

# Accurate Scaling Functions of the Scaled Schrödinger Equation. II. Variational Examination of the Correct Scaling Functions with the Free Complement Theory Applied to the Helium Atom

Hiroshi Nakatsuji\* and Hiroyuki Nakashima



Cite This: <https://doi.org/10.1021/acs.jctc.4c00263>



Read Online

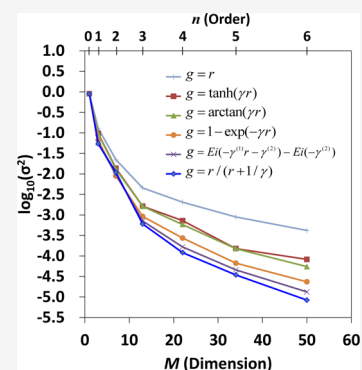
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

**ABSTRACT:** In a previous paper [*Phys. Rev. Lett.* **2004**, 93, 030403.], one of the authors introduced the scaled Schrödinger equation (SSE),  $g(H - E)\psi = 0$  for atoms and molecules, where the scaling function  $g$  is the positive function of the electron–nuclear (e–n) and electron–electron (e–e) distances. The SSE is equivalent to the Schrödinger equation (SE),  $(H - E)\psi = 0$ , that governs the chemical world but does not have the divergence difficulty that occurs when we try to solve the SE to obtain the exact solution. The  $g$  function is essential not only to prevent this divergence difficulty but also to obtain the exact wave function of the SE or SSE. In paper I of this series [*J. Chem. Phys.* **2022**, 156, 014113.], we introduced five analytical  $g$  functions that behave correctly at both the coalescence and asymptotic regions, but we examined them only for the e–e part. In this paper, we examine these correct  $g$  functions for both e–n and e–e parts by applying the free complement (complete-element) (FC) theory variationally to the He atom. However, even for the two-electron He atom, the analytical integral formulas were not obtained when we use the correct  $g$  functions for both e–n and e–e parts, except for  $g = 1 - \exp(-\gamma r)$ , but we were able to perform variational FC calculations by employing numerical integration schemes. We examined not only the energy and wave function but also the H-square error (defined by eq 14 of the text), energy lower bound, and e–n and e–e cusp properties. For the energy lower bound, we applied our FC wave functions to the method proposed recently by Pollak, Martinazzo, and others and could obtain good results. With the use of the correct-group  $g$  functions, the convergence of the FC theory to the exact analytical solution of the SE or SSE became efficient, and the performance was particularly good with the  $g$  functions,  $r/(r + 1/\gamma)$ ,  $Ei$ , and  $1 - \exp(-\gamma r)$  in this order. These results were always superior to those obtained with  $g = r$ .



## 1. INTRODUCTION

The scaled Schrödinger equation (SSE) given by

$$g(H - E)\psi = 0 \quad (1)$$

was proposed by one of the authors<sup>1,2</sup> to solve the original Schrödinger equation (SE)

$$(H - E)\psi = 0 \quad (2)$$

exactly for atoms and molecules. In the above equations,  $H$  is the Hamiltonian of atoms and molecules written as

$$H = - \sum_i \frac{1}{2} \Delta_i - \sum_A \frac{1}{2} \Delta_A - \sum_{i,A} \frac{Z_A}{r_{iA}} + \sum_{i<j} \frac{1}{r_{ij}} + \sum_{A<B} \frac{Z_A Z_B}{r_{AB}} \quad (3)$$

The first two terms represent the kinetic operators of electrons and nuclei, respectively. The next three terms represent the Coulombic potentials among the electrons and nuclei. They diverge to plus or minus infinity when the two-particle coalescence (or collision) occurs. In the Born–Oppenheimer (BO) approximation, the second term of eq 3

is omitted and the last term is not a variable but a constant. In the SSE given by eq 1, the scaling function  $g$  is the positive function of the electron–nuclear (e–n) and electron–electron (e–e) distances,  $r_{iA}$  and  $r_{ij}$  respectively, as given by<sup>1,2</sup>

$$g = \sum_{i,A} g_{iA}(r_{iA}) + \sum_{i<j} g_{ij}(r_{ij}) \quad (4)$$

These  $g$  functions must satisfy the relations

$$\lim_{r \rightarrow 0} g(r)V(r) = a \quad (5)$$

to eliminate the singularity of the Coulombic potential  $V(r)$  in  $H$  at the coalescence region, and  $a$  is a constant. A “reasonable” choice often used was  $g_{iA}(r_{iA}) = r_{iA}$ ,  $g_{ij}(r_{ij}) = r_{ij}$ , and  $g_{AB}(r_{AB}) = r_{AB}$ .

**Received:** February 29, 2024

**Revised:** April 9, 2024

**Accepted:** April 12, 2024

The SE implies that when  $H$  is given, the SE gives the exact wave function  $\psi$  and the exact energy  $E$ . Therefore, we may write the exact wave function as a functional of  $H$ , namely,  $\tilde{\psi}(H)$  (tilde means some functional). The divergence difficulty of the variational equation of the SE is  $\langle \delta\tilde{\psi}|H - E|\tilde{\psi} \rangle = \pm\infty$ , which always occurs because there are three  $V(r)$  in the integrand. To prevent such a divergence, the SSE given by eq 1 was introduced.<sup>1,2</sup> Because  $g$  is a positive function, we can always divide eq 1 by  $g$  without affecting the solution, which means that the solutions of the SSE must be identical to the solutions of the SE.

The formal solution of the SSE is easily obtained through the following formula<sup>1,2</sup>

$$\psi_n = [1 + C_n g(H - E_{n-1})]\psi_{n-1} \quad (6)$$

which was named as the simplest iterative configuration interaction (SICI) formula,<sup>1-5</sup> where  $\psi_n$ ,  $E_n$ , and  $C_n$  represent the wave function, energy, and coefficients, respectively, at order  $n$  of the iteration. We note that here in the SICI, eq 6, the scaling function  $g$  enters into the *central* part, though in the SSE, eq 1,  $g$  was like an attachment in front of the SE and could be divided by itself without affecting the (hidden) exact solutions we want to solve. This shows clearly how important is the scaling function  $g$  for really solving the SE. Based on this SICI formula eq 6, our useful theory called the free complement (complete element) (FC) theory was formulated. From the explicit expansion of the order  $n$  wave function on the right-hand side of  $\psi_n$ , we collect all the independent nondiverging analytical functions  $\{\phi_I\}$ , and by a linear combination of them, we describe the system as

$$\psi_n = \sum_I^M c_I \phi_I \quad (7)$$

The set of analytical functions  $\{\phi_I\}$  is called complete-element (complement) functions (cfs), and this theory was called the FC theory.  $M$  is the number of the cfs (dimension) at order  $n$ . The mathematical transformation from eq 6, SICI to the formula of the FC theory, eq 7, is easily coded<sup>1,2</sup> by using the mathematical software, Maple.<sup>6</sup> The coefficients  $\{c_I\}$  are determined by the variational method or with the local Schrödinger equation (LSE) method,<sup>7,8</sup> the latter being a sampling-type procedure applicable to any systems even though the wave function includes explicit  $r_{ij}$  variables. As the name shows, the FC formula is composed of the free complete elements of the analytical functions  $\{\phi_I\}$  that are the building blocks of the exact wave function. For determining  $\{c_I\}$ , we may use the formula of SSE,  $\langle \delta\tilde{\psi}|g(H - E)|\tilde{\psi} \rangle = 0$ , or that of the SE,  $\langle \delta\tilde{\psi}|H - E|\tilde{\psi} \rangle = 0$ , but the latter was usually more quickly convergent than the former.<sup>1,2,7</sup> The FC theory is guaranteed to become exact as the order  $n$  of the original eq 6 increases. The chemical accuracy, higher than kcal/mol accuracy for the absolute energy, has usually been realized at around orders 2 or 3.

The FC theory has been proven to be a very tough, exact methodology for solving the SE.<sup>9-16</sup> Since 2004, this theory has produced highly accurate solutions of the SEs of many atoms and molecules, for example, from He<sup>10-12</sup> and H<sub>2</sub><sup>13</sup> to simple organic and inorganic molecules.<sup>14-16</sup> Recently, the potential curves of all the nine valence states of the Li<sub>2</sub> molecule were calculated with complete agreement with the experimentally observed RKR potential curves to high

accuracy.<sup>16</sup> These results already show the potential of the FC theory as an *exact* quantum chemistry theory.

In paper I of this series,<sup>17</sup> we have listed many candidate functions of the scaling function and classified them into three groups: “correct”, “reasonable”, and “approximate”. Among them, the “correct”  $g$  functions that satisfy, in addition to the condition of eq 5 at  $r \rightarrow 0$ , the following condition

$$\lim_{r \rightarrow \infty} g(r) = 1 \text{ or } a \quad (8)$$

at  $r \rightarrow \infty$  is important, where  $a$  is some constant. Namely, when the interparticle distance  $r$  becomes very large, the SSE must converge to the SE. As such “correct”  $g$  functions, we considered the following five functions<sup>17</sup>

$$g = 1 - \exp(-\gamma r) \quad (9a)$$

$$g = \frac{r}{r + 1/\gamma} \quad (9b)$$

$$g = Ei(-\gamma^{(1)}r - \gamma^{(2)}) - Ei(-\gamma^{(2)}) \quad (9c)$$

$$g = \arctan(\gamma r) \quad (9d)$$

$$g = \tanh(\gamma r) \quad (9e)$$

where  $\gamma$  is a parameter related to the cusp value and  $Ei$  is the exponential integral function. For understanding the natures of these functions, the following Taylor expansions are useful

$$1 - \exp(-r) = r - \frac{1}{2}r^2 + \frac{1}{6}r^3 - \frac{1}{24}r^4 + \frac{1}{120}r^5 + O(r^6) \quad (10a)$$

$$\frac{r}{r+1} = r - r^2 + r^3 - r^4 + r^5 + O(r^6) \quad (10b)$$

$$Ei(-er - 1) - Ei(-1) = r - er^2 + \frac{5}{6}e^2r^3 - \frac{2}{3}e^3r^4 + \frac{13}{24}e^4r^5 + O(r^6) \quad (10c)$$

$$\arctan(r) = r - \frac{1}{3}r^3 + \frac{1}{5}r^5 + O(r^6) \quad (10d)$$

$$\tanh(r) = r - \frac{1}{3}r^3 + \frac{2}{15}r^5 + O(r^6) \quad (10e)$$

where  $e$  in eq 10c is Napier's constant (or Euler's number,  $e = 2.718\ 281\ 828\ 459\ 045\ \dots$ ). We used this digit of accuracy in the present calculations, but for more highly accurate calculations, we used the numbers of corresponding accuracies. In eq 10a, we put  $\gamma = 1$  for simplicity. The first three functions include all powers of  $r$ , but the latter two include only the odd powers of  $r$ . In paper 1 of this series,<sup>17</sup> we examined these functions by using them only for the two-electron  $g_{ij}(r_{ij})$  part of the FC calculations of the helium (He) atom and showed that they give generally better results than the other classes of the  $g$  functions.

In this paper, we investigate the role and the quality of each correct  $g$  function by solving the SE of the He atom with the variational integral method of the FC theory. We use these correct functions for both e-n  $g_{iA}(r_{iA})$  and e-e  $g_{ij}(r_{ij})$  functions. The variational analytical integration method is an accurate reliable method but became difficult when we use the correct  $g$  functions to both e-n and e-e parts, except for the function given by eq 9a. But, for the small He atom, this is

possible with the numerical integration method explained below. This method is, however, not adequate for highly accurate calculations like the 40 decimal-figure accuracy of the energy as we did before by using different simpler  $g$  functions.<sup>10–12</sup> Thus, the purpose here is to compare the performances of the different correct  $g$  functions given by eq 9a in the practical calculations for the He atom and to see which function is the best for the calculations of energies, related properties, and some other properties. For the function  $g = 1 - \exp(-\gamma r)$  of eq 9a, the explicit analytical integral method is possible; such a highly accurate study is in progress<sup>18</sup> and will be published elsewhere in the literature.

## 2. THEORETICAL AND COMPUTATIONAL DETAILS

We examine here the five correct  $g$  functions of eq 9a in solving the SE or SSE of the He atom. The initial function of the FC theory is a simple Slater function given by<sup>19</sup>

$$\psi_0 = (1 + P_{12})[e^{-\alpha r_{1A}} e^{-\alpha r_{2A}}] \quad (11)$$

where  $P_{12}$  is the electron exchange operator and  $\alpha$  is the orbital exponent. We apply the FC theory starting from this initial function. In the present case, differently from the case of  $g = r$ , we obtain the cf's that include the inverse powers of  $r$  like  $g/r$ ,  $g^2/r^2$ , etc. However, as explained in the Appendix, when we include these functions into the FC calculations, we meet the difficulty caused by the redundancy existing in the calculations, namely, the cf's  $g\phi$  and  $(g/r)\phi$  are nearly redundant. This was shown in Table A1 for  $g = 1 - \exp(-\gamma r)$  of eq 9a. Actually, among the correct  $g$  functions shown in eq 9a, the function  $g = r/(r + \gamma)$  is special because it satisfies the relation

$$1 = g + \frac{g}{\gamma r} \quad (12)$$

as easily seen, which shows that for this  $g$  function, the two functions  $g\phi$  and  $(g/r)\phi$  are completely redundant for any  $\phi$ : we must neglect the subfunction  $(g/r)\phi$  for eliminating the redundancy. Because of the functional similarity among the correct functions, the relation given by eq 12 is nearly satisfied even for other  $g$  functions given in eq 9a. This is the origin of the redundancy difficulty caused by the  $g$  functions shown in eq 9a. Furthermore, as shown in the Appendix, these  $(g/r)$ -type subfunctions were not effective enough to improve the wave function. For these reasons, we decided not to include these  $(g/r)$ -type functions in the present calculations.

Thus, starting from the initial function given by eq 11, the cf's of the present FC calculations are written as

$$\phi_I = (1 + P_{12})[g_{1A}^{a_I} g_{2A}^{b_I} g_{12}^{c_I} e^{-\alpha r_{1A}} e^{-\alpha r_{2A}}] \quad (13)$$

with the non-negative integers  $a_I$ ,  $b_I$ , and  $c_I$ . We performed the FC calculations to order  $n = 6$ , namely,  $a_I + b_I + c_I \leq 6$ . We examined all 25 patterns of the combinations of the five  $g_{iA}$  and five  $g_{ij}$  functions of eq 9a. As a reference, we also examined the case of  $g_{iA} = r_{iA}$  and  $g_{ij} = r_{ij}$  which is a reasonable-group function.<sup>17</sup> The parameters  $\gamma_{iA}$  and  $\gamma_{ij}$  in the correct-group  $g$  functions were determined by considering the electron–nucleus (e–n) and e–e cusp values, which are  $-2.0$  (e–n) and  $0.5$  (e–e).<sup>20</sup> For the e–n coalescence, as the orbital exponent of  $\psi_0$  was  $1.6875$ ,  $\gamma_{iA} = 0.3125$  ( $=2.0 - 1.6875$ ) was used. For the e–e case,  $\gamma_{ij} = 0.5$  was used because  $\psi_0$  does not contain any  $r_{ij}$  term. For the  $Ei$  function (eq 9c),  $\gamma_{iA}^1 = 0.1078$ ,  $\gamma_{iA}^2 = 0.2647$ ,  $\gamma_{ij}^1 = 0.1725$ , and  $\gamma_{ij}^2 = 0.2647$  were used. These values are due to the same criteria as above. We used different

orbital exponents  $\alpha$  for the cf's generated at different orders,  $\alpha = 1.6875, 1.5945, 1.4942, 1.5718, 1.5463, 1.5482, \text{ and } 1.5569$ , respectively, for  $n = 0, 1, 2, 3, 4, 5, \text{ and } 6$ . They were roughly optimized for the case  $g_{iA} = 1 - \exp(-\gamma_{iA} r_{iA})$  and  $g_{ij} = 1 - \exp(-\gamma_{ij} r_{ij})$ . Interestingly, their optimal  $\alpha$  values did not change much, independent of the order  $n$ . On the contrary, for  $g_{iA} = r_{iA}$  and  $g_{ij} = r_{ij}$  their optimal  $\alpha$  values became larger as  $n$  increases:  $\alpha = 1.687, 1.813, 1.814, 1.906, 2.038, 2.113, \text{ and } 2.236$ , respectively. This stability of the correct-group  $g_{iA}$  function is due to its correct shape from near the cusp region to the boundary region of the atom.

The coefficients  $\{c_I\}$  of eq 7 were determined by the variational method, whose Hamiltonian and overlap integrals were calculated by the numerical integration method. Even for the He atom that is expressed with only the three coordinates,  $r_{1A}$ ,  $r_{2A}$  and  $r_{12}$ , we could not find the analytical integral formulas for the overlap and Hamiltonian integrals including the  $g$  functions given by eq 9a (except for eq 9a). Therefore, we employed three-dimensional numerical integration schemes available through the numerical integration package of a Python library SciPy,<sup>18</sup> whose core computational parts were performed with a Fortran library QuadPack.<sup>22</sup> This made us possible to examine variationally all combinations of the correct-type  $g$  functions of the FC theory applied to the He atom. However, SciPy is available only within the double-precision floating-point accuracy (around 15 digits), though its computational speed was fast. For higher accuracy than double precision, we also employed another Python library mpmath,<sup>21</sup> which enabled multiple-precision computations, though its computational speed was slow. We used it to check the numerical accuracy of the above integrals to within 25 digits precision. Then, it turned out to be unnecessary: the double precision SciPy was shown to have enough accuracy for the present purpose.

In the Supporting Information, we presented all the primitive data of the present calculations using various  $g$  functions. We also described the details of the numerical integrations used in the present calculations. We examined the accuracies of the integrals by comparing the numerical integrations with the analytical ones for  $g_{iA} = 1 - \exp(-\gamma_{iA} r_{iA})$  and  $g_{iA} = 1 - \exp(-\gamma_{ij} r_{ij})$ , for which the analytical integrations are possible in high accuracy using the schemes presented by Harris et al.<sup>23</sup> and by us.<sup>18</sup> For the arithmetic evaluations in high precision, we used the MAPLE software.<sup>6</sup> As a consequence, as shown in the Supporting Information, the numerical accuracies with SciPy (around 15 digits) were enough for the present calculations up to  $n = 6$ .

In this paper, we study the quality (exactness) of the wave functions calculated by the FC theory through not only the energy upper bound obtained by the present variational treatment but also the H-square error defined below by eq 14, the energy lower bound, and the e–n and e–e cusp values that are very local properties.

**2.1. H-Square Error.** The H-square error  $\sigma^2$  is defined by

$$\sigma^2 = \langle \psi | (H - E)^2 | \psi \rangle \quad (14)$$

where  $\psi$  is a normalized wave function. It is important to note that the H-square error  $\sigma^2$  is an absolute measure of the exactness of the wave function  $\psi$ . It is always positive and becomes zero only when  $\psi$  is truly exact and vice versa. So, before, we have examined this quantity in the highly accurate FC calculations of the He atom.<sup>11</sup> To calculate the H-square error, the integral over the  $H^2$  operator is necessary, but it is

much difficult due to the existence of the square of the singular potential operators, i.e.,  $1/r^2$ . In the present study, however, they were readily evaluated using the numerical integration scheme, and therefore, we could use this quantity to judge the exactness of the wave function. We performed the H-square-error minimization at each FC order, using for  $E$  in eq 14 the Ritz variational energy.

**2.2. Energy Lower Bounds.** When the exact energy of the system is not known, the variational energy gives the upper bound of the exact energy and therefore, if we can have an accurate knowledge of the lower bound at the same time, it is very helpful. When we use the variational method, the energy upper bound is accurate because it is correct to the square of the error included in the wave function. On the other hand, the energy lower bounds are estimated using the H-square error and/or the  $H^2$  matrix.<sup>11,24–28</sup> Various methods have been proposed since Temple<sup>24</sup> first derived an expression of the energy lower bound in 1928 and then by Weinstein<sup>25</sup> in 1934. The Weinstein method was simple and needs only  $\sigma^2$  of eq 14 of the target state, but the quality of this lower bound energy is generally not good enough. The Temple's lower bound was generally more accurate than the Weinstein's one but still far from the accuracy of the energy upper bound.<sup>11–13</sup> If the estimate of the energy lower bound is crude, it is meaningless for the exact-level accurate theories like the present one, as also seen from our previous highly accurate variational study on the He atom.<sup>11–13</sup>

Recently, Pollak and Martinazzo<sup>26</sup> proposed an impressive idea to produce tighter energy lower bounds than those of the previous methods. This method was referred to as PM method.<sup>26–28</sup> In the PM method, one computes the eigenvalue of the following  $(L + 1) \times (L + 1)$  dimensional  $\mathbf{K}(\varepsilon)$  matrix

$$\mathbf{K}(\varepsilon) = \begin{pmatrix} \lambda_1 & 0 & \cdots & 0 & \sigma_1 \\ 0 & \lambda_2 & \cdots & 0 & \sigma_2 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \cdots & \lambda_L & \sigma_L \\ \sigma_1 & \sigma_2 & \cdots & \sigma_L & \varepsilon + \sum_{k=1}^L \frac{\sigma_k^2}{\lambda_k - \varepsilon} \end{pmatrix} \quad (15)$$

and the ground-state energy lower bound is obtained directly from its lowest eigenvalue. In eq 15,  $L$  is a dimension of a given function space,  $\lambda_k$  and  $\sigma_k^2$  denote the Ritz variational energy and the corresponding variance (H-square error),  $\sigma_k^2 = \langle \psi_k | H^2 | \psi_k \rangle - \langle \psi_k | H | \psi_k \rangle^2$  of the  $k$ -th state wave function  $\psi_k$ , respectively, and  $\sigma_k$  is the positive square root of  $\sigma_k^2$ . Furthermore,  $\varepsilon$  is a parameter that needs to satisfy the condition  $\lambda_1 < \varepsilon \leq E_1^{\text{exact}}$ , where  $E_1^{\text{exact}}$  denotes the exact energy of the first excited state in the same symmetry as the ground state, and the best choice of  $\varepsilon$  should be  $\varepsilon = E_1^{\text{exact}}$ . If one does not know that, the Weinstein's or related lower bound of the first excited state may be used for  $\varepsilon$ . The details about the strict condition for  $\varepsilon$  were given in their original papers.<sup>26–28</sup>

The PM method may compute accurate energy lower bounds by using functional space of the higher excited states. This idea is related to the chemical formula theory<sup>29</sup> proposed from the standpoint of the exact theory.

**2.3. Electron–Nucleus and Electron–Electron Cusp Values.** So far, we have studied the energy related properties. Here, we examine how the calculated wave functions satisfy the Kato's cusp conditions for both the e–n and e–e

coalescences.<sup>20</sup> The cusp values themselves are not physical observables, but the conditions themselves are important necessary conditions for the exact wave function to satisfy. The Kato's cusp values for the e–n and e–e coalescences are  $-2.0$ , corresponding to the nuclear charge, and  $0.5$ , respectively, for the present ground  $^1S$  state of the He atom. These are the lowest-order cusp values, and therefore, the following integral forms

$$e - n \text{ cusp} = \frac{\langle \psi | \delta(r_{1A}) | \partial \psi / \partial r_{1A} \rangle}{\langle \psi | \delta(r_{1A}) | \psi \rangle} \quad (16a)$$

$$e - e \text{ cusp} = \frac{\langle \psi | \delta(r_{12}) | \partial \psi / \partial r_{12} \rangle}{\langle \psi | \delta(r_{12}) | \psi \rangle} \quad (16b)$$

could be useful and accurate, where  $\delta$  is the delta function. The purpose of the present study is to examine the qualities of the correct set of the  $g$  functions that are closely related to the coalescences, and the  $g$  functions themselves were introduced by one of the authors<sup>1</sup> to eliminate the divergence difficulties of the SE originating from the singularities of the Coulombic potentials included in the Hamiltonian. Therefore, the examination of the cusp values is of special importance. Different from the energy and the H-square error, the cusp values are not the bounded properties. So, it is also interesting to examine how the calculated values approach the exact values.

### 3. RESULTS AND DISCUSSION

The He atom is important in quantum chemistry. Starting from the hydrogen atom, which is solvable exactly with the SE, the He atom is the first complex atom. For this reason, there is a long history of the accurate calculations of the energy and the wave function of the He atom.<sup>11–13,30–42</sup> Starting from the Hylleraas's pioneering work,<sup>30</sup> Kinoshita suggested the importance of the negative powers of the Hylleraas's coordinate  $s = r_{1A} + r_{2A}$ .<sup>31</sup> Frankowski and Pekeris<sup>32</sup> performed the numerical calculations including the logarithm basis function theoretically suggested by Bartlett Jr.,<sup>33</sup> Gronwall<sup>34</sup> and Fock,<sup>35</sup> Drake et al.,<sup>38</sup> Sims and Hagstrom,<sup>39</sup> and Korobov et al.<sup>40,41</sup> performed the generalized Hylleraas-like calculations with a large number of basis functions. Schwartz systematically performed the extremely accurate calculations with the basis functions including the logarithm functions constructed by his excellent intuitions.<sup>42,43</sup> In the first paper of the SSE, the He atom was one of the first subjects to which the FC theory was applied and its high potentiality was revealed.<sup>1</sup> We had also performed higher-order FC calculations and obtained the energies accurate to over 40 significant digits.<sup>10–12</sup> All these calculations have been performed variationally with the basis functions whose analytical integrations are possible.

We perform here the FC calculations of the He atom on the variational ground, using the numerical integration methods. We present below the energy difference from the reference exact energy<sup>10–12</sup>

$$E_{\text{exact}} = -2.903\ 724\ 377\ 034\ 119\ 598\ 311 \text{ a. u.} \quad (17)$$

correct to 21 digits after the decimal point, denoted by  $\Delta E$  in kcal/mol, the H-square error as an absolute measure of the exactness, the energy lower bound, and the e–n and e–e cusp values and give the extensive discussions on these results. Furthermore, in Table S1 of the Supporting Information, we

**Table 1.**  $\Delta E$ , the Energy Differences from the Exact Energy and the Ritz Variational Energies Obtained from the FC Variational Calculations Summarized for the Ground State of the He Atom with All the Combinations of the Correct-type  $g_A$  and  $g_j$  Scaling Functions and the Additional Case of  $g_A = r_{iA}$  and  $g_j = r_{ij}$

$g_A$	$g_j$		$n = 1, M = 3^a$		$n = 2, M = 7$		$n = 3, M = 13$		$n = 4, M = 22$		$n = 5, M = 34$		$n = 6, M = 50$	
	rank	$\Delta E$ (kcal/mol) <sup>b</sup>	rank	$\Delta E$ (kcal/mol)	rank	$\Delta E$ (kcal/mol)	rank	$\Delta E$ (kcal/mol)	rank	$\Delta E$ (kcal/mol)	rank	$\Delta E$ (kcal/mol)	rank	$\Delta E$ (kcal/mol)
$1 - \exp(-\gamma_{iA} r_{iA})$	12	6.208	3	0.195	7	0.017 38	9	0.003 41	9	0.000 655	11	0.000 170 1		
$r_{ij}/(\gamma_{ij} + 1/\gamma_{ij})$	15	6.663	2	0.172	2	0.010 62	5	0.001 94	2	0.000 379	5	0.000 077 5		
$Ei(-\gamma_{ij}^{-1} r_{ij} - \gamma_{ij}^{-2}) - Ei(-\gamma_{ij}^{-2})$	13	6.301	1	0.171	4	0.012 81	6	0.002 24	6	0.000 446	6	0.000 094 2		
$\arctan(\gamma_{ij} r_{ij})$	11	6.144	9	0.260	10	0.020 74	13	0.004 52	15	0.000 970	12	0.000 201 7		
$\tanh(\gamma_{ij} r_{ij})$	14	6.551	20	0.352	21	0.052 95	23	0.017 23	23	0.005 447	22	0.002 695 5		
(average)		6.373		0.230		0.022 90		0.005 87		0.001 580		0.000 647 8		
$r_{iA}/(r_{iA} + 1/\gamma_{iA})$	2	5.277	18	0.338	15	0.029 34	7	0.002 80	11	0.000 689	8	0.000 143 7		
$r_{ij}/(\gamma_{ij} + 1/\gamma_{ij})$	6	5.677	14	0.300	5	0.016 63	1	0.001 38	3	0.000 404	1	0.000 046 1		
$Ei(-\gamma_{ij}^{-1} r_{ij} - \gamma_{ij}^{-2}) - Ei(-\gamma_{ij}^{-2})$	3	5.354	15	0.303	9	0.020 18	3	0.001 60	6	0.000 462	3	0.000 059 2		
$\arctan(\gamma_{ij} r_{ij})$	1	5.254	22	0.413	19	0.037 88	11	0.004 08	16	0.000 975	10	0.000 163 1		
$\tanh(\gamma_{ij} r_{ij})$	4	5.594	25	0.521	25	0.085 99	22	0.017 03	24	0.005 927	24	0.002 838 5		
(average)		5.431		0.375		0.038 00		0.005 38		0.001 691		0.000 650 1		
$Ei(-\gamma_{iA}^{-1} r_{iA} - \gamma_{iA}^{-2}) - Ei(-\gamma_{iA}^{-2})$	7	5.693	6	0.244	6	0.016 82	8	0.002 83	8	0.000 596	7	0.000 142 3		
$r_{ij}/(\gamma_{ij} + 1/\gamma_{ij})$	10	6.119	4	0.214	1	0.009 17	2	0.001 41	1	0.000 348	2	0.000 049 3		
$Ei(-\gamma_{ij}^{-1} r_{ij} - \gamma_{ij}^{-2}) - Ei(-\gamma_{ij}^{-2})$	8	5.777	5	0.215	3	0.011 37	4	0.001 65	4	0.000 406	4	0.000 064 2		
$\arctan(\gamma_{ij} r_{ij})$	5	5.651	16	0.315	11	0.021 25	10	0.003 92	12	0.000 823	9	0.000 159 1		
$\tanh(\gamma_{ij} r_{ij})$	9	6.025	21	0.413	22	0.058 45	21	0.016 85	22	0.005 366	23	0.002 740 1		
(average)		5.853		0.280		0.023 41		0.005 33		0.001 508		0.000 631 0		
$1 - \exp(-\gamma_{ij} r_{ij})$	20	7.133	13	0.286	14	0.027 77	18	0.006 37	13	0.000 828	16	0.000 284 3		
$r_{ij}/(\gamma_{ij} + 1/\gamma_{ij})$	25	7.626	12	0.278	8	0.019 90	15	0.005 11	7	0.000 594	13	0.000 202 1		
$Ei(-\gamma_{ij}^{-1} r_{ij} - \gamma_{ij}^{-2}) - Ei(-\gamma_{ij}^{-2})$	21	7.238	11	0.271	12	0.023 01	16	0.005 51	10	0.000 661	14	0.000 225 4		
$\arctan(\gamma_{ij} r_{ij})$	18	7.037	19	0.342	17	0.030 66	20	0.006 92	18	0.001 076	18	0.000 304 0		
$\tanh(\gamma_{ij} r_{ij})$	23	7.490	24	0.425	23	0.058 61	24	0.019 03	21	0.005 173	21	0.002 658 4		
(average)		7.304		0.320		0.031 99		0.008 59		0.001 666		0.000 734 8		
$1 - \exp(-\gamma_{ij} r_{ij})$	17	7.003	10	0.270	18	0.036 70	17	0.005 88	19	0.001 081	19	0.000 355 1		
$r_{ij}/(\gamma_{ij} + 1/\gamma_{ij})$	24	7.494	8	0.256	13	0.025 96	12	0.004 46	17	0.000 984	15	0.000 279 4		
$Ei(-\gamma_{ij}^{-1} r_{ij} - \gamma_{ij}^{-2}) - Ei(-\gamma_{ij}^{-2})$	19	7.109	7	0.251	16	0.029 81	14	0.004 81	14	0.000 969	17	0.000 286 6		
$\arctan(\gamma_{ij} r_{ij})$	16	6.911	17	0.329	20	0.042 23	19	0.006 85	20	0.001 695	20	0.000 390 7		
$\tanh(\gamma_{ij} r_{ij})$	22	7.352	23	0.415	24	0.075 53	25	0.019 28	25	0.006 517	25	0.002 898 7		
(average)		7.174		0.304		0.042 05		0.008 25		0.002 249		0.000 842 1		
$r_{iA}$	26	9.239	26	1.141	26	0.124 77	26	0.045 91	26	0.015 942	26	0.006 021 9		

<sup>a</sup> $n$  and  $M$  denote the order of the FC theory and the number of the cfs (dimension), respectively. <sup>b</sup> $\Delta E$  denotes the energy differences from the exact energy given by eq 17.

summarized all the results of the energy, the H-square error, and the e-n and e-e cusp values up to the FC order of  $n = 6$  for all the combinations of the correct-group  $g_{iA}$  and  $g_{ij}$  scaling functions shown in eq 9a, together with the results for  $g_{iA} = r_{iA}$  and  $g_{ij} = r_{ij}$  as a reference.

**3.1. Energy Convergence to the Exact Solution of the SE.** From the variational principle, the energy value of  $\Delta E$  defined above is an important measure to judge the quality of the different  $g_{iA}$ - $g_{ij}$  pair. Table 1 summarizes the  $\Delta E$  value for each  $g_{iA}$ - $g_{ij}$  pair at each order  $n$ . Table 1 also shows the ranking of  $\Delta E$  from the smallest to largest ones at each order  $n$ . As  $n$  increases,  $\Delta E$  of each  $g_{iA}$ - $g_{ij}$  pair decreases steadily and monotonously toward zero from above, as the variational principle implies.

Whereas the FC theory guarantees the convergence to the exact solution with any choice of  $g_{iA}$  and  $g_{ij}$ , the convergence efficiency depends on each choice of  $g_{iA}$  and  $g_{ij}$ . At any order from  $n = 1$  to 6, the case of  $g_{iA} = r_{iA}$  and  $g_{ij} = r_{ij}$  was worst at rank 26, compared to all the cases of the correct  $g$  functions considered here. This implies that the asymptotic condition of the correct  $g$  function expressed by eq 8 is significantly important for the quality of the scaling function. Overall, the performances of the three correct functions  $g = 1 - \exp(-\gamma r)$ ,  $g = Ei(-\gamma^{(1)} r - \gamma^{(2)}) - Ei(-\gamma^{(2)})$ , and  $g = r/(r + 1/\gamma)$  were better than those of the other functions  $g = \arctan(\gamma r)$  and  $g = \tanh(\gamma r)$  for both  $g_{iA}$  and  $g_{ij}$  especially at higher orders. Prominent differences between these two classes of the correct scaling functions are seen in their Taylor expansion series given by eq 10a; the first three functions are expanded with all orders,  $r, r^2, r^3, r^4, r^5, \dots$  but the last two ones are expanded with only the odd ones:  $r, r^3, r^5, \dots$ . This may suggest that the last two functions may lose the functional flexibilities in comparison with the other three. The best  $g_{iA}$  and  $g_{ij}$  combinations for  $\Delta E$  at the order  $n = 1$  to 6 were

$n = 1$ ,  $\Delta E = 5.254$  kcal/mol:  $r_{iA}/(r_{iA} + 1/\gamma_{iA})$  and  $\arctan(\gamma_{ij} r_{ij})$

$n = 2$ ,  $\Delta E = 0.171$  kcal/mol:  $1 - \exp(-\gamma_{iA} r_{iA})$  and  $Ei(-\gamma_{ij}^1 r_{ij} - \gamma_{ij}^2) - Ei(-\gamma_{ij}^2)$

$n = 3$ ,  $\Delta E = 0.00917$  kcal/mol:  $Ei(-\gamma_{iA}^1 r_{iA} - \gamma_{iA}^2) - Ei(-\gamma_{iA}^2)$  and  $r_{ij}/(r_{ij} + 1/\gamma_{ij})$

$n = 4$ ,  $\Delta E = 0.00138$  kcal/mol:  $r_{iA}/(r_{iA} + 1/\gamma_{iA})$  and  $r_{ij}/(r_{ij} + 1/\gamma_{ij})$

$n = 5$ ,  $\Delta E = 0.000348$  kcal/mol:  $Ei(-\gamma_{iA}^1 r_{iA} - \gamma_{iA}^2) - Ei(-\gamma_{iA}^2)$  and  $r_{ij}/(r_{ij} + 1/\gamma_{ij})$

$n = 6$ ,  $\Delta E = 0.0000461$  kcal/mol:  $r_{iA}/(r_{iA} + 1/\gamma_{iA})$  and  $r_{ij}/(r_{ij} + 1/\gamma_{ij})$ .

Except for  $n = 1$ , the best results were obtained from the combinations within the three functions,  $g = r/(r + 1/\gamma)$ ,  $g = Ei(-\gamma^{(1)} r - \gamma^{(2)}) - Ei(-\gamma^{(2)})$ , and  $g = 1 - \exp(-\gamma r)$ . For  $g_{iA}$ ,  $r/(r + 1/\gamma)$  was best at  $n = 1, 4$ , and 6, and  $Ei(-\gamma^{(1)} r - \gamma^{(2)}) - Ei(-\gamma^{(2)})$  was best at  $n = 3, 5$ , and  $1 - \exp(-\gamma r)$  at  $n = 3$ . For  $g_{ij}$ ,  $r/(r + 1/\gamma)$  was best four times at  $n = 3, 4, 5$ , and 6, and  $Ei(-\gamma^{(1)} r - \gamma^{(2)}) - Ei(-\gamma^{(2)})$  and  $\arctan(\gamma r)$  were best at  $n = 2$  and 1, respectively. Among others, the best performance of the function  $r/(r + 1/\gamma)$ , particularly for  $g_{ij}$  was impressive.

The best three of  $\Delta E$  at  $n = 6$  were

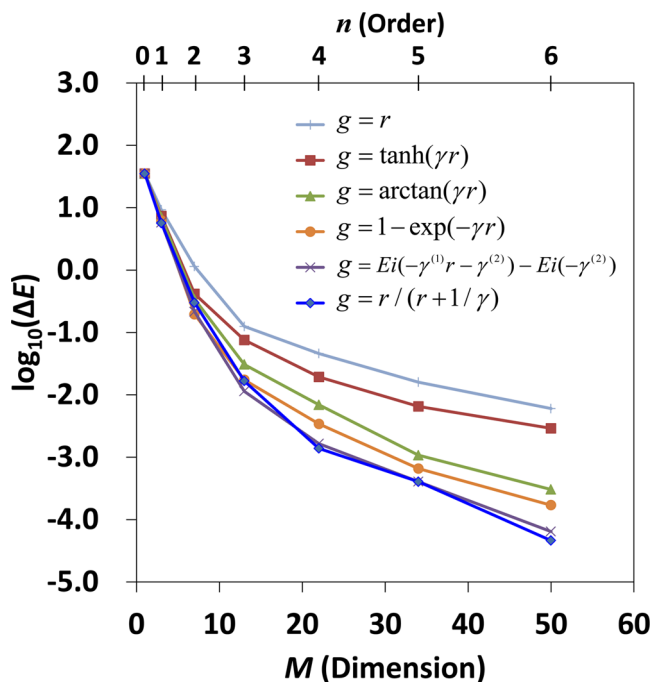
1st,  $\Delta E = 0.0000461$  kcal/mol:  $r_{iA}/(r_{iA} + 1/\gamma_{iA})$  and  $r_{ij}/(r_{ij} + 1/\gamma_{ij})$

2nd,  $\Delta E = 0.0000493$  kcal/mol:  $Ei(-\gamma_{iA}^1 r_{iA} - \gamma_{iA}^2) - Ei(-\gamma_{iA}^2)$  and  $r_{ij}/(r_{ij} + 1/\gamma_{ij})$

3rd,  $\Delta E = 0.0000592$  kcal/mol:  $r_{iA}/(r_{iA} + 1/\gamma_{iA})$  and  $Ei(-\gamma_{ij}^1 r_{ij} - \gamma_{ij}^2) - Ei(-\gamma_{ij}^2)$ .

The performance of the function  $g = 1 - \exp(-\gamma r)$  was slightly worse than those of the other two functions,  $g = r/(r + 1/\gamma)$  and  $g = Ei(-\gamma^{(1)} r - \gamma^{(2)}) - Ei(-\gamma^{(2)})$ .

Figure 1 shows the plots of  $\Delta E$  on a log scale,  $\log_{10}(\Delta E)$  against the dimension  $M$  and the order  $n$  for the six patterns of



**Figure 1.** Convergence of  $\log_{10}(\Delta E)$  against the dimension  $M$  (lower) and the orders  $n$  (upper) for the six cases of the identical  $g_{iA}$  and  $g_{ij}$  functions, where  $\Delta E$  (kcal/mol) is the difference between the exact energy given by eq 17 and the energy calculated here for the ground state of the He atom.

the  $g_{iA}$  and  $g_{ij}$  functions of the same functional form. The best performance was obtained at  $n = 6$  from  $g_{iA} = r_{iA}/(r_{iA} + 1/\gamma_{iA})$  and  $g_{ij} = r_{ij}/(r_{ij} + 1/\gamma_{ij})$ , which was 130 times more accurate than the case,  $g_{iA} = r_{iA}$  and  $g_{ij} = r_{ij}$ , and 63 times more accurate than the case,  $\tanh(\gamma_{iA} r_{iA})$  and  $\tanh(\gamma_{ij} r_{ij})$ , and 6.6 times more accurate than the case,  $\arctan(\gamma_{iA} r_{iA})$  and  $\arctan(\gamma_{ij} r_{ij})$ . However, the performance of the combination  $g_{iA} = r_{iA}/(r_{iA} + 1/\gamma_{iA})$  and  $g_{ij} = r_{ij}/(r_{ij} + 1/\gamma_{ij})$  was not the best at the orders 1, 2, and 3, but became superior at higher orders. As discussed in Sec. II, since the function  $g = r/(r + 1/\gamma)$  contains completely the  $g/r$  partner functions within its form as denoted by eq 12, the convergence efficiency with respect to the dimension might be better than the others.

In the Supporting Information, we showed the plots of  $\Delta E$  for all the five patterns of the  $g_{iA}$  and  $g_{ij}$  and also of  $g_{ij}$  and  $g_{iA}$ .

**3.2. H-Square Error as an Absolute Measure of the Exactness.** Table 2 summarizes the H-square errors obtained for the  $g_{iA}$ - $g_{ij}$  pairs at different orders  $n$ . The H-square error minimization was done fixing the energy  $E$  in eq 14 to the Ritz variational energy obtained above. Because the FC theory is exact, the H-square errors also steadily and monotonously converge (decrease) to the exact value, zero in all the  $g_{iA}$ - $g_{ij}$  pairs. This behavior is quite similar to that of the variational energy  $E$  and  $\Delta E$ , but the difference is that for the H-square error, the best value is always zero, a known number, but for the energy, the best value is definite, but not known generally. Thus, the H-square error obtained by the integral method is an

**Table 2. H-Square Errors Obtained by the H-Square Error Minimization Using the Ritz Variational Energy of Table 1 as the Reference Energy  $E$  in Eq 14 Summarized for the Ground State of the He Atom with All the Combinations of the Correct-type  $g_{iA}$  and  $g_{ij}$  Scaling Functions and the Additional Case of  $g_{iA} = r_{iA}$  and  $g_{ij} = r_{ij}$**

$g_{iA}$	$n = 1, M = 3^a$		$n = 2, M = 7$		$n = 3, M = 13$		$n = 4, M = 22$		$n = 5, M = 34$		$n = 6, M = 50$	
	rank	H-square error <sup>b</sup>	rank	H-square error	rank	H-square error	rank	H-square error	rank	H-square error	rank	H-square error
$1 - \exp(-\gamma_{iA} r_{iA})$	11	0.067 103 4	3	0.008 911 3	9	0.000 918 2	9	0.000 273 2	9	0.000 066 9	9	0.000 023 4
$r_{ij}/(\gamma_{ij} + 1/\gamma_{ij})$	14	0.073 855 9	1	0.007 998 8	3	0.000 693 7	5	0.000 181 2	5	0.000 046 3	5	0.000 014 6
$Ei(-\gamma_{ij}^1 r_{ij} - \gamma_{ij}^2) - Ei(-\gamma_{ij}^2)$	12	0.068 731 6	2	0.008 158 3	6	0.000 803 4	7	0.000 210 7	7	0.000 054 9	7	0.000 017 7
$\arctan(\gamma_{ij} r_{ij})$	13	0.072 702 2	16	0.012 051 8	19	0.001 287 8	18	0.000 433 5	20	0.000 112 3	17	0.000 038 0
$\tanh(\gamma_{ij} r_{ij})$	15	0.074 241 3	19	0.012 910 1	20	0.001 315 7	23	0.000 590 2	21	0.000 119 4	23	0.000 068 3
(average)		0.071 326 9		0.010 006 0		0.001 003 8		0.000 337 7		0.000 080 0		0.000 032 4
$r_{iA}/(r_{iA} + 1/\gamma_{iA})$	1	0.049 451 9	15	0.011 965 4	8	0.000 843 5	6	0.000 207 4	6	0.000 050 3	6	0.000 015 6
$r_{ij}/(\gamma_{ij} + 1/\gamma_{ij})$	3	0.054 339 0	13	0.010 856 1	2	0.000 601 4	1	0.000 120 6	1	0.000 034 5	1	0.000 008 4
$Ei(-\gamma_{ij}^1 r_{ij} - \gamma_{ij}^2) - Ei(-\gamma_{ij}^2)$	2	0.050 261 6	14	0.011 092 7	5	0.000 716 6	3	0.000 146 8	3	0.000 040 8	2	0.000 010 7
$\arctan(\gamma_{ij} r_{ij})$	5	0.056 247 0	24	0.015 330 2	16	0.001 242 0	14	0.000 373 5	14	0.000 090 3	11	0.000 028 0
$\tanh(\gamma_{ij} r_{ij})$	6	0.056 864 1	25	0.016 240 3	21	0.001 320 3	19	0.000 526 4	18	0.000 104 3	21	0.000 061 5
(average)		0.053 432 7		0.013 096 9		0.000 944 8		0.000 275 0		0.000 064 1		0.000 024 8
$Ei(-\gamma_{iA}^1 r_{iA} - \gamma_{iA}^2) - Ei(-\gamma_{iA}^2)$	4	0.055 898 9	12	0.010 484 9	7	0.000 830 6	8	0.000 226 8	8	0.000 056 3	8	0.000 018 5
$r_{ij}/(\gamma_{ij} + 1/\gamma_{ij})$	8	0.061 561 6	8	0.009 457 0	1	0.000 601 1	2	0.000 139 2	2	0.000 038 6	3	0.000 010 8
$Ei(-\gamma_{ij}^1 r_{ij} - \gamma_{ij}^2) - Ei(-\gamma_{ij}^2)$	7	0.057 044 2	9	0.009 666 4	4	0.000 711 9	4	0.000 166 1	4	0.000 045 8	4	0.000 013 3
$\arctan(\gamma_{ij} r_{ij})$	9	0.062 208 5	21	0.013 743 5	14	0.001 212 2	15	0.000 387 3	16	0.000 098 3	14	0.000 031 7
$\tanh(\gamma_{ij} r_{ij})$	10	0.063 221 4	23	0.014 618 9	18	0.001 257 1	20	0.000 543 7	19	0.000 108 3	22	0.000 063 6
(average)		0.059 987 0		0.011 594 1		0.000 922 6		0.000 292 6		0.000 069 4		0.000 027 6
$1 - \exp(-\gamma_{ij} r_{ij})$	17	0.090 235 6	11	0.009 923 7	17	0.001 245 0	17	0.000 428 9	17	0.000 098 4	16	0.000 037 1
$r_{ij}/(\gamma_{ij} + 1/\gamma_{ij})$	25	0.098 633 4	6	0.009 241 8	10	0.000 998 7	11	0.000 329 4	10	0.000 070 4	10	0.000 025 8
$Ei(-\gamma_{ij}^1 r_{ij} - \gamma_{ij}^2) - Ei(-\gamma_{ij}^2)$	19	0.092 592 1	7	0.009 270 7	13	0.001 119 2	13	0.000 367 0	13	0.000 082 7	13	0.000 030 5
$\arctan(\gamma_{ij} r_{ij})$	21	0.094 696 9	18	0.012 891 0	23	0.001 613 1	22	0.000 583 5	23	0.000 150 6	20	0.000 054 9
$\tanh(\gamma_{ij} r_{ij})$	23	0.097 112 0	22	0.013 821 9	24	0.001 631 5	25	0.000 730 9	25	0.000 151 4	24	0.000 080 4
(average)		0.094 654 0		0.011 029 8		0.001 321 5		0.000 487 9		0.000 110 7		0.000 045 7
$1 - \exp(-\gamma_{ij} r_{ij})$	16	0.089 631 9	10	0.009 798 0	15	0.001 240 3	16	0.000 416 9	15	0.000 095 4	18	0.000 038 2
$r_{ij}/(\gamma_{ij} + 1/\gamma_{ij})$	24	0.098 000 9	4	0.009 092 9	11	0.000 999 1	10	0.000 321 2	11	0.000 071 4	12	0.000 028 6
$Ei(-\gamma_{ij}^1 r_{ij} - \gamma_{ij}^2) - Ei(-\gamma_{ij}^2)$	18	0.091 986 9	5	0.009 134 2	12	0.001 118 4	12	0.000 355 8	12	0.000 081 5	15	0.000 032 3
$\arctan(\gamma_{ij} r_{ij})$	20	0.094 110 8	17	0.012 788 2	22	0.001 610 5	21	0.000 571 5	22	0.000 147 0	19	0.000 053 9
$\tanh(\gamma_{ij} r_{ij})$	22	0.096 450 5	20	0.013 698 9	25	0.001 636 0	24	0.000 725 2	24	0.000 151 4	25	0.000 082 5
(average)		0.094 036 2		0.010 902 4		0.001 320 9		0.000 478 1		0.000 109 3		0.000 047 1
$r_{iA}$	26	0.128 632 3	26	0.022 088 5	26	0.004 545 6	26	0.002 041 8	26	0.000 894 3	26	0.000 419 1

<sup>a</sup> $n$  and  $M$  denote the order of the FC theory and the number of the cfs (dimension), respectively. <sup>b</sup>Defined by eq 14.

absolute measure of the exactness of the wave function. Therefore, this convergence to zero is a numerical proof of the exactness of the theory. Although the variational energy is calculated with possibly occurring cancelations, the H-square error is constructed with the summation (integration) of always positive local values of  $[(H - E)\psi(\mathbf{r})]^2$  at local coordinates  $\mathbf{r}$ , as shown in eq 14. Thus, if the H-square error converges to zero, then all the local energy becomes identical to the exact energy at any coordinate  $\mathbf{r}$  of the system. Therefore, the H-square error minimization principle is a more stringent principle than the variational principle, for the energy, wave function, and all the other properties. The present result, therefore, shows that the FC theory is powerful not only for the variational energy principle but also for the H-square error minimization principle. Some years ago, we have shown such a behavior for the local energy of the SE.<sup>11</sup>

Table 2 further shows the behavior of the H-square error that is roughly similar to that of the variational energy  $\Delta E$  shown in Table 1. The worst case was always  $g_{iA} = r_{iA}$  and  $g_{ij} = r_{ij}$  at all orders  $n$ . The performances with  $g = r/(r + 1/\gamma)$ ,  $g = Ei(-\gamma^{(1)}r - \gamma^{(2)}) - Ei(-\gamma^{(2)})$ , and  $g = 1 - \exp(-\gamma r)$  were better than those with  $g = \arctan(\gamma r)$  and  $g = \tanh(\gamma r)$  for both  $g_{iA}$  and  $g_{ij}$  especially at higher orders. The best  $g_{iA}$  and  $g_{ij}$  patterns of the H-square error at each order  $n = 1$  to 6 were

$n = 1$ ,  $\sigma^2 = 0.0494519$ :  $r_{iA}/(r_{iA} + 1/\gamma_{iA})$  and  $1 - \exp(-\gamma_{ij}r_{ij})$   
 $n = 2$ ,  $\sigma^2 = 0.0079988$ :  $1 - \exp(-\gamma_{iA}r_{iA})$  and  $r_{ij}/(r_{ij} + 1/\gamma_{ij})$   
 $n = 3$ ,  $\sigma^2 = 0.0006011$ :  $Ei(-\gamma_{iA}^1 r_{iA} - \gamma_{iA}^2) - Ei(-\gamma_{iA}^2)$  and  $r_{ij}/(r_{ij} + 1/\gamma_{ij})$

$n = 4$ ,  $\sigma^2 = 0.0001206$ :  $r_{iA}/(r_{iA} + 1/\gamma_{iA})$  and  $r_{ij}/(r_{ij} + 1/\gamma_{ij})$   
 $n = 5$ ,  $\sigma^2 = 0.0000345$ :  $r_{iA}/(r_{iA} + 1/\gamma_{iA})$  and  $r_{ij}/(r_{ij} + 1/\gamma_{ij})$   
 $n = 6$ ,  $\sigma^2 = 0.0000084$ :  $r_{iA}/(r_{iA} + 1/\gamma_{iA})$  and  $r_{ij}/(r_{ij} + 1/\gamma_{ij})$ .

This result of the H-square error minimization principle seems to be highly accurate. The H-square error decreases quite rapidly with increasing  $n$ , the order. The function  $g = r/(r + 1/\gamma)$  was best at  $n = 1, 4, 5$ , and 6 for  $g_{iA}$  and at  $n = 2, 3, 4, 5$ , and 6 for  $g_{ij}$ . The good performance of this function for the H-square error is impressive, since the H-square error is an absolute measure of the exactness of the calculated wave function. The other two functions,  $g = 1 - \exp(-\gamma r)$  and  $g = Ei(-\gamma^{(1)}r - \gamma^{(2)}) - Ei(-\gamma^{(2)})$ , appeared as a partner of the function  $g = r/(r + 1/\gamma)$  at  $n = 1, 2$ , and 3. From  $n = 4$  to 6, the unique pair of the same  $g$  function,  $g_{iA} = r_{iA}/(r_{iA} + 1/\gamma_{iA})$  and  $g_{ij} = r_{ij}/(r_{ij} + 1/\gamma_{ij})$  showed always the best performance.

The best three of the H-square error at  $n = 6$  were  
 1st,  $\sigma^2 = 0.0000084$ :  $r_{iA}/(r_{iA} + 1/\gamma_{iA})$  and  $r_{ij}/(r_{ij} + 1/\gamma_{ij})$   
 2nd,  $\sigma^2 = 0.0000107$ :  $r_{iA}/(r_{iA} + 1/\gamma_{iA})$  and  $Ei(-\gamma_{ij}^1 r_{ij} - \gamma_{ij}^2) - Ei(-\gamma_{ij}^2)$ .  
 3rd,  $\sigma^2 = 0.0000108$ :  $Ei(-\gamma_{iA}^1 r_{iA} - \gamma_{iA}^2) - Ei(-\gamma_{iA}^2)$  and  $r_{ij}/(r_{ij} + 1/\gamma_{ij})$

This ranking was almost the same as the case of  $\Delta E$  (2nd and third was swapped), showing the secondary importance of the  $Ei$  function. Thus, at  $n = 6$ , the best H-square error by  $g_{iA} = r_{iA}/(r_{iA} + 1/\gamma_{iA})$  and  $g_{ij} = r_{ij}/(r_{ij} + 1/\gamma_{ij})$  was 50 times more precise than the worst case of  $g_{iA} = r_{iA}$  and  $g_{ij} = r_{ij}$ . In the case of  $\Delta E$ , this ratio was 130 times. This implies that the performance of the pair,  $g_{iA} = r_{iA}$  and  $g_{ij} = r_{ij}$  was tolerable in comparison with those of the correct  $g$  functions, in particular, the function  $g = r/(r + 1/\gamma)$ .

Figure 2 shows the plots of the H-square error  $\sigma^2$  in a log scale  $\log_{10}(\sigma^2)$  against the dimension  $M$  and the order  $n$  for the six patterns of the identical  $g_{iA}$  and  $g_{ij}$  functions. Similarly to the  $\Delta E$  case, all the plots monotonically decrease as increasing the order  $n$ . For  $g = \arctan(\gamma r)$  and  $g = \tanh(\gamma r)$ , however, the plots

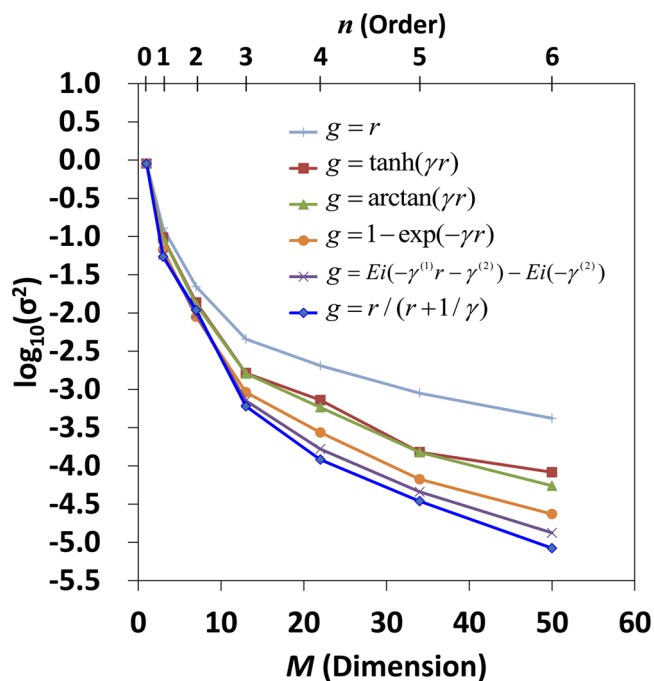


Figure 2. Convergence of  $\log_{10}(\sigma^2)$ , i.e., H-square error, obtained by the H-square error minimization using the Ritz variational energy against the dimension  $M$  (lower) and the orders  $n$  (upper) for the six cases of the identical  $g_{iA}$  and  $g_{ij}$  functions, calculated by the FC variational method for the ground state of the He atom.

look slightly bumpy, i.e.,  $\sigma^2$  improved largely at odd  $n$  ( $n = 1, 3$ , and 5) but slightly at even  $n$  ( $n = 2, 4$ , and 6). This behavior may be related to the behaviors of the Taylor expansion given by eq 10a, i.e.,  $\arctan(\gamma r)$  and  $\tanh(\gamma r)$  include only the odd powers of  $r$ . Thus, also from the performance of the H-square error,  $g = \arctan(\gamma r)$  and  $g = \tanh(\gamma r)$  were the worst two, though they performed much better than  $g = r$ . The three correct  $g$  functions  $g = r/(r + 1/\gamma)$ ,  $g = Ei(-\gamma^{(1)}r - \gamma^{(2)}) - Ei(-\gamma^{(2)})$ , and  $g = 1 - \exp(-\gamma r)$  showed excellent performances in this order: the best one was again  $g = r/(r + 1/\gamma)$ .

**3.3. Energy Lower Bound.** The FC theory is exact. Therefore, its variational calculations lead to the highly accurate energy lower bound. Then, if we can calculate the upper bound energy with the similar accuracy, we can predict the energy of the system in high accuracy. Here, we apply the PM (Pollak and Martinazzo) theory<sup>26</sup> for calculating the lower bound using the various scaling functions given in eq 9a. We used the results of the H-square errors presented above.

In Table 3, we summarized the energy upper bounds (Ritz variational energy) of the He atom shown in the above section and the lower bounds calculated with the PM method from the FC wave functions of the order  $n = 1$  to 6. We showed only the five patterns of the identical  $g$  functions for both  $g_{iA}$  and  $g_{ij}$  together with the case of  $g_{iA} = r_{iA}$  and  $g_{ij} = r_{ij}$ . The energy differences  $\Delta E$  from the exact energy given in eq 7 are shown for all the upper and lower bound energies. Note that  $\Delta E$  for the energy upper bounds should be positive and that for the lower bounds should be negative. For the PM method, we need the parameter  $\epsilon$  and we employed the best possible choice:  $\epsilon = -2.145\ 974\ 046\ 054\ 417$  a.u. (used in the present calculations that is correct to 15 digits after the decimal point), which is the reference exact energy of the excited  $2^1S$  state of



**Table 3. Summary of the Energy Upper Bound (Ritz Variational Energy) and the Energy Lower Bound Based on the PM Method Calculated by the FC Variational Method for the Ground State of the He Atom Using the Five Patterns of the Correct-type  $g_{iA}$  and  $g_{ij}$  Scaling Functions, and the Additional Case of  $g_{iA} = r_{iA}$  and  $g_{ij} = r_{ij}$ .  $\Delta E$  Is the Energy Difference from the Exact Energy Given by Eq 17**

energy upper or lower bounds	$n = 1, M = 3^a$		$n = 2, M = 7$		$n = 3, M = 13$	
	energy (a.u.)	$\Delta E$ (kcal/mol) <sup>b</sup>	energy (a.u.)	$\Delta E$ (kcal/mol)	energy (a.u.)	$\Delta E$ (kcal/mol)
			$g_{iA} = 1 - \exp(-\gamma_{iA} r_{iA}), g_{ij} = 1 - \exp(-\gamma_{ij} r_{ij})$			
upper	-2.893 831 344	6.208	-2.903 413 787	0.195	-2.903 696 682	0.0174
lower (PM)	-2.920 951 673	-10.810	-2.904 756 662	-0.648	-2.903 772 192	-0.0300
			$g_{iA} = r_{iA}/(r_{iA} + 1/\gamma_{iA}), g_{ij} = r_{ij}/(r_{ij} + 1/\gamma_{ij})$			
upper	-2.894 677 458	5.677	-2.903 246 859	0.300	-2.903 697 873	0.016 6
lower (PM)	-2.917 148 398	-8.424	-2.904 821 044	-0.688	-2.903 743 788	-0.012 2
			$g_{iA} = Ei(-\gamma_{iA}^1 r_{iA} - \gamma_{iA}^2) - Ei(-\gamma_{iA}^2), g_{ij} = Ei(-\gamma_{ij}^1 r_{ij} - \gamma_{ij}^2) - Ei(-\gamma_{ij}^2)$			
upper	-2.894 518 307	5.777	-2.903 381 851	0.215	-2.903 706 262	0.011 4
lower (PM)	-2.916 985 618	-8.322	-2.904 664 391	-0.590	-2.903 754 107	-0.018 7
			$g_{iA} = \arctan(\gamma_{iA} r_{iA}), g_{ij} = \arctan(\gamma_{ij} r_{ij})$			
upper	-2.892 510 692	7.037	-2.903 179 326	0.342	-2.903 675 510	0.030 7
lower (PM)	-2.933 236 561	-18.519	-2.906 352 236	-1.649	-2.903 891 341	-0.105
			$g_{iA} = \tanh(\gamma_{iA} r_{iA}), g_{ij} = \tanh(\gamma_{ij} r_{ij})$			
upper	-2.892 008 214	7.352	-2.903 062 405	0.415	-2.903 604 016	0.075 5
lower (PM)	-2.935 127 019	-19.705	-2.906 648 259	-1.835	-2.903 814 504	-0.056 6
			$g_{iA} = r_{iA}, g_{ij} = r_{ij}$			
upper	-2.889 001 272	9.239	-2.901 905 673	1.141	-2.903 525 542	0.125
lower (PM)	-2.945 637 391	-26.301	-2.908 125 579	-2.762	-2.904 192 637	-0.294
energy upper or lower bounds	$n = 4, M = 22$		$n = 5, M = 34$		$n = 6, M = 50$	
	energy (a.u.)	$\Delta E$ (kcal/mol)	energy (a.u.)	$\Delta E$ (kcal/mol)	energy (a.u.)	$\Delta E$ (kcal/mol)
			$g_{iA} = 1 - \exp(-\gamma_{iA} r_{iA}), g_{ij} = 1 - \exp(-\gamma_{ij} r_{ij})$			
upper	-2.903 718 938	0.003 41	-2.903 723 333	0.000 655	-2.903 724 106	0.000 170
lower (PM)	-2.903 738 037	-0.008 57	-2.903 726 106	-0.001 08	-2.903 724 949	-0.000 359
			$g_{iA} = r_{iA}/(r_{iA} + 1/\gamma_{iA}), g_{ij} = r_{ij}/(r_{ij} + 1/\gamma_{ij})$			
upper	-2.903 722 176	0.001 38	-2.903 723 733	0.000 404 2	-2.903 724 304	0.000 046 1
lower (PM)	-2.903 727 872	-0.002 19	-2.903 724 854	-0.000 299 2	-2.903 724 497	-0.000 075 3
			$g_{iA} = Ei(-\gamma_{iA}^1 r_{iA} - \gamma_{iA}^2) - Ei(-\gamma_{iA}^2), g_{ij} = Ei(-\gamma_{ij}^1 r_{ij} - \gamma_{ij}^2) - Ei(-\gamma_{ij}^2)$			
upper	-2.903 721 750	0.001 65	-2.903 723 731	0.000 406	-2.903 724 275	0.000 064 2
lower (PM)	-2.903 730 353	-0.003 75	-2.903 725 414	-0.000 651	-2.903 724 623	-0.000 154
			$g_{iA} = \arctan(\gamma_{iA} r_{iA}), g_{ij} = \arctan(\gamma_{ij} r_{ij})$			
upper	-2.903 713 355	0.006 92	-2.903 722 663	0.001 08	-2.903 723 893	0.000 304
lower (PM)	-2.903 766 265	-0.026 3	-2.903 731 932	-0.004 74	-2.903 726 246	-0.001 17
			$g_{iA} = \tanh(\gamma_{iA} r_{iA}), g_{ij} = \tanh(\gamma_{ij} r_{ij})$			
upper	-2.903 693 647	0.019 3	-2.903 713 992	0.006 52	-2.903 719 758	0.002 90
lower (PM)	-2.903 778 117	-0.033 7	-2.903 729 405	-0.003 16	-2.903 725 599	-0.000 767
			$g_{iA} = r_{iA}, g_{ij} = r_{ij}$			
upper	-2.903 651 223	0.045 9	-2.903 698 971	0.015 9	-2.903 714 781	0.006 02
lower (PM)	-2.903 866 418	-0.089 1	-2.903 767 861	-0.027 3	-2.903 739 324	-0.009 38

<sup>a</sup> $n$  and  $M$  denote the order of the FC theory and the number of the cf's (dimension), respectively. <sup>b</sup>Energy differences from the exact energy given by eq 17.

the He atom obtained previously by the FC theory.<sup>44</sup> It should be correct at least up to this digit.

As seen from Table 3, the variational energy upper bound approaches the exact energy from above closer and closer as increasing the order  $n$ , while the energy lower bounds approach the exact energy from below closer and closer as increasing the order  $n$ . This is seen in all patterns of  $g_{iA}$  and  $g_{ij}$ . Comparing the  $\Delta E$  values for the upper and lower bounds, we were impressed to see that the calculated PM's energy lower bounds  $\Delta E$  were roughly in the same order as those of the upper bound; the  $\Delta E$  values of the calculated lower bounds were roughly in the same order as those of the variational energy upper bounds in many cases. Note that the  $\Delta E$  value was calculated using the exact energy of the ground state of the

He atom shown in eq 17. If the absolute values of the two bounds are the same, their average is just the exact energy.

Looking at the whole table, the best results were obtained again for the case of  $g_{iA} = r_{iA}/(r_{iA} + 1/\gamma_{iA})$  and  $g_{ij} = r_{ij}/(r_{ij} + 1/\gamma_{ij})$ . This is the same result as the cases of the Ritz variational energies and the H-square errors discussed above. In this case, the calculated energy upper  $E_{\text{upper}}$  and lower bounds  $E_{\text{lower}}^{\text{PM}}$  at order  $n = 6$  were

$E_{\text{upper}} = -2.903 724 304$  a.u. with  $\Delta E = 0.000 046 1$  kcal/mol

$E_{\text{lower}}^{\text{PM}} = -2.903 724 497$  a.u. with  $\Delta E = -0.000 075 3$  kcal/mol.

Thus, we may conclude that the value  $E_{\text{lower}}^{\text{PM}}$  was very accurate with the same-order correct digits as  $E_{\text{upper}}$ . This

remarkable result is due to the good collaboration of the reliable PM method and the exact FC theory. From the energy upper and lower bounds obtained here, we can safely conclude that the energy up to six digits after the decimal point,  $-2.903\ 724$  a.u. is guaranteed to be correct.

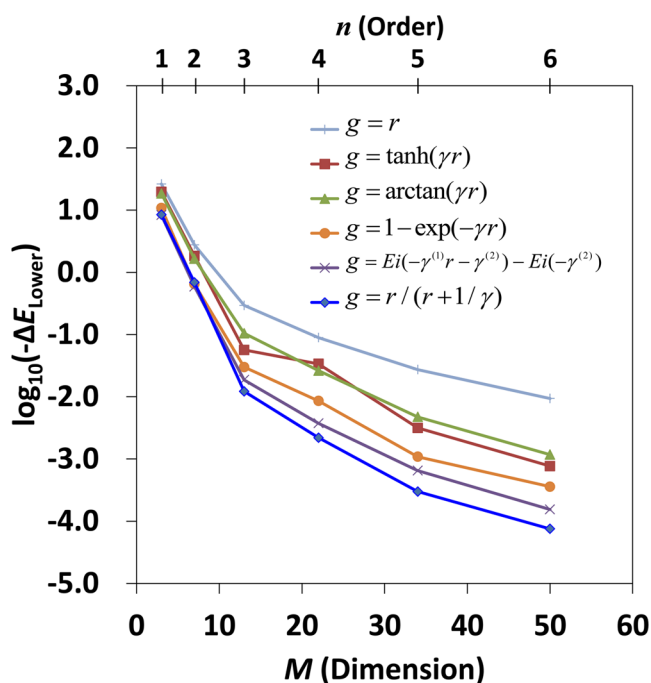
On the other hand, the worst results were again with the case of  $g_{iA} = r_{iA}$  and  $g_{ij} = r_{ij}$ . In this case, the calculated energy upper and lower bounds at order  $n = 6$  were

$$E_{\text{upper}}^{\text{PM}} = -2.903\ 714\ 781 \text{ a.u. with } \Delta E = 0.006\ 02 \text{ kcal/mol}$$

$$E_{\text{lower}}^{\text{PM}} = -2.903\ 739\ 324 \text{ a.u. with } \Delta E = -0.009\ 38 \text{ kcal/mol}$$

In this case, although the accuracies of  $E_{\text{upper}}^{\text{PM}}$  and  $E_{\text{lower}}^{\text{PM}}$  were also almost same, the energy only up to four digits after the decimal point  $-2.903\ 7$  a.u. was guaranteed to be correct. Thus, even with the exact FC theory, the use of the correct scaling function is necessary. Among the correct scaling functions, the functions  $g = r/(r + 1/\gamma)$ ,  $g = Ei(-\gamma^{(1)}r - \gamma^{(2)}) - Ei(-\gamma^{(2)})$ , and  $g = 1 - \exp(-\gamma r)$  are recommended in this order.

Figure 3 shows the plots of the energy difference of the energy lower bound,  $-\Delta E_{\text{lower}}$ , in a log scale  $\log_{10}(-\Delta E_{\text{lower}})$



**Figure 3.** Convergence of  $\log_{10}(-\Delta E_{\text{lower}})$  against the dimension  $M$  (lower) and the orders  $n$  (upper) for the six cases of the identical  $g_{iA}$  and  $g_{ij}$  functions, where  $\Delta E_{\text{lower}}$  (kcal/mol) is the energy difference between the exact energy given by eq 17 and the energy lower bounds obtained here with the PM method for the ground state of the He atom.

against the dimension  $M$  for the six patterns of the identical  $g_{iA}$  and  $g_{ij}$  functions. Although all these plots decrease monotonically as the order  $n$  increases, like in the cases of the energy upper bound and the H-square error, only  $g = \tanh(\gamma r)$  showed a large fluctuation. Then,  $g = \tanh(\gamma r)$  may not be a good member of the correct  $g$  functions.

**3.4. Electron–Nucleus and Electron–Electron Cusp Properties.** The cusp values are very local properties of the wave functions under the e–n and e–e coalescence regions. We evaluated the e–n and e–e cusp values with eqs 16a and 16b from the variational FC wave functions of the He atom at orders  $n = 0$  to 6. The results were summarized in Tables 4 and

5 for the e–n and e–e cusps, respectively. There, we marked the ranking orders according to the smallness of the deviation from the exact values,  $-2.0$  and  $0.5$  for the e–n and e–e cusps, respectively. Because they are not bounded properties, they did not monotonically converge to their exact values as seen from Figures 4 and 5. As seen from Tables 4 and 5 and Figures 4 and 5, the convergence was not monotonous but oscillating from above or from below particularly for the e–e case, but the values approached on the whole to the exact values. The e–n values were generally more accurate than the e–e values because the e–n coalescence favorably occurs due to the attractive potential but the e–e coalescence is unfavorable due to the repulsion. The amplitudes of the wave function around the e–e coalescence are expected to be small, and therefore, the e–e cusp values were not effectively improved by the energy-variational procedures.

For the e–n cusp value, the worst case at all orders was seen again for the case of  $g_{iA} = r_{iA}$  and  $g_{ij} = r_{ij}$  except for  $n = 1$ . The best 6 ranking of the e–n cusp values at  $n = 6$  was

1st, e–n cusp =  $-1.999\ 962$ :  $1 - \exp(-\gamma_{iA} r_{iA})$  and  $\arctan(\gamma_{ij} r_{ij})$

2nd, e–n cusp =  $-1.999\ 843$ :  $r_{iA}/(r_{iA} + 1/\gamma_{iA})$  and  $1 - \exp(-\gamma_{ij} r_{ij})$

3rd, e–n cusp =  $-2.000\ 217$ :  $Ei(-\gamma_{iA}^1 r_{iA} - \gamma_{iA}^2) - Ei(-\gamma_{iA}^2)$  and  $\arctan(\gamma_{ij} r_{ij})$

4th, e–n cusp =  $-1.999\ 733$ :  $r_{iA}/(r_{iA} + 1/\gamma_{iA})$  and  $Ei(-\gamma_{ij}^1 r_{ij} - \gamma_{ij}^2) - Ei(-\gamma_{ij}^2)$

5th, e–n cusp =  $-1.999\ 721$ :  $r_{iA}/(r_{iA} + 1/\gamma_{iA})$  and  $r_{ij}/(r_{ij} + 1/\gamma_{ij})$

6th, e–n cusp =  $-1.999\ 695$ :  $Ei(-\gamma_{iA}^1 r_{iA} - \gamma_{iA}^2) - Ei(-\gamma_{iA}^2)$  and  $\tanh(\gamma_{ij} r_{ij})$ .

The readers may be surprised by the differences from the similar rankings given before for the energetic properties. However, because this is for the e–n cusp,  $-2.0$ , the nuclear charge, the excellent  $g_{iA}$  functions were normal, like  $r_{iA}/(r_{iA} + 1/\gamma_{iA})$ ,  $Ei(-\gamma_{iA}^1 r_{iA} - \gamma_{iA}^2) - Ei(-\gamma_{iA}^2)$ , and  $1 - \exp(-\gamma_{iA} r_{iA})$ , but the  $g_{ij}$  function were somewhat abnormal:  $\arctan(\gamma_{ij} r_{ij})$  and  $\tanh(\gamma_{ij} r_{ij})$  entered in first, third, and sixth positions. When we observe Table 4,  $n = 6$ , the Rank column, we clearly notice that the small numbers below 10 gather at the rows of  $g_{iA} = r_{iA}/(r_{iA} + 1/\gamma_{iA})$  and  $g_{iA} = Ei(-\gamma_{iA}^1 r_{iA} - \gamma_{iA}^2) - Ei(-\gamma_{iA}^2)$ . Furthermore, the large Rank numbers ( $>16$ ) gather mostly at the rows of  $g_{iA} = \arctan(\gamma_{iA} r_{iA})$  and  $g_{iA} = \tanh(\gamma_{iA} r_{iA})$ :  $g_{iA} = \tanh(\gamma_{iA} r_{iA})$  is the worst. Furthermore, the e–n cusp values of the high Rank (small numbers  $<6$ ) were very close to each other: at  $n = 6$ , the e–n cusp value is almost converging to  $-2.0$ , the nuclear charge, as seen in Table 4 and from Figure 4.

We next examine the e–e cusp values shown in Table 5 and Figure 5. Here, in Table 5, the first and second columns were reversed to that of Table 4 because for the e–e cusp values,  $g_{ij}$  is more important than  $g_{iA}$ . First, we show again first that the worst case at each order was  $g_{ij} = r_{ij}$  and  $g_{iA} = r_{iA}$  at every order  $n$ , except for  $n = 2$ . Thus, both e–n and e–e cusp values using the correct-group  $g$  functions were totally more accurate than the case of  $g_{iA} = r_{iA}$  and  $g_{ij} = r_{ij}$ . The best 6 ranking of the e–e cusp values at  $n = 6$  was

1st, e–e cusp =  $0.499\ 918$ :  $Ei(-\gamma_{ij}^1 r_{ij} - \gamma_{ij}^2) - Ei(-\gamma_{ij}^2)$  and  $\arctan(\gamma_{iA} r_{iA})$

2nd, e–e cusp =  $0.499\ 366$ :  $r_{ij}/(r_{ij} + 1/\gamma_{ij})$  and  $1 - \exp(-\gamma_{iA} r_{iA})$

3rd, e–e cusp =  $0.501\ 370$ :  $r_{ij}/(r_{ij} + 1/\gamma_{ij})$  and  $\arctan(\gamma_{iA} r_{iA})$

4th, e–e cusp =  $0.498\ 392$ :  $r_{ij}/(r_{ij} + 1/\gamma_{ij})$  and  $Ei(-\gamma_{iA}^1 r_{iA} - \gamma_{iA}^2) - Ei(-\gamma_{iA}^2)$

**Table 4. Summary of the e-n Cusp Values Defined by Eq 16a for the FC Variational Calculations of the Ground State of the He Atom with All the Combinations of the Correct-Type  $g_{iA}$  and  $g_{ij}$  Scaling Functions and the Additional Case of  $g_{iA} = r_{iA}$  and  $g_{ij} = r_{ij}$**

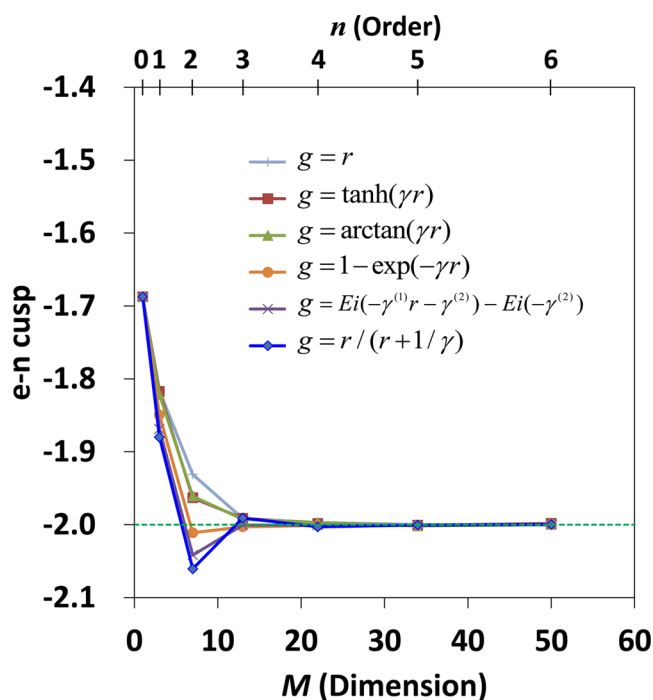
$g_{iA}$	$g_{ij}$		$n = 1, M = 3^a$		$n = 2, M = 7$		$n = 3, M = 13$		$n = 4, M = 22$		$n = 5, M = 34$		$n = 6, M = 50$	
	rank <sup>b</sup>	e-n cusp	rank	e-n cusp	rank	e-n cusp	rank	e-n cusp	rank	e-n cusp	rank	e-n cusp	rank	e-n cusp
$1 - \exp(-\gamma_{iA} r_{iA})$	12	-1.851 950	3	-1.996 695	4	-1.998 299	10	-1.997 845	11	-1.999 694	12	-1.999 145		
$r_{ij}/(r_{ij} + 1/\gamma_{ij})$	15	-1.845 668	5	-1.994 650	2	-2.000 752	12	-1.997 733	15	-2.000 471	15	-1.998 944		
$Ei(-\gamma_{ij}^2 r_{ij} - \gamma_{ij}^2) - Ei(-\gamma_{ij}^2)$	13	-1.850 108	4	-1.995 523	1	-1.999 688	11	-1.997 778	5	-2.000 192	13	-1.999 029		
$\arctan(\gamma_{ij} r_{ij})$	11	-1.855 086	2	-1.997 621	6	-1.997 387	6	-1.998 798	20	-1.999 063	1	-1.999 962		
$\tanh(\gamma_{ij} r_{ij})$	14	-1.849 565	1	-1.998 491	9	-1.995 640	15	-1.997 605	23	-1.998 104	14	-1.998 977		
(average)		-1.850 475		-1.996 596		-1.998 353		-1.997 952		-1.999 505		-1.999 211		
$1 - \exp(-\gamma_{iA} r_{iA})$	2	-1.888 866	13	-2.044 477	14	-1.990 526	5	-2.001 198	14	-1.999 549	2	-1.999 843		
$r_{ij}/(r_{ij} + 1/\gamma_{ij})$	5	-1.882 698	11	-2.042 336	11	-1.991 075	3	-2.000 969	6	-2.000 198	5	-1.999 721		
$Ei(-\gamma_{ij}^2 r_{ij} - \gamma_{ij}^2) - Ei(-\gamma_{ij}^2)$	3	-1.887 123	12	-2.043 115	12	-1.990 595	4	-2.001 143	2	-2.000 016	4	-1.999 733		
$\arctan(\gamma_{ij} r_{ij})$	1	-1.891 717	14	-2.045 422	13	-1.990 553	14	-2.002 384	19	-1.999 106	11	-2.000 610		
$\tanh(\gamma_{ij} r_{ij})$	4	-1.886 282	15	-2.047 280	15	-1.989 690	1	-2.000 401	25	-1.997 517	10	-1.999 504		
(average)		-1.887 337		-2.044 526		-1.990 488		-2.001 219		-1.999 277		-1.999 882		
$1 - \exp(-\gamma_{iA} r_{iA})$	7	-1.873 302	8	-2.026 340	7	-1.996 726	8	-1.998 327	13	-1.999 558	7	-1.999 659		
$r_{ij}/(r_{ij} + 1/\gamma_{ij})$	10	-1.867 025	6	-2.024 282	3	-1.999 032	9	-1.998 271	7	-2.000 205	9	-1.999 512		
$Ei(-\gamma_{ij}^2 r_{ij} - \gamma_{ij}^2) - Ei(-\gamma_{ij}^2)$	8	-1.871 507	7	-2.025 081	5	-1.998 008	7	-1.998 341	1	-2.000 013	8	-1.999 540		
$\arctan(\gamma_{ij} r_{ij})$	6	-1.876 311	9	-2.027 239	8	-1.995 892	2	-1.999 217	21	-1.999 023	3	-2.000 217		
$\tanh(\gamma_{ij} r_{ij})$	9	-1.870 741	10	-2.028 652	10	-1.993 973	13	-1.997 694	24	-1.997 968	6	-1.999 695		
(average)		-1.871 777		-2.026 319		-1.996 726		-1.998 370		-1.999 353		-1.999 725		
$1 - \exp(-\gamma_{iA} r_{iA})$	19	-1.820 427	23	-1.948 730	21	-1.987 144	23	-1.991 018	3	-1.999 945	19	-1.997 858		
$r_{ij}/(r_{ij} + 1/\gamma_{ij})$	26	-1.814 252	25	-1.946 607	16	-1.989 125	25	-1.990 880	18	-2.000 791	21	-1.997 726		
$Ei(-\gamma_{ij}^2 r_{ij} - \gamma_{ij}^2) - Ei(-\gamma_{ij}^2)$	22	-1.818 548	24	-1.947 636	18	-1.988 289	24	-1.990 943	12	-2.000 395	20	-1.997 775		
$\arctan(\gamma_{ij} r_{ij})$	17	-1.823 692	21	-1.949 762	23	-1.986 478	21	-1.991 851	17	-1.999 224	17	-1.998 328		
$\tanh(\gamma_{ij} r_{ij})$	23	-1.818 353	19	-1.949 879	24	-1.985 123	22	-1.991 086	22	-1.998 839	18	-1.998 103		
(average)		-1.819 054		-1.948 523		-1.987 232		-1.991 156		-1.999 839		-1.997 958		
$1 - \exp(-\gamma_{iA} r_{iA})$	18	-1.821 729	18	-1.950 928	20	-1.987 146	18	-1.993 349	10	-1.999 735	22	-1.997 421		
$r_{ij}/(r_{ij} + 1/\gamma_{ij})$	25	-1.815 574	22	-1.948 817	17	-1.988 833	20	-1.992 953	4	-1.999 882	24	-1.997 190		
$Ei(-\gamma_{ij}^2 r_{ij} - \gamma_{ij}^2) - Ei(-\gamma_{ij}^2)$	20	-1.819 842	20	-1.949 813	19	-1.988 145	19	-1.993 135	8	-1.999 766	23	-1.997 307		
$\arctan(\gamma_{ij} r_{ij})$	16	-1.824 967	17	-1.951 965	22	-1.986 572	16	-1.994 762	16	-1.999 761	16	-1.998 830		
$\tanh(\gamma_{ij} r_{ij})$	21	-1.819 727	16	-1.952 239	25	-1.985 105	17	-1.993 358	16	-1.999 363	25	-1.996 645		
(average)		-1.820 368		-1.950 752		-1.987 160		-1.993 511		-1.999 701		-1.997 479		
$r_{iA}$	24	-1.816 827	26	-1.922 264	26	-1.982 833	26	-1.990 083	26	-1.994 594	26	-1.996 611		

<sup>a</sup> $n$  and  $M$  denote the order of the FC theory and the number of the cfs (dimension), respectively. <sup>b</sup>Ranking from the smallest of  $[e-n \text{ cusp}] - (-2.0)$ .

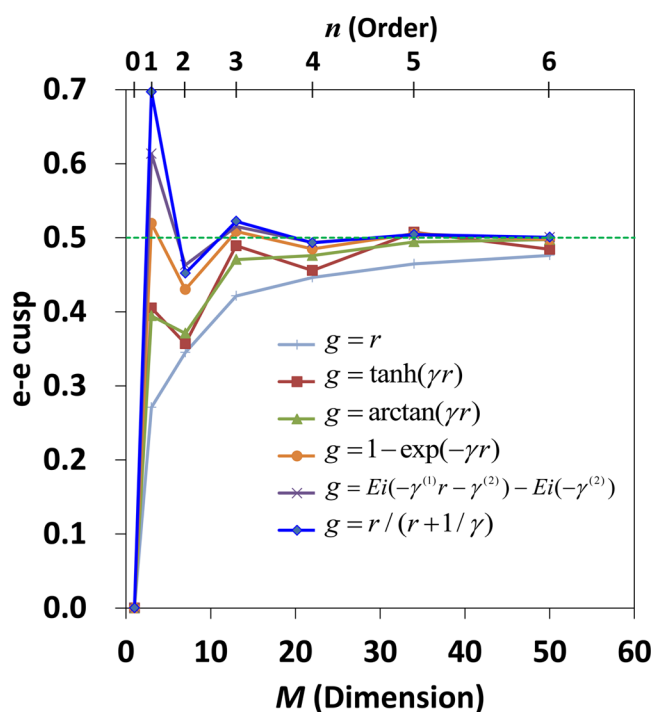
**Table S. Summary of the e-e Cusp Values Defined by Eq 16b for the FC Variational Calculations of the Ground State of the He Atom with All the Combinations of the Correct-Type  $g_{ij}$  and  $g_{iA}$  Scaling Functions and the Additional Case of  $g_{ij} = r_{ij}$  and  $g_{iA} = r_{iA}$**

$g_{ij}$	$n = 1, M = 3^a$		$n = 2, M = 7$		$n = 3, M = 13$		$n = 4, M = 22$		$n = 5, M = 34$		$n = 6, M = 50$		
	rank <sup>b</sup>	e-e cusp	rank	e-e cusp	rank	e-e cusp	rank	e-e cusp	rank	e-e cusp	rank	e-e cusp	
$1 - \exp(-\gamma_{ij} r_{ij})$	1	0.500 231	13	0.417 526	1	0.500 084	13	0.476 742	6	0.500 874	13	0.493 002	
	5	0.498 876	15	0.406 750	5	0.497 704	15	0.473 563	4	0.500 519	16	0.491 625	
	$r_{iA}/(r_{iA} + 1/\gamma_{iA})$	2	0.499 754	14	0.412 764	4	0.499 036	14	0.475 297	7	0.501 088	14	0.492 380
		4	0.498 977	11	0.422 578	3	0.500 936	11	0.481 063	12	0.502 486	11	0.494 892
	$\arctan(\gamma_{iA} r_{iA})$	3	0.499 593	12	0.421 534	2	0.499 413	12	0.480 048	8	0.501 129	10	0.495 947
		(average)	0.499 486	0.416 230	0.499 435	0.477 342	0.501 219	0.493 569					
	$r_{ij}/(r_{ij} + 1/\gamma_{ij})$	24	0.668 759	7	0.447 958	19	0.518 932	5	0.490 378	10	0.502 045	2	0.499 366
		23	0.668 734	10	0.438 714	11	0.514 906	8	0.487 070	5	0.500 756	6	0.497 783
	$Ei(-\gamma_{iA}^3 r_{iA} - \gamma_{iA}^2) - Ei(-\gamma_{iA}^2)$	25	0.669 101	8	0.444 358	14	0.517 590	7	0.488 454	9	0.501 195	4	0.498 392
		21	0.665 441	4	0.450 202	18	0.518 757	2	0.495 637	14	0.504 096	3	0.501 370
	$\tanh(\gamma_{iA} r_{iA})$	22	0.666 428	5	0.449 836	15	0.517 631	1	0.496 611	18	0.511 025	12	0.505 628
		(average)	0.667 693	0.446 214	0.517 563	0.491 630	0.503 823	0.500 508					
	$Ei(-\gamma_{ij}^3 r_{ij} - \gamma_{ij}^2) - Ei(-\gamma_{ij}^2)$	10	0.589 832	3	0.453 939	9	0.508 098	6	0.488 739	2	0.500 284	5	0.497 894
		7	0.588 604	9	0.443 592	6	0.505 394	10	0.485 192	3	0.499 615	9	0.496 442
	$r_{iA}/(r_{iA} + 1/\gamma_{iA})$	9	0.589 487	6	0.449 587	7	0.506 919	9	0.486 916	1	0.499 904	8	0.497 132
		6	0.587 969	1	0.457 887	10	0.508 545	3	0.493 805	11	0.502 057	1	0.499 918
	$\arctan(\gamma_{iA} r_{iA})$	8	0.588 696	2	0.456 981	8	0.507 680	4	0.493 635	15	0.505 480	7	0.502 286
		(average)	0.588 917	0.452 397	0.507 327	0.489 658	0.501 468	0.498 734					
	$1 - \exp(-\gamma_{iA} r_{iA})$	17	0.381 598	18	0.354 443	23	0.460 449	18	0.463 076	24	0.486 380	17	0.490 378
		20	0.379 975	22	0.343 973	22	0.460 683	20	0.460 121	23	0.486 525	19	0.489 581
	$r_{iA}/(r_{iA} + 1/\gamma_{iA})$	19	0.380 911	19	0.349 567	25	0.460 218	19	0.462 058	22	0.486 759	18	0.490 295
		18	0.381 207	16	0.360 426	21	0.461 173	16	0.466 687	21	0.487 694	15	0.492 045
$\arctan(\gamma_{iA} r_{iA})$	16	0.381 605	17	0.359 122	24	0.460 324	17	0.464 146	25	0.483 967	20	0.489 193	
	(average)	0.381 059	0.353 506	0.460 569	0.463 217	0.486 265	0.490 298						
$1 - \exp(-\gamma_{iA} r_{iA})$	11	0.392 605	23	0.342 048	13	0.482 932	23	0.442 945	17	0.510 245	23	0.473 667	
	13	0.392 215	26	0.332 228	20	0.478 170	25	0.439 806	16	0.510 134	25	0.471 683	
$r_{iA}/(r_{iA} + 1/\gamma_{iA})$	12	0.392 558	24	0.337 570	17	0.481 284	24	0.441 631	20	0.511 439	24	0.472 807	
	15	0.391 129	20	0.347 038	12	0.484 712	21	0.446 480	19	0.511 234	22	0.475 629	
$\arctan(\gamma_{iA} r_{iA})$	14	0.391 771	21	0.346 412	16	0.481 411	22	0.445 041	13	0.503 037	21	0.476 550	
	(average)	0.392 056	0.341 059	0.481 702	0.443 181	0.509 218	0.474 067						
$r_{iA}$	26	0.262 511	25	0.335 380	26	0.411 621	26	0.436 703	26	0.455 988	26	0.468 706	

<sup>a</sup> $n$  and  $M$  denote the order of the FC theory and the number of the cfs (dimension), respectively. <sup>b</sup>Ranking from the smallest of  $g$  of [e-e cusp]  $-0.51$ .



**Figure 4.** Convergence of the e–n cusp values defined by eq 16a against the dimension  $M$  (lower) and the orders  $n$  (upper) for the six cases of the identical  $g_{iA}$  and  $g_{ij}$  functions, calculated by the FC variational method for the ground state of the He atom. The green dashed line is the exact e–n cusp value, i.e.,  $-2.0$ .



**Figure 5.** Convergence of the e–e cusp values defined by eq 16b against the dimension  $M$  (lower) and the orders  $n$  (upper) for the six cases of the identical  $g_{iA}$  and  $g_{ij}$  functions, calculated by the FC variational method for the ground state of the He atom. The green dashed line is the exact e–e cusp value, i.e.,  $0.5$ .

5th, e–e cusp =  $0.497\ 894$ :  $Ei(-\gamma_{ij}^1 r_{ij} - \gamma_{ij}^2) - Ei(-\gamma_{ij}^2)$  and  $1 - \exp(-\gamma_{iA} r_{iA})$

6th, e–e cusp =  $0.497\ 783$ :  $Ei(-\gamma_{ij}^1 r_{ij} - \gamma_{ij}^2) - Ei(-\gamma_{ij}^2)$  and  $r_{iA}/(r_{iA} + 1/\gamma_{iA})$ .

Because this is for the e–e cusp values, the excellent  $g_{ij}$  functions were  $Ei(-\gamma_{ij}^1 r_{ij} - \gamma_{ij}^2) - Ei(-\gamma_{ij}^2)$  and  $Ei(-\gamma_{ij}^1 r_{ij} - \gamma_{ij}^2) - Ei(-\gamma_{ij}^2)$  alone, which is impressive not including  $1 - \exp(-\gamma_{ij} r_{ij})$ . For the  $g_{iA}$  function pairs, there appeared the four functions,  $\arctan(\gamma_{iA} r_{iA})$ ,  $1 - \exp(-\gamma_{iA} r_{iA})$ ,  $Ei(-\gamma_{iA}^1 r_{iA} - \gamma_{iA}^2) - Ei(-\gamma_{iA}^2)$ , and  $r_{iA}/(r_{iA} + 1/\gamma_{iA})$ , except for  $\tanh(\gamma_{iA} r_{iA})$ . Among them, the role of the first pair,  $Ei(-\gamma_{ij}^1 r_{ij} - \gamma_{ij}^2) - Ei(-\gamma_{ij}^2)$  and  $\arctan(\gamma_{iA} r_{iA})$  is interesting because it gave the most accurate cusp value of  $0.499\ 919$ , as seen from Table 5. When we observe Table 5,  $n = 6$ , the Rank column, we clearly notice that the small numbers below 10 gather at the rows of  $g_{ij} = r_{ij}/(r_{ij} + 1/\gamma_{ij})$  and  $g_{ij} = Ei(-\gamma_{ij}^1 r_{ij} - \gamma_{ij}^2) - Ei(-\gamma_{ij}^2)$ . Furthermore, the large Rank numbers ( $>15$ ) gather mostly at the rows of  $g_{ij} = \arctan(\gamma_{ij} r_{ij})$  and  $g_{ij} = \arctan(\gamma_{ij} r_{ij})$ :  $g_{ij} = \tanh(\gamma_{ij} r_{ij})$  is the worst. These behaviors are the same as the e–n cusp case discussed above.

Figures 4 and 5 show the e–n and e–e cusp values against the dimension  $M$  for the six patterns of the identical  $g_{iA}$  and  $g_{ij}$  functions. In both figures, the vertical axis is set to the same scale. All the plots in both figures converged to their exact values:  $-2.0$  and  $0.5$  as increasing the order  $n$ . We also see at first glance that the e–n cusp values are generally more accurate than the e–e cusp values. The e–n cusp value at  $n = 0$  was  $-1.6875$ , which is equal to the orbital exponent of  $\psi_0$ . At  $n = 1$ , the e–n cusp values of all the  $g_{iA} g_{ij}$  pairs lowered and were improved, but at  $n = 2$ , these values for  $g = r/(r + 1/\gamma)$  and  $g = Ei(-\gamma^{(1)} r - \gamma^{(2)}) - Ei(-\gamma^{(2)})$  slightly overshoot  $-2.0$ . At  $n = 3$ , most of these values were slightly higher than  $-2.0$ . Then, from  $n = 4$ , the e–n cusp values approached the exact value with slight fluctuation.

In the e–e cusp case shown in Figure 5, larger zigzag plots were observed. At  $n = 0$ , the calculated e–e cusp value is  $0$  because there are no correlated functions including  $r_{ij}$ . At  $n = 1$ , these values jumped up to near  $0.5$  except for  $g = r$ , but some overshoot to higher than  $0.5$ . At  $n = 2$ , in all the cases except for  $g = r$ , the e–e cusp values are lowered. Then, as  $n$  increases, the e–e cusp values approach the exact value with fluctuation: the e–e cusp values tend to become higher at odd order  $n$  and lower at even order  $n$ .

#### 4. CONCLUDING REMARKS

In this study, we have investigated the qualities of the five correct-type scaling functions<sup>17</sup> of the SSE for use in the FC theory applied to general atoms and molecules. We adopted the variational method because of its universal simplicity and reliability and applied the FC theory to the ground state of the He atom. The difficulty of the analytical integrations that occur when we use these correct  $g$  functions in both e–n and e–e parts was circumvented by using the numerical integration scheme over the three coordinates,  $r_{1A}$ ,  $r_{2A}$ , and  $r_{12}$ . Though highly accurate calculations like those we already performed for this system<sup>10–12</sup> were not possible, we could understand the general natures and the qualities of these correct  $g$  functions, which was the purpose of the present study.

With all the combinations of the correct scaling functions  $g$  for the e–n and e–e interactions, we calculated the energies, wave functions, H-square errors, energy lower bounds, and e–n and e–e cusp values of the He atom. Among them, the H-square error is an absolute measure of the exactness of the wave function and therefore very important to judge the exactness of the wave functions achieved by the use of these

Table A1. Overlap Matrix Elements<sup>a</sup> for the cfs with the  $g/r$ -Type Functions at the FC Order  $n = 2$ ,  $M = 18$  Calculations with  $g_{iA} = 1 - \exp(-r_{iA}r_{iA})$  and  $g_{ij} = 1 - \exp(-r_{ij}r_{ij})$  of the FC Variational Calculations of the Ground State of the He Atom

cfs <sup>b,c</sup>	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
1	1.0000																		
2	$g_{iA}$	1.0000																	
3	$g_{iA}/r_{iA}$	0.9279	1.0000																
4	$g_{i2}$	0.9760	0.9297	1.0000															
5	$g_{i2}/r_{i2}$	0.9017	0.9946	0.8894	1.0000														
6	$g_{iA}^2$	0.7523	0.9368	0.7624	0.8992	0.7210	1.0000												
7	$g_{iA}^2/r_{iA}$	0.9149	0.9995	0.9208	0.9725	0.8945	0.9415	1.0000											
8	$g_{iA}^2/r_{iA}^2$	0.9992	0.9362	0.9997	0.9370	0.9927	0.7775	0.9293	1.0000										
9	$g_{iA} g_{i2A}$	0.7274	0.9198	0.7368	0.8624	0.7021	0.9302	0.7502	1.0000										
10	$g_{iA}/r_{iA} g_{i2A}$	0.9118	0.9991	0.9181	0.9755	0.8897	0.9487	0.9986	0.9271	0.9254	1.0000								
11	$g_{iA}/r_{iA} g_{i2A}/r_{i2A}$	0.9994	0.9348	0.9998	0.9353	0.9933	0.7742	0.9281	0.9999	0.7489	0.9254	1.0000							
12	$g_{iA} g_{i2}$	0.7702	0.9402	0.7796	0.9354	0.7270	0.9443	0.7936	0.9584	0.9497	0.7907	1.0000							
13	$g_{iA}/r_{iA} g_{i2}$	0.9177	0.9772	0.9230	0.9997	0.8816	0.9740	0.9309	0.8713	0.9776	0.9290	0.9437	1.0000						
14	$g_{iA} g_{i2}/r_{i2}$	0.9292	0.9932	0.9343	0.9514	0.9188	0.9149	0.9927	0.9414	0.9052	0.9405	0.9025	0.9514	1.0000					
15	$g_{iA}/r_{iA} g_{i2}/r_{i2}$	0.9961	0.9100	0.9956	0.8964	0.9998	0.7342	0.9030	0.9941	0.8985	0.9947	0.7393	0.8891	0.9265	1.0000				
16	$g_{i2}^2$	0.7794	0.9243	0.7881	0.9514	0.7275	0.9462	0.9252	0.8011	0.9049	0.7979	0.9868	0.9581	0.8757	0.7386	1.0000			
17	$g_{i2}^2/r_{i2}$	0.9467	0.9831	0.9511	0.9955	0.9189	0.8897	0.9793	0.9573	0.9805	0.9560	0.9158	0.9940	0.9687	0.9253	0.9236	1.0000		
18	$g_{i2}^2/r_{i2}^2$	0.9825	0.8782	0.9811	0.8499	0.9957	0.6913	0.8712	0.9783	0.8650	0.9793	0.6847	0.8417	0.9049	0.9949	0.6759	0.8860	1.0000	

<sup>a</sup>Values larger than 0.99 are written in a bold face. Only the lower triangle part of the symmetric matrix is shown. <sup>b</sup>Abbreviated expressions of the cfs. <sup>c</sup>First term is the initial function and next four terms are generated at  $n = 1$  and the others are generated at  $n = 2$ .

**Table A2.** Comparison of the FC Processes at Increasing Orders with and without the  $g/r$  Functions for the Case of  $g_{iA} = 1 - \exp(-\gamma_{iA}r_{iA})$  and  $g_{ij} = 1 - \exp(-\gamma_{ij}r_{ij})$  in the Calculations of the Ground State of the He atom. Energy and  $\Delta E$  Converged and the Minimum Eigenvalue of the Overlap Matrix are Summarized

$n^a$	with $g/r$ functions				without $g/r$ functions			
	$M^b$	energy (a.u.)	$\Delta E$ (kcal/mol) <sup>c</sup>	min. eig. v. of overlap <sup>d</sup>	$M^b$	energy (a.u.)	$\Delta E$ (kcal/mol) <sup>c</sup>	min. eig. v. of overlap <sup>d</sup>
0	1	-2.847 656 250	35.183 282	1.0	1	-2.847 656 250	35.183 282	1.0
1	5	<b>-2.903 349 537</b>	0.235 216	$7.95 \times 10^{-6}$	3	-2.893 831 344	6.207 972	$7.95 \times 10^{-2}$
2	18	<b>-2.903 700 165</b>	0.015 193	$1.78 \times 10^{-12}$	7	<b>-2.903 413 787</b>	0.194 898	$7.24 \times 10^{-4}$
3	50	<b>-2.903 722 928</b>	0.000 909	$(1.26 \times 10^{-16})^e$	13	<b>-2.903 696 682</b>	0.017 379	$1.47 \times 10^{-5}$
4	not converged				22	<b>-2.903 718 938</b>	0.003 413	$9.33 \times 10^{-7}$
5	not converged				34	<b>-2.903 723 333</b>	0.000 655	$2.70 \times 10^{-8}$
6	not converged				50	<b>-2.903 724 106</b>	0.000 170	$6.18 \times 10^{-10}$
exact		-2.903 724 377	0			-2.903 724 377	0	

<sup>a</sup>Order of the FC theory. <sup>b</sup>Number of the cf's (dimension). <sup>c</sup>Energy differences from the exact energy given by eq 17. <sup>d</sup>Minimum eigenvalue of the overlap matrix. <sup>e</sup>Exceed the precision of the double-precision floating-point number.

special correct  $g$  functions. Also, using this quantity, the energy lower bounds could be calculated. Between the first three energetic properties and the last cusp properties, there were some differences in the effects gained by the use of the correct  $g$  functions.

For the energetic properties, both  $g_{iA}$  and  $g_{ij}$  functions were important almost equally. The correct  $g$  functions were much superior to the conventional function  $r$ . Among the five correct functions, the performances of  $g = r/(r + 1/\gamma)$ ,  $g = Ei(-\gamma^{(1)}r - \gamma^{(2)}) - Ei(-\gamma^{(2)})$ , and  $g = 1 - \exp(-\gamma r)$  were better in this order than those of  $g = \arctan(\gamma r)$  and  $g = \tanh(\gamma r)$ .  $g = \tanh(\gamma r)$  was not good within the examined five correct  $g$  functions. The best performance for  $\Delta E$  and the H-square error at  $n = 6$  was obtained with  $g_{iA} = r_{iA}/(r_{iA} + 1/\gamma_{iA})$  and  $g_{ij} = r_{ij}/(r_{ij} + 1/\gamma_{ij})$ . A reason for such a good performance of  $g = r/(r + 1/\gamma)$  might be due to the fact that it includes in itself the function  $g/r$  as seen from eq 12.

The smooth convergence of the H-square error to zero shown in Table 2 supports the exactness of the FC theory with any scaling function: the H-square error is an absolute measure of the exactness of both the energy and the wave function. From the variational upper bound energy and the lower bound energy obtained from the H-square errors, we could give the mathematically strict correct energy of **-2.903 724** a.u. at  $n = 6$  as the best energy obtained by this study. This energy is correct up to the six digits after the decimal point. Though this energy is much poorer than our previously reported energies<sup>10–12</sup> accurate to over 40 digits, due to the limited accuracy of the present numerical integration method, it is sufficient for the purpose of this study. For the correct scaling function  $g = 1 - \exp(-\gamma r)$ , however, fully analytic integrations are possible for its Slater function form. The results will be published soon.<sup>18</sup>

For the cusp properties, the effects of the  $g$  functions were different from those for the energetic properties. In short, for the e–n cusp condition, the e–n  $g$  function  $g_{iA}$  was of primary importance, and for the e–e cusp condition, the e–e  $g$  function  $g_{ij}$  was of primary importance. This is reasonable because the cusp values and the scaling functions are both local near the e–n and e–e coalescence regions. As the  $g$  functions that are efficient for the cusp conditions, the  $g$  functions  $g = r/(r + 1/\gamma)$  and  $g = Ei(-\gamma^{(1)}r - \gamma^{(2)}) - Ei(-\gamma^{(2)})$  were important. With the FC theory, we could obtain the accurate cusp values close to -2.0 and 0.5, respectively, for the e–n and e–e cusp values of the He atom.

For general applications of the FC theory to the systems of chemical interests, the basic integrals are limited only to the one-electron part of the theory. However, when we introduce a sampling type methodology,<sup>7,8,45</sup> the FC theory can be applied to any system without any limitation. Since the Schrödinger equation and the SSE are local equations, the sampling-type theory is very suitable for the exact theory. In the FC theory, the wave function is given in the form of eq 7, where  $\{\phi_i\}$  is the set of the analytical functions, called complement functions (cf's), that describe the exact wave function  $\psi$ . All we have to do is to determine the coefficients  $\{c_i\}$ , and this is possible with a simple sampling methodology called the direct (or inverse-transformation) local sampling method.<sup>45</sup> The present study has given the basic information for developing the FC theories using the accurate scaling functions given by eq 9a.

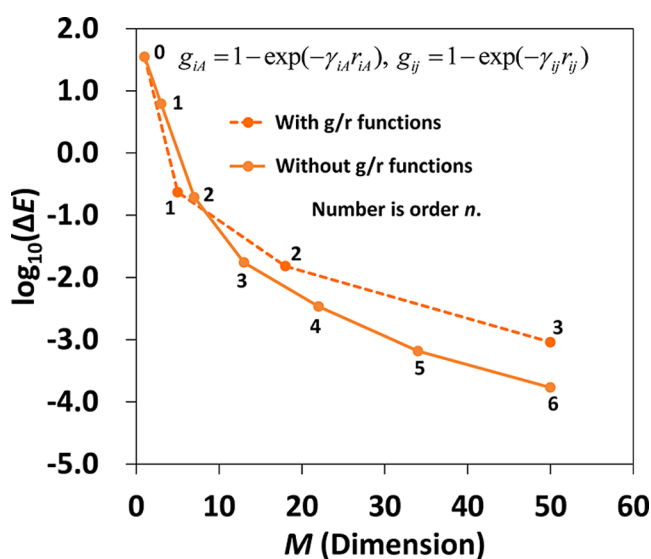
## APPENDIX

### Examination of the $g/r$ Functions

We examined numerically here the  $g/r$  functions that are produced as byproducts of the cf generation step when we use the correct  $g$  functions of eq 9a except for  $g = r/(r + 1/\gamma)$ . For this purpose, we performed the FC calculations of the ground state of the He atom with and without the  $g/r$  functions for the case of  $g = 1 - \exp(-\gamma r)$  for both e–n and e–e scaling functions.

Table A1 shows the overlap matrix elements for the cf's with the  $g/r$  functions at order  $n = 2$  with dimension  $M = 18$ . The first one is the initial function. The next four cf's are generated at  $n = 1$ , and the others are generated at  $n = 2$ . In this table, the values larger than 0.99 are shown in a bold face. We see that very large overlaps exist only in the elements including the  $g/r$  functions. This may cause the redundancy difficulty in the calculations, which was really observed, as seen from Table A2.

Table A2 summarizes the energy convergence and the minimum eigenvalues of the overlap matrices in the FC calculational processes with and without the  $g/r$  functions. Figure A1 shows the plots of  $\log_{10}(\Delta E)$  against the dimension  $M$ . With the  $g/r$  functions, the dimension  $M$  rapidly increased, but  $\Delta E$  was not efficiently improved, compared to the case without these functions. An exception may be seen at order  $n = 1$ , but  $M$  is small and this exception is not important. From Table A2, we see that the minimum eigenvalues of overlap matrix become almost zero when  $g/r$  functions exist. This value at  $n = 3–4$  already exceeded the precision of the double-precision floating-point number and caused a trouble in the



**Figure A1.** Convergence of  $\log_{10}(\Delta E)$  against the dimension  $M$  for the cases with (real line) and without (dotted line) the  $g/r$ -type functions for the case of  $g_{iA} = 1 - \exp(-\gamma_{iA}r_{iA})$  and  $g_{ij} = 1 - \exp(-\gamma_{ij}r_{ij})$ , where  $\Delta E$  (kcal/mol) is the energy difference between the exact energy given by eq 17 and the energy calculated from the FC variational method for the ground state of the He atom. The numbers in the graph denote order  $n$ .

calculations, like numerical instabilities. Thus, the  $g/r$  functions may be used only at lower orders of the FC calculations, though here, they were thrown out from the calculations.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jctc.4c00263>.

All the primitive data of the present calculations except for the energy lower bound and details of the numerical integration methods used in the present calculations (PDF)

## AUTHOR INFORMATION

### Corresponding Author

Hiroshi Nakatsuji – Quantum Chemistry Research Institute, Sakyo-ku, Kyoto 606-8305, Japan; [orcid.org/0000-0002-8162-3220](https://orcid.org/0000-0002-8162-3220); Email: [h.nakatsuji@qcri.or.jp](mailto:h.nakatsuji@qcri.or.jp)

### Author

Hiroyuki Nakashima – Quantum Chemistry Research Institute, Sakyo-ku, Kyoto 606-8305, Japan; [orcid.org/0000-0002-3758-5159](https://orcid.org/0000-0002-3758-5159)

Complete contact information is available at: <https://pubs.acs.org/10.1021/acs.jctc.4c00263>

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

We acknowledge the computer centers of the Research Center for Computational Science in the Institute for Molecular Science (IMS), Okazaki, Japan, for the huge support and encouragement given to our research project (Project: 23-IMS-C011). In particular, we would like to appreciate Prof.

Masahiro Ehara and Dr. Motoshi Kamiya for their generous and technical support in using their superparallel machines efficiently. This work was also supported by JSPS KAKENHI grant numbers 22H02045 and 23H01930.

## REFERENCES

- (1) Nakatsuji, H. Scaled Schrödinger equation and the exact wave function. *Phys. Rev. Lett.* **2004**, *93*, 030403.
- (2) Nakatsuji, H. General method of solving the Schrödinger equation of atoms and molecules. *Phys. Rev. A* **2005**, *72*, 062110.
- (3) Nakatsuji, H. Structure of the exact wave function. *J. Chem. Phys.* **2000**, *113*, 2949–2956.
- (4) Nakatsuji, H.; Davidson, E. R. Structure of the exact wave function. II. Iterative configuration interaction method. *J. Chem. Phys.* **2001**, *115*, 2000–2006.
- (5) Nakatsuji, H.; Ehara, M. Structure of the exact wave function. V. Iterative configuration interaction method for molecular systems within finite basis. *J. Chem. Phys.* **2002**, *117*, 9–12.
- (6) Maplesoft, See <https://www.maplesoft.com/>.
- (7) Nakatsuji, H.; Nakashima, H.; Kurokawa, Y.; Ishikawa, A. Solving the Schrödinger equation of atoms and molecules without analytical integration based on the free iterative-complement-interaction wave function. *Phys. Rev. Lett.* **2007**, *99*, 240402.
- (8) Nakatsuji, H.; Nakashima, H. Free-complement local-Schrödinger-equation method for solving the Schrödinger equation of atoms and molecules: Basic theories and features. *J. Chem. Phys.* **2015**, *142*, 084117.
- (9) Nakatsuji, H. Discovery of a general method of solving the Schrödinger and Dirac equations that opens a way to accurately predictive quantum chemistry. *Acc. Chem. Res.* **2012**, *45*, 1480–1490.
- (10) Nakashima, H.; Nakatsuji, H. Solving the Schrödinger equation for helium atom and its isoelectronic ions with the free iterative complement interaction (ICI) method. *J. Chem. Phys.* **2007**, *127*, 224104.
- (11) Nakashima, H.; Nakatsuji, H. How accurately does the free complement wave function of a helium atom satisfy the Schrödinger equation? *Phys. Rev. Lett.* **2008**, *101*, 240406.
- (12) Kurokawa, Y.; Nakashima, H.; Nakatsuji, H. Solving the Schrödinger equation of helium and its isoelectronic ions with the exponential integral (Ei) function in the free iterative complement interaction method. *Phys. Chem. Chem. Phys.* **2008**, *10*, 4486.
- (13) Kurokawa, Y.; Nakashima, H.; Nakatsuji, H. Free iterative-complement-interaction calculations of the hydrogen molecule. *Phys. Rev. A* **2005**, *72*, 062502.
- (14) Nakatsuji, H.; Ehara, M. Iterative CI general singles and doubles (ICIGSD) method for calculating the exact wave functions of the ground and excited States of molecules. *J. Chem. Phys.* **2005**, *122*, 194108 1.
- (15) Nakatsuji, H.; Nakashima, H.; Kurokawa, Y. I. Solving the Schrödinger equation of atoms and molecules with the free-complement chemical-formula theory: First-row atoms and small molecules. *J. Chem. Phys.* **2018**, *149*, 114106.
- (16) Nakatsuji, H.; Nakashima, H. Potential curves of the lower nine states of  $\text{Li}_2$  molecule: Accurate calculations with the free complement theory and the comparisons with the SAC/SAC-CI results. *J. Chem. Phys.* **2022**, *157*, 094109.
- (17) Nakatsuji, H.; Nakashima, H.; Kurokawa, Y. I. Accurate scaling functions of the scaled Schrödinger equation. *J. Chem. Phys.* **2022**, *156*, 014113.
- (18) Kurokawa, Y. I.; Nakatsuji, H. to be submitted.
- (19) Slater, J. C. Atomic shielding constants. *Phys. Rev.* **1930**, *36*, 57–64.
- (20) Kato, T. On the eigenfunctions of many-particle systems in quantum mechanics. *Commun. Pure Appl. Math.* **1957**, *10*, 151–177.
- (21) Python, See <https://www.python.org/> for Python and <https://scipy.org/> for SciPy library and <https://mpmath.org/for-mpmathlibrary>.
- (22) quadpack, see <https://www.netlib.org/quadpack/>.



- (23) Harris, F. E.; Frolov, A. M.; Smith, V. H. Singular and nonsingular three-body integrals for exponential wave functions. *J. Chem. Phys.* **2004**, *121*, 6323–6333.
- (24) Temple, G. The theory of Rayleigh's principle as applied to continuous systems. *Proc. R. Soc. A* **1928**, *119*, 276.
- (25) Weinstein, D. H. Modified Ritz method. *Proc. Natl. Acad. Sci. U.S.A.* **1934**, *20*, 529–532.
- (26) Pollak, E.; Martinazzo, R. Lower bounds for Coulombic systems. *J. Chem. Theory Comput.* **2021**, *17*, 1535–1547.
- (27) Ireland, R. T.; Jeszenszki, P.; Mátyus, E.; Martinazzo, R.; Ronto, M.; Pollak, E. Lower bounds for nonrelativistic atomic energies. *ACS Phys. Chem. Au* **2022**, *2*, 23–37.
- (28) Ronto, M.; Jeszenszki, P.; Mátyus, E.; Pollak, E. Lower bounds on par with upper bounds for few-electron atomic energies. *Phys. Rev. A* **2023**, *107*, 012204.
- (29) Nakatsuji, H.; Nakashima, H.; Kurokawa, Y. I. Solving the Schrödinger equation of atoms and molecules: Chemical-formula theory, free-complement chemical-formula theory, and intermediate variational theory. *J. Chem. Phys.* **2018**, *149*, 114105.
- (30) Hylleraas, E. A. Neue Berechnung der Energie des Heliums im Grundzustande, Sowie des Tiefsten Terms von Ortho-Helium. *Z. Phys.* **1929**, *54*, 347–366.
- (31) Kinoshita, T. Ground state of the helium atom. *Phys. Rev.* **1957**, *105*, 1490–1502.
- (32) Frankowski, K.; Pekeris, C. L. Logarithmic terms in the wave functions of the ground state of two-electron atoms. *Phys. Rev.* **1966**, *146*, 46–49.
- (33) Bartlett, J. H. The helium wave equation. *Phys. Rev.* **1937**, *51*, 661–669.
- (34) Gronwall, T. H. The helium wave equation. *Phys. Rev.* **1937**, *51*, 655–660.
- (35) Fock, V. A. On the Schrödinger equation of the helium atom. *Izv. Akad. Nauk SSSR, Ser. Fiz.* **1954**, *18*, 161.
- (36) Thakkar, A. J.; Koga, T. Ground-state energies for the helium isoelectronic series. *Phys. Rev. A* **1994**, *50*, 854–856.
- (37) Goldman, S. P. Uncoupling correlated calculations in atomic physics: Very high accuracy and ease. *Phys. Rev. A* **1998**, *57*, R677–R680.
- (38) Drake, G. W. F.; Cassar, M. M.; Nistor, R. A. Ground-state energies for helium,  $H^-$ , and  $Ps^-$ . *Phys. Rev. A* **2002**, *65*, 054501.
- (39) Sims, J. S.; Hagstrom, S. A. High-precision Hy-CI variational calculations for the ground state of neutral helium and helium-like ions. *Int. J. Quantum Chem.* **2002**, *90*, 1600–1609.
- (40) Korobov, V. I. Nonrelativistic ionization energy for the helium ground state. *Phys. Rev. A* **2002**, *66*, 024501.
- (41) Aznabaev, D. T.; Bekbaev, A. K.; Korobov, V. I. Nonrelativistic energy levels of helium atoms. *Phys. Rev. A* **2018**, *98*, 012510.
- (42) Schwartz, C. Experiment and theory in computations of the He atom ground state. *Int. J. Mod. Phys. E* **2006**, *15*, 877–888.
- (43) Schwartz, C. Further computations of the He atom ground State. *arXiv* **2006**, arXiv:math-ph/0605018.
- (44) Nakashima, H.; Hijikata, Y.; Nakatsuji, H. Solving the electron and electron-nuclear Schrödinger equations for the excited states of helium atom with the free iterative-complement-interaction method. *J. Chem. Phys.* **2008**, *128*, 154108.
- (45) Nakatsuji, H.; Nakashima, H. Direct local sampling method for solving the Schrödinger equation with the free complement - local Schrödinger equation theory. *Chem. Phys. Lett.* **2022**, *806*, 140002.