.038 for n = 1–4.
[s] (α, a) = (1.725, 2.507), (1.753, 1.338), (1.598, 0.923), (1.556, 0.850) for n = 1–4.
[t] $(\alpha, \gamma_1, \gamma_2, \gamma_3, c_1, c_2, c_3)$ = (1.751, 6.700, 0.827, 0.0734, 1.0000, 1.8478, 10.0675), (1.804, 16.250, 1.784, 0.108, 1.0000, 2.4567, 14.8452), (1.766, 5.584, 1.117, 0.125, 1.0000, 0.6630, 0.9127), (1.982, 38.028, 4.442, 0.151, 1.0000, 2.4104, 40.2206) for n = 1–4.

TABLE II. (*Continued.*)

[u](α, γ) = (1.732, 0.517), (1.764, 0.812), (1.569, 1.115), (1.716, 1.038) for n = 1–4.
[v]$(\alpha, \gamma_1, \gamma_2, c_1, c_2)$ = (1.759, 0.148, 4.182, 1.0000, 0.1447), (1.795, 0.176, 5.252, 1.0000, 0.1278), (1.735, 0.178, 3.633, 1.0000, 1.4969), (1.876, 0.170, 3.593, 1.0000, 0.7651) for n = 1–4.
[w](α, γ) = (1.772, 0.361), (1.781, 0.492), (1.735, 0.513), (2.070, 0.412) for n = 1–4.
[x]$(\alpha, \gamma_1, \gamma_2, \gamma_3, c_1, c_2, c_3)$ = (1.764, 3.291, 0.605, 0.0488, 1.0000, 0.5907, 0.3479), (1.808, 4.829, 0.965, 0.0580, 1.0000, 0.9551, 0.5580), (1.845, 6.977, 1.370, 0.0538, 1.0000, 0.7185, 0.5168), (2.089, 9.397, 1.771, 0.0455, 1.0000, 0.6738, 0.5001) for n = 1–4.
[y](α, γ) = (1.880, 0.0858), (1.806, 0.119), (2.007, 0.102), (2.205, 0.0908) for n = 1–4.
[z]$(\alpha, \gamma, c_1, c_2, c_3)$ = (1.799, 0.240, 1.0000, −0.1266, 0.030 78), (1.804, 0.257, 1.0000, −0.1649, 0.044 23), (1.915, 0.210, 1.0000, −0.09720, 0.014 842), (2.093, 0.222, 1.0000, −0.1169, 0.021 53) for n = 1–4.
[aa](α, γ) = (2.018, 0.0807), (1.938, 0.117), (2.310, 0.0913), (2.310, 0.125) for n = 1–4.
[bb]$(\alpha, \gamma, c_1, c_2)$ = (1.974, 0.596, 1.0000, 0.6008), (1.946, 0.784, 1.0000, 0.5972), (2.341, 1.302, 1.0000, 0.2143), (2.386, 0.393, 1.0000, 1.6695) for n = 1–4.
[cc]α = 2.041, 1.994, 2.422, 2.496 for n = 1–4.

3 and 4. Note that these functions satisfy the asymptotic condition, even though s_{12} itself does not satisfy it. If the integrals of these functions are available, we can use them for general atoms and molecules using the variational principle.

Next, we examine the results obtained by using the *multiple* g_{12} functions shown in the right half of Table II. The dimensions M of their cfns are the same as those of the single g_{12} functions because the *multiple* functions were expressed by a linear combination of some single g_{12} functions, as expressed in Eqs. (15), (18), and (20).

The scaling functions G_{16} to G_{21} are composed of only the correct functions. It is very important to note that at each order, the ΔE values obtained from the multiple scaling functions are all very similar within a given order n. In other words, the result of the multiple function is very close to the average value of each order, in contrast to the single function case given in the left half of Table II. This value would be the most accurate value, i.e., the limiting value at each order with the p-alone method. This demonstrates the converging effect that occurred with the use of the multiple g_{12} functions.

Next, we examine the result obtained from each multiple function. The function G_{16} is a sum of the correct functions G_4 and G_3. The energy result is certainly better than that obtained with G_4 or with G_3 alone, demonstrating the collaborative effect of these two functions. Similar collaborative effects are seen in general; that is, when we use multiple correct functions, the accuracy is improved in comparison to the single-function case. However, an interesting exception can be seen for the Ei function at n = 4. The single-function result of G_1 in the left half of Table II was ΔE = 0.001 31 kcal/mol, while the corresponding multiple-function results, G_{21} of right-half of Table II, were again 0.001 31 kcal/mol, the same as above, indicating a lack of the collaborative effect. Furthermore, ΔE = 0.001 31 kcal/mol is the *best* result among all the present results. This may suggest that the Ei function is suitable for the accurate descriptions of the wave functions at higher order. This was the reason why we used the Ei function to obtain the most highly accurate results of the He atom published in 2008.[7] We anticipate that the evaluation of the integrals over this function for general atoms and molecules will become possible in the near future.

The functions G_{22} to G_{24} are the multiple functions of the reasonable function $\sin(\gamma_{12} r_{12})$ with the correct functions or with the reasonable function r_{12}. Again, we note the stability of the results within the same order. The multiple functions gave much better results than the independent functions. The last multiple function (G_{24}) was the worst of the three, as expected.

Finally, we examine the multiple g_{12} functions G_{25} to G_{29}, which belong to the "approximate" functions composed of the s_{12} functions alone. Let us first emphasize that even with the s_{12} functions alone, we could obtain many ΔE results of chemical accuracy (indicated by boldface in Table II) starting from order 2. In particular, the results of the functions G_{25}, G_{26}, and G_{27} were ΔE = 0.16–0.36 kcal/mol at order 2, 0.128–0.0416 kcal/mol at order 3, and 0.0237–0.0595 kcal/mol at order 4, which are useful accurate results. Remarkably, some results are one order of magnitude better than the chemical accuracy for n = 3 and 4. These results are much improved in comparison with the results obtained from the single approximate functions (G_{10} to G_{15}), demonstrating that the multiple combinations of the scaled s_{12} functions can lead to the highly accurate g_{12} functions. Thus, developing a useful method for evaluating the integrals over these multiple functions will lead to accurate variational methods for solving SEs of atoms and molecules.

C. Cusp values and mean r_{1A} and r_{12} separations

We examine here the e–n and e–e cusp values of the helium atom summarized in Table III, where the way of presentation is the same as that in Table II. The cusp values were calculated using the expression $\langle\psi|\delta(r_{pq}) \cdot \partial/\partial r_{pq}|\psi\rangle/\langle\psi|\delta(r_{pq})|\psi\rangle$ given by Pachucki and Komasa.[51] The present calculations were performed changing the e–e g_{12} functions while fixing the e–n g_{iA} function to r_{iA}. Therefore, we examine first the e–e cusp values, whose exact value is 0.5.

With the single correct functions, $G_1 \sim G_5$, the e–e cusp value is improved, as seen from the average value, as the order n of FC theory increases, like roughly 0.39 (n = 1), 0.43 (n = 2), 0.49 (n = 3), and 0.49 (n = 4). However, within the same order, the e–e cusp values are strongly dependent on the g_{12} function. We next compare the e–e cusp values between the correct and reasonable $G_6 \sim G_9$ g_{12} functions using the average values. The average values of the correct functions are certainly better than those of the reasonable functions, 0.39 vs 0.37 (n = 1), 0.43 vs 0.40 (n = 2), 0.49 vs 0.46 (n = 3), and 0.49 vs 0.47 (n = 4). With the approximate g_{12} functions, the e–e cusp values are all zero.

With the multiple functions, the result of the correct functions becomes better at lower orders (n = 1 and 2) but overshoots the correct value, 0.5, at higher orders (n = 3 and 4). With the reasonable functions, the e–e cusp values are smaller than the correct case and

TABLE III. Electron–nucleus (e–n) and electron–electron (e–e) cusp values of the helium atom obtained from the free-complement variational calculations using different e–e scaling functions g_{12} (G_1 to G_{29}) of the scaled Schrödinger equation. See Table II for the details of the calculations.

		$n=1, M=3$		$n=2, M=7$		$n=3, M=13$		$n=4, M=22$				$n=1, M=3$		$n=2, M=7$		$n=3, M=13$		$n=4, M=22$	
	g_{12}	e–n	e–e	e–n	e–e	e–n	e–e	e–n	e–e		g_{12}	e–n	e–e	e–n	e–e	e–n	e–e	e–n	e–e
	Correct										**Correct**								
G_1	$Ei(-\gamma_1 r_{12}-\gamma_2)-Ei(-\gamma_2)$	−1.8446	0.4066	−1.9971	0.4778	−1.9931	0.5262	−2.0025	0.5263	G_{16}	$c_1[1-\exp(-\gamma_1 r_{12})]+c_2\arctan(\gamma_2 r_{12})$	−1.8444	0.5152	−1.9989	0.4785	−1.9942	0.5173	−2.0018	0.5035
G_2	$r_{12}/(r_{12}+a)$	−1.8449	0.4025	−1.9967	0.4501	−1.9914	0.5127	−2.0016	0.4921	G_{17}	$\sum_{k=1}^{3} c_k[1-\exp(-\gamma_k r_{12})]$	−1.8445	0.4189	−1.9986	0.4977	−1.9936	0.5585	−2.0023	0.5196
G_3	$\arctan(\gamma r_{12})$	−1.8481	0.3618	−1.9979	0.3934	−1.9912	0.4758	−2.0011	0.4765	G_{18}	$c_1 r_{12}/(r_{12}+a)+c_2[1-\exp(-\gamma r_{12})]$	−1.8453	0.5172	−1.9985	0.5041	−1.9937	0.5631	−2.0018	0.5233
G_4	$1-\exp(-\gamma r_{12})$	−1.8455	0.3962	−1.9970	0.4337	−1.9905	0.4944	−2.0013	0.4879	G_{19}	$c_1 r_{12}/(r_{12}+a)+c_2\arctan(\gamma r_{12})$	−1.8454	0.5127	−1.9985	0.5141	−1.9937	0.5627	−2.0024	0.4942
G_5	$\tanh(\gamma r_{12})$	−1.8491	0.3598	−1.9987	0.3923	−1.9900	0.4655	−2.0013	0.4750	G_{20}	$c_1 r_{12}/(r_{12}+a_1)+c_2 r_{12}/(r_{12}+a_2)$	−1.8449	0.4025	−1.9986	0.5006	−1.9937	0.5649	−2.0025	0.5093
	Average	−1.8464	0.3854	−1.9975	0.4295	−1.9912	0.4949	−2.0016	0.4916	G_{21}	$c_1[Ei(-\gamma_1 r_{12}-\gamma_2)-Ei(-\gamma_2)]+c_2 r_{12}/(r_{12}+a)$	−1.8456	0.4691	−1.9988	0.4893	−1.9930	0.5350	−2.0025	0.5288
											Average	−1.8452	0.4726	−1.9987	0.4974	−1.9937	0.5503	−2.0022	0.5131
	Reasonable										**Reasonable**								
G_6	$r_{12}\exp(-\gamma r_{12})$	−1.8459	0.3930	−1.9972	0.4275	−1.9900	0.4858	−2.0013	0.4854	G_{22}	$c_1\arctan(\gamma_1 r_{12})+c_2\sin(\gamma_2 r_{12})$	−1.8458	0.4020	−1.9999	0.4165	−1.9932	0.5029	−2.0020	0.4816
G_7	$r_{12}\exp(-\gamma s_{12})$	−1.8502	0.3581	−1.9992	0.3914	−1.9892	0.4588	−2.0015	0.4734	G_{23}	$c_1[1-\exp(-\gamma_1 r_{12})]+c_2\sin(\gamma_2 r_{12})$	−1.8458	0.4447	−1.9994	0.4662	−1.9915	0.5057	−2.0019	0.4909
G_8	$\sin(\gamma r_{12})$	−1.8504	0.3578	−1.9993	0.3912	−1.9891	0.4578	−2.0015	0.4731	G_{24}	$c_1 r_{12}+c_2\sin(\gamma r_{12})$	−1.8479	0.3845	−1.9996	0.4189	−1.9904	0.4710	−2.0019	0.4816
G_9	r_{12}	−1.8540	0.3549	−2.0009	0.3880	−1.9882	0.4483	−2.0020	0.4684										
	Average	−1.8501	0.3660	−1.9992	0.3995	−1.9891	0.4627	−2.0016	0.4751		Average	−1.8465	0.4104	−1.9996	0.4339	−1.9917	0.4932	−2.0019	0.4847
	Approximate										**Approximate**								
G_{10}	$s_{12}/(s_{12}+a)$	−1.8322	0.0	−1.9878	0.0	−1.9886	0.0	−2.0021	0.0	G_{25}	$\sum_{k=1}^{3} c_k[1-\exp(-\gamma_k s_{12})]$	−1.8449	0.0	−1.9979	0.0	−1.9973	0.0	−2.0009	0.0
G_{11}	$\arctan(\gamma s_{12})$	−1.8265	0.0	−1.9879	0.0	−1.9874	0.0	−2.0051	0.0	G_{26}	$c_1[1-\exp(-\gamma_1 s_{12})]+c_2\arctan(\gamma_2 s_{12})$	−1.8450	0.0	−1.9961	0.0	−1.9959	0.0	−2.0054	0.0
G_{12}	$1-\exp(-\gamma s_{12})$	−1.8368	0.0	−1.9934	0.0	−1.9958	0.0	−2.0042	0.0	G_{27}	$\sum_{k=1}^{3} c_k s_{12}\exp(-\gamma_k s_{12})$	−1.8499	0.0	−1.9988	0.0	−1.9897	0.0	−2.0050	0.0
G_{13}	$s_{12}\exp(-\gamma s_{12})$	−1.8410	0.0	−2.0012	0.0	−1.9762	0.0	−2.0128	0.0	G_{28}	$\sum_{k=1}^{3} c_k {s_{12}}^k\exp(-\gamma s_{12})$	−1.8452	0.0	−2.0014	0.0	−1.9857	0.0	−2.0131	0.0
G_{14}	$\sin(\gamma s_{12})$	−1.8196	0.0	−2.0202	0.0	−1.9694	0.0	−2.0353	0.0	G_{29}	$c_1 s_{12}+c_2\sin(\gamma s_{12})$	−1.8326	0.0	−2.0285	0.0	−1.9689	0.0	−2.0152	0.0
G_{15}	s_{12}	−1.8144	0.0	−2.0348	0.0	−1.9745	0.0	−2.0143	0.0		Average	−1.8435	0.0	−2.0045	0.0	−1.9875	0.0	−2.0079	0.0
	Average	−1.8284	0.0	−2.0042	0.0	−1.9820	0.0	−2.0123	0.0										
	Exact value	−2.0	0.5	−2.0	0.5	−2.0	0.5	−2.0	0.5			−2.0	0.5	−2.0	0.5	−2.0	0.5	−2.0	0.5

TABLE IV. Expectation values of $\langle r_1 \rangle$ and $\langle r_{12} \rangle$ (a.u.) for the free-complement variational calculations of the helium atom using different e–e scaling functions g_{12} (G_1 to G_{29}) of the scaled Schrödinger equation. The values obtained for ψ_0 and those obtained for ψ_{HF} using the Mclean–Yoshimine basis set (Table II of Ref. 53) are given as footnote.[a] See Table II for the details of the calculations.

		$n=1, M=3$		$n=2, M=7$		$n=3, M=13$		$n=4, M=22$				$n=1, M=3$		$n=2, M=7$		$n=3, M=13$		$n=4, M=22$	
	g_{12}	$\langle r_1 \rangle$	$\langle r_{12} \rangle$	$\langle r_1 \rangle$	$\langle r_{12} \rangle$	$\langle r_1 \rangle$	$\langle r_{12} \rangle$	$\langle r_1 \rangle$	$\langle r_{12} \rangle$		g_{12}	$\langle r_1 \rangle$	$\langle r_{12} \rangle$	$\langle r_1 \rangle$	$\langle r_{12} \rangle$	$\langle r_1 \rangle$	$\langle r_{12} \rangle$	$\langle r_1 \rangle$	$\langle r_{12} \rangle$
	Single function										**Multiple function**								
	Correct										**Correct**								
G_1	$Ei(-\gamma_1 r_{12} - \gamma_2) - Ei(-\gamma_2)$	0.897 46	1.372 98	0.929 50	1.421 53	0.929 16	1.421 23	0.929 46	1.422 05	G_{16}	$c_1[1-\exp(-\gamma_1 r_{12})] + c_2 \arctan(\gamma_2 r_{12})$	0.897 84	1.373 60	0.929 51	1.421 76	0.929 20	1.421 48	0.929 46	1.422 03
G_2	$r_{12}/(r_{12}+a)$	0.897 49	1.373 11	0.929 43	1.421 21	0.929 15	1.421 23	0.929 46	1.422 02	G_{17}	$\sum_{k=1}^{3} c_k[1-\exp(-\gamma_k r_{12})]$	0.897 59	1.373 23	0.929 50	1.421 74	0.929 18	1.421 45	0.929 46	1.422 04
G_3	$\arctan(\gamma r_{12})$	0.897 66	1.373 88	0.929 15	1.420 49	0.929 17	1.421 26	0.929 45	1.421 98	G_{18}	$c_1 r_{12}/(r_{12}+a) + c_2[1-\exp(-\gamma r_{12})]$	0.898 06	1.374 18	0.929 50	1.421 72	0.929 18	1.421 44	0.929 46	1.422 04
G_4	$1-\exp(-\gamma r_{12})$	0.897 53	1.373 26	0.929 35	1.421 00	0.929 13	1.421 25	0.929 45	1.422 00	G_{19}	$c_1 r_{12}/(r_{12}+a) + c_2 \arctan(\gamma r_{12})$	0.898 07	1.374 21	0.929 49	1.421 71	0.929 18	1.421 44	0.929 46	1.422 04
G_5	$\tanh(\gamma r_{12})$	0.897 80	1.374 31	0.929 08	1.420 47	0.929 13	1.421 25	0.929 44	1.421 97	G_{20}	$c_1 r_{12}/(r_{12}+a_1) + c_2 r_{12}/(r_{12}+a_2)$	0.897 47	1.373 03	0.929 50	1.421 74	0.929 18	1.421 43	0.929 46	1.422 05
	Average	0.897 59	1.373 51	0.929 30	1.420 94	0.929 15	1.421 24	0.929 45	1.422 00	G_{21}	$c_1[Ei(-\gamma_1 r_{12} - \gamma_2) - Ei(-\gamma_2)] + c_2 r_{12}/(r_{12}+a)$	0.898 15	1.374 38	0.929 50	1.421 75	0.929 18	1.421 45	0.929 46	1.422 05
											Average	0.897 86	1.373 77	0.929 50	1.421 74	0.929 18	1.421 45	0.929 46	1.422 04
	Reasonable										**Reasonable**								
G_6	$r_{12}\exp(-\gamma r_{12})$	0.897 56	1.373 38	0.929 31	1.420 92	0.929 12	1.421 26	0.929 44	1.421 99	G_{22}	$c_1 \arctan(\gamma_1 r_{12}) + c_2 \sin(\gamma_2 r_{12})$	0.898 06	1.374 27	0.929 44	1.421 59	0.929 20	1.421 47	0.929 45	1.422 02
G_7	$r_{12}\exp(-\gamma s_{12})$	0.897 96	1.374 79	0.929 05	1.420 47	0.929 09	1.421 26	0.929 43	1.421 97	G_{23}	$c_1[1-\exp(-\gamma_1 r_{12})] + c_2 \sin(\gamma_2 r_{12})$	0.898 15	1.374 42	0.929 51	1.421 76	0.929 16	1.421 39	0.929 45	1.422 02
G_8	$\sin(\gamma r_{12})$	0.897 99	1.374 91	0.929 04	1.420 47	0.929 09	1.421 26	0.929 43	1.421 97	G_{24}	$c_1 r_{12} + c_2 \sin(\gamma r_{12})$	0.898 35	1.375 12	0.929 43	1.421 55	0.929 14	1.421 38	0.929 44	1.422 01
G_9	r_{12}	0.898 70	1.377 09	0.928 93	1.420 49	0.929 05	1.421 30	0.929 42	1.421 97		Average	0.898 19	1.374 60	0.929 46	1.421 63	0.929 17	1.421 41	0.929 45	1.422 02
	Average	0.898 05	1.375 04	0.929 08	1.420 59	0.929 09	1.421 27	0.929 43	1.421 98										
	Approximate										**Approximate**								
G_{10}	$s_{12}/(s_{12}+a)$	0.893 87	1.362 47	0.929 43	1.415 87	0.929 16	1.419 99	0.929 46	1.420 87	G_{25}	$\sum_{k=1}^{3} c_k[1-\exp(-\gamma_k s_{12})]$	0.897 96	1.373 90	0.929 41	1.421 33	0.929 26	1.421 51	0.929 42	1.421 83
G_{11}	$\arctan(\gamma s_{12})$	0.893 06	1.358 34	0.929 44	1.412 88	0.929 18	1.419 05	0.929 44	1.419 82	G_{26}	$c_1[1-\exp(-\gamma_1 s_{12})] + c_2 \arctan(\gamma_2 s_{12})$	0.897 66	1.373 03	0.929 21	1.420 13	0.929 26	1.421 27	0.929 44	1.421 65
G_{12}	$1-\exp(-\gamma s_{12})$	0.894 57	1.363 64	0.928 91	1.413 44	0.929 27	1.418 97	0.929 28	1.419 56	G_{27}	$\sum_{k=1}^{3} c_k s_{12} \exp(-\gamma_k s_{12})$	0.898 01	1.374 05	0.929 13	1.420 20	0.929 11	1.421 03	0.929 37	1.421 66
G_{13}	$s_{12}\exp(-\gamma s_{12})$	0.895 98	1.369 10	0.928 27	1.412 57	0.928 67	1.417 72	0.929 09	1.419 03	G_{28}	$\sum_{k=1}^{3} c_k {s_{12}}^k \exp(-\gamma s_{12})$	0.896 05	1.368 94	0.928 90	1.418 08	0.928 92	1.419 21	0.929 18	1.420 01
G_{14}	$\sin(\gamma s_{12})$	0.897 60	1.377 61	0.926 29	1.413 77	0.927 18	1.417 68	0.928 82	1.419 01	G_{29}	$c_1 s_{12} + c_2 \sin(\gamma s_{12})$	0.898 58	1.378 35	0.927 05	1.417 00	0.927 73	1.418 57	0.928 79	1.419 79
G_{15}	s_{12}	0.898 55	1.380 92	0.926 18	1.41739	0.927 18	1.418 71	0.928 54	1.421 09		Average	0.897 65	1.373 65	0.928 74	1.419 35	0.928 86	1.420 32	0.929 24	1.420 99
	Average	0.895 61	1.368 68	0.928 09	1.414 32	0.928 44	1.418 69	0.929 11	1.419 90										

[a] $\langle r_1 \rangle$ and $\langle r_{12} \rangle$ for ψ_0 with $\alpha = 1.6875$ were 0.888 889 and 1.296 296 a.u., respectively. Those for the Hartree–Fock wave function ψ_{HF} using the Mclean–Yoshimine basis set (Table II of Ref. 53) were 0.927 266 and 1.362 111 a.u., respectively.

the variations against orders are similar. We will not try to explain more details.

Next, we examine the e–n cusp values. Because the e–n g_{iA} functions are r_{iA} for all calculations, we are examining the indirect effects of the e–e g_{12} functions on the e–n cusp values, which should be smaller than the direct effects discussed above. Compared to the exact value of −2.0, the calculated values are all very close except for the $n = 1$ case. Generally, this value becomes close to −2.0 as the order increases for all cases of correct, reasonable, and approximate.

Finally, we examine the average e–n distance, r_{1A} (=r_{2A}) and the average e–e distance, r_{12} of the two electrons of the helium atom. Table IV summarizes the expectation values of these quantities. In footnote a of Table II, we gave the calculated values of $\langle r_{1A} \rangle$ and $\langle r_{12} \rangle$ for the initial function ψ_0 of the present FC calculations, which is Hartree–Fock with the single-zeta Slater-type orbital[52] of $\alpha = 1.6875$. We have also given these values calculated from the Hartree–Fock wave function with the McLean and Yoshimine's extended Slater basis set.[53] Starting from the Hartree–Fock results, we see that both $\langle r_{1A} \rangle$ and $\langle r_{12} \rangle$ increase as the quality of the wave function increases by increasing the order n of the FC theory. However, from order 2, the change is very small: a saturation occurs. Furthermore, the effect of changing the e–e scaling function on the distances, $\langle r_{1A} \rangle$ and $\langle r_{12} \rangle$, are quite small: only the order of the FC theory affects these quantities. This is true even when we change the single g function to multiple one. Interestingly, the improving effects of the approximate functions are also similar to those of the correct and reasonable functions, although with the approximate functions, the $\langle r_{12} \rangle$ value is more slowly improved than the $\langle r_{1A} \rangle$ value.

V. CONCLUDING REMARKS

In atoms and molecules, the electrons and nuclei interact through Coulombic potentials that are singular at the collisional regions. For such systems, the variational formula of the potentially exact wave function of the original SE suffers from the divergence difficulty. However, by virtue of SSE, the variational formula does not encounter such a difficulty, allowing the exact solution of SE to be obtained with FC theory.[3,4]

In this paper, we have generalized the scaling function g of SSE and investigated its general behaviors. From the behavior in the collisional region, which is related to the cusp condition, the coalescent condition given by Eq. (11) was formulated. From the relationship between SSE and the original SE in the non-collisional region, the asymptotic condition given by Eq. (12) was formulated. For the g functions to be "correct," they must satisfy both of these two limiting conditions. The "reasonable" g functions satisfy only the coalescent condition. The distinction of the correct functions from the reasonable functions based on the asymptotic condition was introduced for the first time in the present study. We studied many analytical functions that belong to the correct and reasonable classes. We have shown that the correct g_{ij} functions are almost always more accurate than the reasonable g_{ij} functions. The popular e–e function r_{ij} belongs to the less-accurate "reasonable" class, and its performance was less accurate than those of the correct functions. We also studied the functions belonging to the "approximate" class, which do not satisfy the coalescent condition but are still practically useful. Typical approximate functions include the Gaussian-type functions[39,40] and the s_{ij} (=r_{ij}^2) function[19] reported previously.

The qualities of many different e–e scaling functions were examined using the robust variational principle for the helium atom for which all the necessary integrals were easily evaluated without any mathematical problems. The e–n scaling function was fixed as $g_{iA} = r_{iA}$. The correct functions were generally most accurate, followed by the reasonable functions. Among them, the popular function r_{ij} showed the worst performance, although it was still very accurate. This result recommends a use of the correct class of g_{ij} functions for their high accuracy. When we constructed multiple functions composed of the correct functions, the results were consistently very accurate and stable. These results are valuable for increasing the accuracy of FC theory. The present study may also be considered as a generalization of the so-called geminal functions[26–40] and Jastrow functions.[41–47] The results of this study, for example, the merit of using the multiple g_{ij} functions, may be useful beyond just SSE because they can easily find applications in QMC as well.

The "approximate" g_{ij} functions defined with s_{ij} were less accurate than the correct and reasonable functions. However, when s_{ij} was used in the framework of the correct function, a better accuracy was obtained. The simple primitive s_{ij} function has a remarkable merit that it can be transformed into solely one-electron functions as given by Eq. (9). This leads to the variational FC s_{ij} theory, which can be performed using only one- and two-electron integrals as reported previously.[19]

Now, let us consider the transferability of the scaling functions. The popular g functions r_{iA} and r_{ij} [Eq. (6)] have no parameters in them and are thus transferable. However, for the correct scaling functions g_{pq}, their parameters such as γ_{pq} should reflect the intrinsic nature of the local interactions between particles p and q, like orbital exponents and spin-dependent parameters; they should depend on the cusp values intrinsic to the e–n pair (the nuclear charge) and the e–e pair (singlet or triplet pairing),[21] whereas they should not depend strongly on other environmental factors.

In FC theory, the e–n g_{iA} function works to improve the local electronic structure near the nucleus A; thus, the orbital exponent of the atomic orbital of A to which the electron i belongs is improved by the g_{iA} function, and thereby, the e–n cusp values are improved at the same time. Therefore, the e–n g_{iA} function is not expected to be transferable, particularly when we start from the Slater orbitals for the initial function ψ_0. However, for the e–e function g_{ij}, the initial function ψ_0 of FC theory does not usually include the explicit e–e dependence. Therefore, the g_{ij} function creates the e–e *geminal* function that is essentially transferable. They depend only on the e–e singlet or triplet paring. This explains why the general functional forms were important for the g_{ij} functions and the uses of the correct functions were important to obtain highly accurate and stable results.

Finally, let us consider how to take advantage of the high accuracy of the correct g_{ij} functions in applications of FC theory to general atoms and molecules. The development of integral-evaluation methods over the correct g_{ij} functions of general atoms and molecules would allow straightforward variational calculations leading to accurate predictive quantum-chemistry. However, even if the variational approach is difficult, we already have an integral-free general method, the LSE method,[11] that uses SEs themselves at the selected local sampling points as the deterministic equations. This method has been successfully used in several applications.[13,14] In the

LSE method, the functional complexity of the e–e g_{ij} functions does not matter because the values of the functions at given sampling points are always easily calculated. FC theory usually deals with the wave functions that are close to the exact limit; thus, the fluctuations of the local energy $\varepsilon(r)$ are expected to be small[12] except near the local collisional regions where the roles of the correct g_{ij} functions are expected to be important.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

REFERENCES

[1] P. A. M. Dirac, Proc. R. Soc. London, Ser. A **123**, 714 (1929).
[2] H. Nakatsuji, J. Chem. Phys. **113**, 2949 (2000); H. Nakatsuji and E. R. Davidson, *ibid.* **115**, 2000 (2001); H. Nakatsuji, *ibid.* **115**, 2465 (2001).
[3] H. Nakatsuji, Phys Rev. Lett. **93**, 030403 (2004); Phys. Rev. A **72**, 062110 (2005).
[4] H. Nakatsuji, Acc. Chem. Res. **45**, 1480 (2012).
[5] H. Nakashima and H. Nakatsuji, Astrophys. J. **725**, 528 (2010).
[6] A. Ishikawa, H. Nakashima, and H. Nakatsuji, Chem. Phys. **401**, 000062 (2012); H. Nakashima and H. Nakatsuji, J. Chem. Phys. **139**, 074105 (2013).
[7] H. Nakashima and H. Nakatsuji, J. Chem. Phys. **127**, 224104 (2007); Y. Kurokawa, H. Nakashima, and H. Nakatsuji, Phys. Chem. Chem. Phys. **10**, 4486 (2008).
[8] Y. Kurokawa, H. Nakashima and H. Nakatsuji, Phys. Rev. A, **72**, 062502 (2005); Phys. Chem. Chem. Phys. **21**, 6327 (2019); **22**, 13489 (2020).
[9] H. Nakatsuji and H. Nakashima, J. Chem. Phys. **150**, 044105 (2019).
[10] H. Nakashima and H. Nakatsuji, Phys. Rev. A **102**, 052835 (2020).
[11] H. Nakatsuji, H. Nakashima, Y. Kurokawa, and A. Ishikawa, Phys. Rev. Lett. **99**, 240402 (2007); H. Nakatsuji and H. Nakashima, J. Chem. Phys. **142**, 084117 (2015).
[12] H. Nakashima and H. Nakatsuji, Phys. Rev. Lett. **101**, 240406 (2008).
[13] H. Nakatsuji and H. Nakashima, J. Chem. Phys. **142**, 194101 (2015).
[14] H. Nakatsuji, H. Nakashima, and Y. I. Kurokawa, J. Chem. Phys. **149**, 114105 (2018); **149**, 114106 (2018).
[15] B. L. Hammond, W. A. Lester, Jr., and P. J. Reynolds, *Monte Carlo Methods in Ab Initio Quantum Chemistry* (World Scientific, Singapore, 1994).
[16] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, J. Chem. Phys. **21**, 1087 (1953).
[17] C. J. Umrigar, Phys. Rev. Lett. **71**, 408 (1993).
[18] L. Devroye, *Non-Uniform Random Variate Generation* (Springer-Verlag, Berlin, 1986).
[19] H. Nakatsuji, H. Nakashima, and Y. Kurokawa, Phys. Rev. A **101**, 062508 (2020).
[20] H. Nakatsuji, H. Nakashima, and Y. Kurokawa, in *Annual Report of the Computer Center of the Institute of Molecular Science* (Research Center for Computational Science, Okazaki, Japan, 2020), Vol. 20, p. 92; Vol. 21, p. 98 (2021).
[21] T. Kato, Commun. Pure Appl. Math. **10**, 151 (1957).
[22] V. A. Rassolov and D. M. Chipman, J. Chem. Phys. **104**, 9908 (1996).
[23] R. T. Pack and W. B. Brown, J. Chem. Phys. **45**, 556 (1966).
[24] Y. I. Kurokawa, H. Nakashima, and H. Nakatsuji, J. Chem. Phys. **139**, 044114 (2013).
[25] M. Nooijen and R. J. Bartlett, J. Chem. Phys. **109**, 8232 (1998).
[26] C. L. Davis and E. N. Maslen, Proc. R. Soc. London, Ser. A, **384**, 89 (1982); E. L. Davis and E. N. Maslen, J. Phys. A: Math. Gen. **16**, 4255 (1983).
[27] C. M. Johnson, A. E. Doran, J. Zhang, E. F. Valeev, and S. Hirata, J. Chem. Phys. **145**, 154115 (2016).
[28] A. Grüneis, S. Hirata, Y. Ohnishi, and S. Ten-no, J. Chem. Phys. **146**, 080901 (2017).
[29] S. Y. Willow, M. R. Hermes, K. S. Kim, and S. Hirata, J. Chem. Theory Comput. **9**, 4396 (2013).
[30] S. Ten-no, Chem. Phys. Lett. **398**, 56 (2004).
[31] S. Ten-no, J. Chem. Phys. **126**, 014108 (2007).
[32] W. Klopper, F. R. Manby, S. Ten-no, and E. F. Valeev, Int. Rev. Phys. Chem. **25**, 427 (2006).
[33] S. Ten-no, Theor. Chem. Acc. **131**, 1070 (2012).
[34] W. Kutzelnigg, Theor. Chim. Acta **68**, 445 (1985).
[35] W. Kutzelnigg and W. Klopper, J. Chem. Phys. **94**, 1985 (1991).
[36] V. Termath, W. Klopper, and W. Kutzelnigg, J. Chem. Phys. **94**, 2002 (1991).
[37] W. Klopper and W. Kutzelnigg, J. Chem. Phys. **94**, 2020 (1991).
[38] J. Noga and W. Kutzelnigg, J. Chem. Phys. **101**, 7738 (1994).
[39] S. F. Boys, Proc. R. Soc. London, Ser. A **258**, 402 (1960).
[40] K. Singer, Proc. R. Soc. London, Ser. A **258**, 412 (1960).
[41] R. Jastrow, Phys. Rev. **98**, 1479 (1955).
[42] P. J. Reynolds, D. M. Ceperley, B. J. Alder, and W. A. Lester, Jr., J. Chem. Phys. **77**, 5593 (1982).
[43] C. Fillippi and C. J. Umrigar, J. Chem. Phys. **105**, 213 (1996).
[44] M. Casula and S. Sorella, J. Chem. Phys. **119**, 6500 (2003).
[45] T. Bouabça, B. Braïda, and M. Caffarel, J. Chem. Phys. **133**, 044111 (2010).
[46] B. Braïda, J. Toulouse, M. Caffarel, and C. J. Umrigar, J. Chem. Phys. **134**, 084108 (2010).
[47] W. Wu, H. Zhang, B. Braïda, S. Shaik, and P. C. Hiberty, Theor. Chem. Acc. **133**, 1441 (2014).
[48] S. Huzinaga, Prog. Theor. Phys. Suppl. **40**, 52 (1967).
[49] E. A. Hylleraas, Z. Phys. **48**, 469 (1928); **54**, 347 (1930).
[50] See http://www.maplesoft.com/ for MAPLE13 code, Cybernet Systems Co. Ltd. in Japan.
[51] K. Pachucki and J. Komasa, Chem. Phys. Lett. **389**, 209 (2004).
[52] E. Clementi and D. L. Raimondi, J. Chem. Phys. **38**, 2686 (1963).
[53] A. D. McLean and M. Yoshimine, "Table of Linear Molecular Wave Functions," IBM J. Res. Dev. **12**, 206 (1968).