How Does the Free Complement Wave Function Become Accurate and Exact Finally for the Hydrogen Atom Starting From the Slater and Gaussian Initial Functions and for the Helium Atom on the Cusp Conditions?

HIROSHI NAKATSUJI, HIROYUKI NAKASHIMA

Quantum Chemistry Research Institute, JST, CREST, Kyodai Katsura Venture Plaza 106,
Goryo Oohara 1-36, Nishikyo-Ku, Kyoto 615-8245, Japan

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ABSTRACT: The free complement (FC) method, or the free iterative-complement-interaction (ICI) method, for generating the exact wave function from an approximate initial wave function has been applied to the hydrogen atom starting from the Slater and Gaussian functions for comparison. The process of improvement was followed by checking the wave function itself and other quantities that have definite exact values. Because the exact wave function is simple in this case, we could make clear analyses for many aspects of the wave function. We examined the energy, the wave function itself, the wave function error, the H-square error, the local energy near the nucleus, and the cusp. Both the Slater and Gaussian functions gave similar convergence rates to the exact function with respect to the order of the FC method, but the number of complement functions at a particular order is three times larger for the Gaussian case than for the Slater case. Although the cusp value of the Gaussian initial function is zero, it grows as the FC calculation proceeds and finally becomes essentially exact at convergence. The same was true for all the quantities studied here, irrespective of the type of the initial wave function. For the helium atom, the cusp conditions including the electron–electron cusp were also examined with the FC wave function calculated before and shown to converge to the exact values. © 2009 Wiley Periodicals, Inc. Int J Quantum Chem 109: 2248–2262, 2009

Correspondence to: H. Nakatsuji; e-mail: h.nakatsuji@qcri.or.jp

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Key words: solve Schrödinger equation; free complement method; complement function; Slater function; Gaussian function; hydrogen atom; helium atom; cusp conditions

Introduction

The Schrödinger equation (SE), $H\psi = E\psi$, provides a governing principle of chemistry, biology, and physics and has accurate and powerful predictive power [1]. For over 80 years after its discovery, however, this equation has been thought not to be soluble except for a few special cases [1, 2]. For this reason, quantum chemistry has long been a science for developing *approximate* practical methods of applying quantum mechanics that lead to *explanations* of the *main* features of chemical phenomena [1]. Actually, even with this limitation, quantum chemistry has produced many important methods and concepts that are useful for understanding and explaining chemical phenomena. Among others, the valence bond method, molecular orbital method, and coupled-cluster method have comprised a main stream of methodology, and many important concepts, such as resonance [3], electronegativity [3, 4], frontier orbital [5], and symmetry conservation [6] have been built up on these theories. However, truly quantitative predictions have been very rare in quantum chemistry, because we had no general method of solving the SE accurately. A formulation of a general theory of solving the SE is important for making quantum chemistry an *accurately predictive science*.

Since 1999, one of the authors has been involved in this difficult task and has published a series of articles to formulate a general method of solving the SE of atoms and molecules in an analytical expansion form [7–25]. First, he clarified the *mathematical structure of the exact wave function* and proposed a method, called the iterative complement (or configuration) interaction (ICI) method that gives a series of functions converging to the exact wave function [7, 8]. This was confirmed by applying the method to the harmonic oscillator [9, 10] and to the finite-basis expansion method based on the second-quantized Hamiltonian [11, 17]. However, this method included the integrals of higher powers of the Hamiltonian, which diverge when the Hamiltonian involves singular operators like Coulomb potentials [12–14]. This problem, called the *singularity problem*, always occurred when we apply the method to atoms and molecules, and so this was a really severe problem. However, this difficulty was solved by introducing the scaled Schrödinger equation (SSE) [13]. The ICI method based on the SSE gives the exact wave function at convergence without encountering the singularity problem. Further, the *free ICI method* was proposed based on this method. It is more easily handled and converges more rapidly than the original ICI method [13]. Combined with the variation principle, this method produced the most accurate solutions of the SE for H_2 [15, 20], He [19, 23, 24], and others. In particular, the applications to He [19, 24] showed numerically that with the free ICI method we can calculate the solutions of the SE to any desired accuracy.

In this article, we show how the free ICI method gives a series of analytical functions that converge to the exact wave function. We use the hydrogen atom as an example because we know its exact wave function in a simple closed form. We show that this convergence is true even when we start from different starting wave functions, such as the Slater function or the Gaussian function. To verify the exactness, we compare our free ICI wave function and the calculated properties with the exact wave function and properties. They are the energy, the wave function error, the H-square error, the local energy near the nucleus, and the cusp value. Recently, we studied for the helium atom the local energy, H-square error, and upper and lower bounds to the exact energy for examining the exactness of our FC wave function [25]. We further examine here the electron–nuclear and electron–electron cusp conditions of the helium atom using the same FC wave function. For many electron atoms and molecules, the electron–electron cusp properties should be important, reflecting a proper description of electron correlations. However, there have been only a few studies that examined these properties [26–29].

Theoretical Background

The SE defines the exact wave function ψ as its solution:

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

For the hydrogen atom in its ground state, the Hamiltonian can be written as:

$$H = -\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr} - \frac{1}{r}, \tag{2}$$

and we know that the exact solution of the SE for this Hamiltonian is:

$$\psi = e^{-r}, \quad E = -\frac{1}{2}. \tag{3}$$

Except for the hydrogen atom, the exact wave functions of atoms and molecules cannot be expressed in closed forms such as Eq. (3). However, a general theory of calculating them in analytical expansion form has been given by one of the present authors. We briefly explain it as it is pertinent to this study. We introduce two equations that are equivalent to the SE. One is the variation principle given by:

$$\langle \psi | H - E | \delta\psi \rangle = 0, \tag{4}$$

and the other is the H-square equation given by:

$$\langle \psi | (H - E)^2 | \psi \rangle = 0. \tag{5}$$

The variation principle gives the best possible solution within the freedom of the given ψ and when it is completely free, this equation gives the exact wave function. On the other hand, the H-square equation is valid only for the exact wave function, and in this sense, it is strictly equivalent to the SE. Comparing Eqs. (4) and (5), we can say that the wave function that includes a variable C in the form:

$$\delta\psi = (H - E)\psi \cdot \delta C, \tag{6}$$

has the structure of the exact wave function, because when we solve the variable C using the variation principle, the solution satisfies the H-square equation, and so must be exact.

An example of a wave function that satisfies Eq. (6) is given by a recursion formula:

$$\psi_{n+1} = [1 + C_n(H - E_n)]\psi_n, \tag{7}$$

where E_n is defined by $\langle \psi_n | H - E_n | \psi_n \rangle = 0$. We can easily show the relation:

$$\langle \delta\psi_{n+1} | \psi_n \rangle = 0, \tag{8}$$

where $\delta\psi_{n+1} = \psi_{n+1} - \psi_n$. At convergence, the solution of Eq. (7) is exact. The proof is very easy: at convergence, everything is n-independent, and so we can remove n from Eq. (7). Then, by differentiating the resultant equation with respect to C, we obtain Eq. (6). (Proof ends.) We refer to the method of solving the SE using Eq. (7) as the simplest iterative complement interaction (SICI) method.

Let us use the SICI method to solve the SE of the hydrogen atom. To do so, we may start from a Slater function of the form:

$$\psi_0 = \exp(-\alpha r), \tag{9}$$

or a Gaussian function of the form:

$$\psi_0 = \exp(-\beta r^2). \tag{10}$$

Using these expressions for ψ_0, we calculate the first-order SICI wave function by $\psi_1 = [1 + C_0(H - E_0)]\psi_0$. Because the Hamiltonian is a sum of the differentiation operators and a potential operator as given by Eq. (2), we can easily formulate ψ_1. The unknown coefficient C_0 is calculated by applying the variation principle and we obtain the secular equation $(\boldsymbol{H}^{\mathrm{SICI}} - E\boldsymbol{S}^{\mathrm{SICI}})\boldsymbol{C} = 0$, where:

$$\begin{aligned} \boldsymbol{H}^{\mathrm{SICI}} &= \begin{pmatrix} \langle \psi_n | H - E_n | \psi_n \rangle & \langle \psi_n | (H - E_n)^2 | \psi_n \rangle \\ \langle \psi_n | (H - E_n)^2 | \psi_n \rangle & \langle \psi_n | (H - E_n)^3 | \psi_n \rangle \end{pmatrix}, \\ \boldsymbol{S}^{\mathrm{SICI}} &= \begin{pmatrix} \langle \psi_n | \psi_n \rangle & \langle \psi_n | H - E_n | \psi_n \rangle \\ \langle \psi_n | H - E_n | \psi_n \rangle & \langle \psi_n | (H - E_n)^2 | \psi_n \rangle \end{pmatrix}, \end{aligned} \tag{11}$$

with $n = 0$ in this case. Note that the dimension of this secular equation is only two. However, when we try to solve this secular equation, we encounter a problem: the integral of Eq. (11) includes infinity in the H-matrix element, $\langle \psi_0 | (H - E_n)^3 | \psi_0 \rangle$, which diverges to infinity except when ψ_0 is exact, i.e., except when α of Eq. (9) is unity. Table I illustrates this. It shows that the integrals of the kth power of a Hamiltonian diverge when k is larger than three, unless ψ is exact. At $n = 0$, the H-matrix element involving H^3 diverges. As the iteration proceeds, it becomes more severe: at $n = 2$, all the H-matrix elements diverge. Although such divergence does not occur when ψ_0 is exact, we never know the exact wave function for general atoms and molecules. It is meaningless to use the exact wave function for ψ_0!

This difficulty is caused by the singularity of the Coulomb potential involved in the Hamiltonian and so is referred to as the singularity problem. It generally occurs for atoms and molecules and is

TABLE I

Integrals of the higher powers of the Hamiltonian of the hydrogen atom over the Slater-type and Gaussian-type orbitals.

	Slater-type ψ		Gaussian-type ψ
Integral[a]	Exact ($\alpha = 1.0$)	Approximate ($\alpha = 0.5$)	$\beta = 1/16$
$\langle\psi\|H\|\psi\rangle/\langle\psi\|\psi\rangle$	–0.5	–0.375	–0.30519228
$\langle\psi\|H^2\|\psi\rangle/\langle\psi\|\psi\rangle$	0.25	0.203125	0.16491287
$\langle\psi\|H^3\|\psi\rangle/\langle\psi\|\psi\rangle$	–0.125	$-\infty$	$-\infty$
$\langle\psi\|H^4\|\psi\rangle/\langle\psi\|\psi\rangle$	0.0625	∞	∞
$\langle\psi\|H^5\|\psi\rangle/\langle\psi\|\psi\rangle$	–0.03125	$-\infty$	$-\infty$
$\langle\psi\|H^6\|\psi\rangle/\langle\psi\|\psi\rangle$	0.015625	∞	∞

[a] $H = -\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr} - \frac{1}{r}$.

certainly a serious problem, because if we have infinity in our formalism, we cannot proceed further. This problem was so severe that no one could have ever overcome this difficulty, until one of the authors found a way to overcome this difficulty by introducing the inverse Schrödinger equation [12] and the scaled Schrödinger equation [13]. Between the two, the latter was more general and easier to use. Actually, some papers describe a similar method to our SICI as a method to formulate an exact wave function [30–32]. However, because of the singularity problem, such methods could not be applied to atoms and molecules to calculate the exact wave functions. Note that when the system does not have a singular potential, for instance a harmonic oscillator, we do not have any problem, and the SICI method gave a fast convergence to the exact wave function when applied to the harmonic oscillator [9, 10].

The scaled Schrödinger equation (SSE) [13] is defined by:

$$g(H - E)\psi = 0, \tag{12}$$

where g is the scaling function, which is always positive but can become zero at singular points. Even there, the g function must satisfy:

$$\lim_{r\to 0} gH \neq 0 < \infty, \tag{13}$$

so as not to eliminate the information of the Hamiltonian at the singular regions. Then, we can define g^{-1} and by multiplying it from the left of Eq. (12), we obtain the SE. The SSE and the SE are therefore equivalent. In the present application to the hydrogen atom, we choose g as:

$$g = r. \tag{14}$$

We can formulate the SICI method based on the SSE and obtain the modified SICI as [13, 14]:

$$\psi_{n+1} = [1 + C_n g(H - E_n)]\psi_n. \tag{15}$$

This SICI was also proved to become exact at convergence [13, 14], and for the existence of the g-function, we do not encounter the singularity problem in the course of the iterative calculations. Here, E_n may be defined by $\langle\psi_n|g(H - E_n)|\psi_n\rangle = 0$; the difference from the previous E_n defined below Eq. (7) is small near the convergence. With this definition of E_n, we can show a relation like Eq. (8).

We now explain the free ICI method. When we do SICI calculations to the nth iteration, the right-hand side of Eq. (15) becomes a sum of products of analytical functions and the coefficients C_i. In the free ICI method, we take all the independent analytical functions from there and group them as $\{\phi_i\}$, which we refer to as complement functions, and using them, we expand our wave function as:

$$\psi_{(n+1)} = \sum_i^{M_n} c_i\phi_i. \tag{16}$$

We refer to this wave function as the free ICI wave function. It converges more quickly to the exact wave function than the original SICI does, because of the increased freedom in the wave function. However, we generally do not have a relation like Eq. (8) in the free ICI case. In the SICI scheme, the $(n+1)$th result, ψ_{n+1}, depends on all the former results, ψ_m and $C_m(m = 0, \cdots, n)$ $(m = 0, \ldots, n)$, but in the free ICI method, all the coefficients C_i are reoptimized at each n, and therefore, this method is not an iterative method. Then, the name free ICI (*iterative* complement interaction) method may be confusing. We therefore use hereafter the new name "free complement (FC)" method instead of the free ICI method. We refer to n of the FC method as an *order*, instead of an iteration number. Thus, the FC method gives a general method of solving the SE in an analytical expansion form.

Applying the variation principle to the FC wave function given by Eq. (16), we obtain the secular equation $(\boldsymbol{H} - E\boldsymbol{S})\boldsymbol{C} = 0$, where the Hamiltonian and overlap matrices are defined by:

$$\boldsymbol{H} = \begin{pmatrix} \cdot & \cdot & \cdot \\ \cdot & \int \phi_i H \phi_j d\tau & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix}, \quad \boldsymbol{S} = \begin{pmatrix} \cdot & \cdot & \cdot \\ \cdot & \int \phi_i \phi_j d\tau & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix}. \tag{17}$$

For the hydrogen atom studied here, these matrix elements are easily calculated. However, for complex atoms and molecules, the analytical integrations involved in the above matrices are often difficult to perform. For such cases, we have proposed the local Schrödinger equation (LSE) method. It is based on the potential exactness of the FC wave function given by Eq. (16) for large n. For more details, refer to Ref. [20]. Using the LSE method, we can calculate the analytic wave function without doing the analytical integrations. The LSE method is very general because it does not rely on the integrations required by Eq. (17), which cannot be performed for the complement functions of complex atoms and molecules.

Exactness Check

We examine in this article how the FC wave function of the hydrogen atom approaches the exact wave function, starting from the approximate Slater or Gaussian initial function. We calculate the following quantities for the nth-order FC wave function, $\psi_{(n)}$, to examine the exactness of the calculated wave function.

1. Energy E_n compared with the exact energy $E = -0.5$ a.u.
2. Wave function error (ψ-square error):

$$|\Delta\psi_{(n)}|^2 = \int |\psi_{(n)} - \psi_{\text{exact}}|^2 d\tau. \tag{18}$$

   This quantity can be calculated only when we know the exact wave function.
3. H-square error:

$$\sigma^2 = \langle \psi_{(n)} | (H - E_n)^2 | \psi_{(n)} \rangle = \int |(H - E_{(n)})\psi_{(n)}|^2 d\tau. \tag{19}$$

   This quantity is considered to be the sum of the squares of the errors of the Schrödinger equation:

$$\delta_n = (H - E_{(n)})\psi_{(n)}.$$

4. Averaged local energy near the nucleus:

$$LE_{(n)} = \frac{\int_0^a E^{\text{loc}}_{(n)} \cdot \psi^2_{(n)} r^2 dr}{\int_0^a \psi^2_{(n)} r^2 dr}. \tag{20}$$

   This is compared with the exact value, −0.5, where $E^{\text{loc}}_{(n)}$ is the local energy defined by $E^{\text{loc}}_{(n)} = H\psi_{(n)}/\psi_{(n)}$. The radius a is set to be $a = 1/100$ a.u.

5. Cusp value:

$$\text{Cusp}_{(n)} = \frac{1}{\psi_{(n)}(r=0)} \cdot \left. \frac{\partial \psi_{(n)}}{\partial r} \right|_{r=0}, \tag{21}$$

   compared with the exact value, –1.

Because we use the variation principle to calculate the energy E_n, we obtain the upper bound of the exact energy. The other quantities from (2) to (5) are stringent tests of the exactness of the calculated wave function. Both the wave function error and the H-square error are the sums of positive elements, and therefore no cancellations are included in the values. In comparison with the H-square error, the wave function error may be referred to as the ψ-square error. As we have shown previously for the helium atom, the local energy is a rather sensitive quantity near the singularity point [25]. Therefore, the average local energy near the nucleus defined by Eq. (20) is also a stringent test of the exactness. The cusp condition [33] is a necessary condition that the exact wave function must satisfy. It is the condition that the local energy at the nucleus does not diverge. Further, it should be equal to the exact energy, i.e.:

$$\left.\frac{H\psi_{(n)}}{\psi_{(n)}}\right|_{r=0} = E. \tag{22}$$

Without assuming the cusp condition, the local energy at the origin diverges, but if we assume the cusp condition, this equation imposes further conditions on the structure of the exact wave function. There are some other related conditions [34]. Because the quantities given by Eqs. (20)–(22) have a common origin, which is the singularity of the nuclear potential at the origin, they are usually difficult to satisfy with an approximate wave function unless the wave function is constrained beforehand to satisfy these conditions.

FC Wave Function of Hydrogen Atom Starting From Slater and Gaussian ψ_0

We calculate the FC wave function and energy of the hydrogen atom starting from two different initial functions ψ_0. One is the Slater function given by Eq. (9) and the other is the Gaussian function given by Eq. (10). The g-function we used is given by Eq. (14). We want to see how the FC method gives the exact wave function starting from different initial functions.

Of particular interests are the cusp properties of the calculated FC wave function. It is well known that the Slater function has a cusp but the Gaussian function does not. Thus, a question is whether the FC wave function starting from the Gaussian function can have a correct cusp value. A similar question for the Slater function is: can an FC wave function starting from a function that has a cusp different from the correct value have a correct cusp after the FC calculations?

It is interesting to note that a set of s-type Gaussian functions can never be complete for describing the hydrogen atom, irrespective of how many Gaussian functions are involved in the set. The proof is simple: it is impossible to produce a cusp from a linear combination of a finite number of s-type Gaussians. The same is true for the correlated Gaussian functions that are used to obtain accurate wave functions.

SLATER INITIAL FUNCTION

We start from the Slater-type initial function, $\psi_0 = e^{-\alpha r}$. The value of α adopted in the present calculation was 0.5. The exact wave function for the ground state is written also with the Slater function of $\alpha = 1.0$. When one applies the FC method using the above ψ_0 and $g = r$, one finds that the FC wave function is written as:

$$\psi_{(n)} = \sum_{i=0}^{n} c_i r^i e^{-\alpha r}, \tag{23}$$

where n is the order of the FC method. Thus, for each increment in the order i, an additional complement function $r^i e^{-\alpha r}$ is generated, and so we have the FC wave function of Eq. (23) at order n.

From Eq. (21), the cusp value is related to the first two coefficients in Eq. (23):

$$\mathrm{Cusp}_{(n)} = \frac{c_1}{c_0} - \alpha, \tag{24}$$

which should be equal to -1 at the exact limit. Because the values of c_0 and c_1 change as the order of the FC calculation increases, the cusp value should be improved as the order n increases.

Another interesting relation is obtained from the local energy condition at the nucleus given by Eq. (22) and the cusp condition given above, that is:

$$\left.\frac{c_2}{c_0}\right|_{\text{at exact}} = \frac{1}{3}(Z^2 - E) + \frac{1}{2}\alpha^2 - Z\alpha, \tag{25}$$

where Z is the nuclear charge, which is unity in the present case. This condition involves the exact energy.

It is interesting to constrain our wave function to satisfy the cusp condition. Then, the ratio c_1/c_0 is constrained to be $\alpha - 1$. Further, when we use the local energy condition given by Eq. (22), the ratio c_2/c_0 is constrained to the right-hand side of Eq. (22), although in general we must replace the exact energy E with some approximate value. Then, both c_1/c_0 and c_2/c_0 are constrained, and the free variations are done only for c_3/c_0 and higher coefficients. (Note that for the normalization condition, c_0 is not actually a variable parameter.) In our FC formalism, the final result must be the exact wave function, so that the result should not depend much on whether or not we constrain such conditions. In the present calculations, we used free variations, although it is interesting to compare the convergence speeds between the calculations with and without the constraints.

Because we know that the exact wave function is e^{-r}, we can easily estimate the exact solution of the FC wave function as:

$$\psi_{(\infty)} = e^{-r} = e^{(\alpha-1)r}e^{-\alpha r} = \left[1 + (\alpha - 1)r + \frac{(\alpha-1)^2}{2}r^2 + \cdots + \frac{(\alpha-1)^k}{k!}r^k + \cdots\right]\psi_0, \quad (26)$$

and the coefficients c_k in Eq. (23) as:

$$\frac{c_k}{c_0} = \frac{(\alpha-1)^k}{k!}. \quad (27)$$

This kind of estimation is impossible for general atoms and molecules, because we do not know the exact wave functions. In the FC method, the coefficients c_i are calculated using the variation principle or the LSE method. Here, we used the variation principle. We calculated the overlap and Hamiltonian matrices given by Eq. (17) and solved the secular equation.

We give a summary of the present results in Table II. The first and second columns show the order n and the number of functions M_n included in the FC wave function. In the present case, $M_n = n + 1$. We performed the calculations up to $n = 50$. The third column shows the energy. As the order n increases, it converges nicely from above to the exact value -0.5. The numbers of correct digits are 4, 8, 17, 26, 36, and 45 for $n = 5$, 10, 20, 30, 40, and 50, respectively. From the nature of the variation principle, the energy converges faster than the wave function itself. The fourth and fifth columns show the coefficient ratios c_1/c_0 and c_2/c_0, which must be -0.5 and 0.125, respectively, from Eqs. (24) and (25) for the exact wave function. They also converge well to the exact values, but the convergence speed is slower than that of the energy. The numbers of correct digits are 1, 3, 7, 12, 16, and 21 for c_1/c_0, and 1, 2, 7, 11, 15, and 20 for c_2/c_0, for $n = 5$, 10, 20, 30, 40, and 50, respectively, and so the numbers of correct digits are about half of those for the energy. The accuracy of c_1/c_0 is better than that of c_2/c_0, and this tendency is general. It is clear that when we terminate the expansion in Eq. (26) at the nth order and calculate each coefficient by the variation principle, as we do in the present FC method, then the effect of termination should be largest on the nth term (the last term), less for the $(n-1)$th term, less again for the $(n-2)$th term, and so on. It is also interesting to note that the values of both ratios, c_1/c_0 and c_2/c_0, approach the exact values from smaller absolute values.

The sixth column shows the wave function error defined by Eq. (18). This quantity shows an average square deviation of the FC wave function at each order n from the exact wave function. This quantity again converges well to the exact value, 0.0. It is interesting to compare this quantity with the H-square error shown at the next column, which is the average of the square of the error of the Schrödinger equation, $\delta_n = (H - E_n)\psi_n$, at each order. The convergence behaviors of these two quantities are similar, although the ψ-square error converges a little faster than the H-square error. These errors at $n = 50$ are quite small: 10^{-46} and 10^{-44}. It is interesting to note that the number of correct digits of the H-square error and the wave function error are almost equal to the number of correct digits of the calculated energy. For the H-square error, they are 4, 8, 17, 26, 35, and 44 for $n = 5$, 10, 20, 30, 40, and 50, respectively, which are almost the same as the numbers of the correct digits of the energy, 4, 8, 17, 26, 36, and 45, shown earlier. In our experience, this is valid in general, and this rule may be used to estimate the accuracy of the calculated energy, because it is easy to calculate the H-square error in the FC method.

The last two columns show the average local energy near the nucleus and the cusp value, which should converge to the exact values, -0.5 and -1, respectively. These quantities are the properties near the nucleus and so are affected strongly by the Coulomb singularity at the nucleus. These values are rather difficult to calculate correctly. Actually, the initial values of these quantities are far from the correct values, particularly on the local energy. Nevertheless, these values calculated from the FC wave function converge well to the exact values. Note that the cusp value and the coefficient ratio c_1/c_0 are essentially the same thing.

TABLE II

The convergence of the energy, coefficients, wave function error, H-square error, average local energy near the nucleus, and the cusp value of the FC wave function starting from the Slater-type initial function.

n[a]	M_n[b]	Energy (a.u.)	c_1/c_0	c_2/c_0	Wave function error	H-square error	*L.E.*	Cusp
0	1	–0.375			3.239×10^{-1}	6.250×10^{-2}	–75.187	–0.500
1	2	**–0.4**58	–0.166		6.460×10^{-2}	5.555×10^{-2}	–50.236	–0.666
2	3	**–0.4**893	–0.302	0.0226	1.223×10^{-2}	2.581×10^{-2}	–29.946	–0.802
3	4	**–0.49**784	–0.394	0.0536	2.295×10^{-3}	7.660×10^{-3}	–16.236	–0.894
4	5	**–0.499**627	–0.447	0.0811	3.969×10^{-4}	1.731×10^{-3}	–8.271	–0.9475
5	6	**–0.4999**408	–0.475	**0.1**004	6.292×10^{-5}	3.356×10^{-4}	–4.117	**–0.9**755
10	11	**–0.49999999**676	**–0.499**677	**0.12**440	3.376×10^{-9}	3.472×10^{-8}	**–0.5**468	**–0.999**677
15	16	**–0.499999999999**885	**–0.49999**723	**0.12499**263	1.174×10^{-13}	1.793×10^{-12}	**–0.500**394	**–0.99999**723
20	21	**–0.49999999999999999**670	**–0.4999999**806	**0.1249999**321	3.370×10^{-18}	6.830×10^{-17}	**–0.50000**272	**–0.9999999**806
25	26	**–0.4999999999999999999999**150	**–0.499999999**878	**0.124999999**473	8.658×10^{-23}	2.187×10^{-21}	**–0.5000000**1678100131	**–0.999999999**878
30	31	**–0.499999999999999999999999999**796	**–0.499999999999**292	**0.12499999999**634	2.069×10^{-27}	6.262×10^{-26}	**–0.5000000000**960	**–0.999999999999**292
35	36	**–0.4999999999999999999999999999999**536	**–0.49999999999999**608	**0.1249999999999**765	4.701×10^{-32}	1.657×10^{-30}	**–0.500000000000**522	**–0.99999999999999**608
40	41	**–0.49999999999999999999999999999999999**898	**–0.4999999999999999**791	**0.124999999999999**857	1.028×10^{-36}	4.141×10^{-35}	**–0.50000000000000**273	**–0.9999999999999999**791
45	46	**–0.4999999999999999999999999999999999999999**783	**–0.499999999999999999**892	**0.124999999999999999**173	2.185×10^{-41}	9.892×10^{-40}	**–0.5000000000000000**138	**–0.999999999999999999**892
50	51	**–0.499999999999999999999999999999999999999999999**550	**–0.499999999999999999999**455	**0.12499999999999999999**537	4.538×10^{-46}	2.280×10^{-44}	**–0.5000000000000000000**689	**–0.999999999999999999999**455
Exact		**–0.5**	**–0.5**	**0.125**	**0**	**0**	**–0.5**	**–1**

[a] Order.

[b] Number of complement functions at order n.

Thus, all the quantities shown in Table II converge to the exact values. From a theoretical basis, this is very natural, because the FC wave function must converge to the exact wave function, but the present result shows numerically that the convergence is quite fast with the FC method. By extrapolating the present result, it is safe to say that the FC method certainly gives the exact wave function at convergence. This had been proved already by the theory, but the present result supports it numerically.

GAUSSIAN INITIAL FUNCTION

We next use the Gaussian function as the initial function of the FC method, i.e., $\psi_0 = e^{-\beta r^2}$. The value of β was fixed to $1/16 = 0.0625$, which is close to the optimally fitted (in a least mean square sense) exponent, 0.0677 of a single Gaussian orbital to a single Slater orbital, $e^{-0.5r}$, used in the previous section. Therefore, the qualities of the initial Slater and Gaussian functions are similar. The scaling function g is r as for the Slater case. Because the Hamiltonians given by Eq. (2) have only the differentiation operator and the potential operator, the free ICI process given by Eq. (15) produces only Gaussian functions at any order. It does not modify the functional type: we obtain only Slater-type functions from the Slater initial function and only Gaussian-type functions from the Gaussian initial function. Therefore, it is interesting to see how the FC wave function satisfies the cusp condition when starting from the Gaussian function.

When one applies the FC method to the Gaussian initial function, the FC wave function is generated as:

$$\psi_{(n)} = \sum_{i=0}^{n}(c_{i,1}r^{3i-4} + c_{i,2}r^{3i-2} + c_{i,3}r^{3i})e^{-\beta r^2} = \sum_{j=0}^{M_n} c_j r^j e^{-\beta r^2}. \quad (28)$$

In the above equation, the powers of r must be nonnegative and so $c_{0,1} = c_{0,2} = c_{1,1} = 0$. The number of terms at order n, M_n is $M_0 = 1$ and $M_n = 3n$ for $n \geq 1$. This is three times larger than for the Slater case.

The cusp value of the FC wave function given by Eq. (28) is calculated as:

$$\mathrm{Cusp}_{(n)} = \frac{c_1}{c_0} = \frac{c_{1,2}}{c_{0,3}}, \quad (29)$$

which should be equal to -1 for the exact wave function. Only the first two coefficients in Eq. (28) are related to the cusp value. Because the values of c_0 and c_1 change as the order of the FC method increases, the cusp value should be improved as the order n increases. In contrast to Eq. (24) of the Slater case, the cusp value in the Gaussian case is independent of the value of β, as is easily expected: it is simply equal to the ratio c_1/c_0. When the Gaussian set includes only s-type Gaussians, $e^{-\beta r^2}$, the cusp value can never be described. This situation is different from the generation of a Slater-type function from a Gaussian function. For example:

$$e^{-\alpha r} = \frac{\alpha}{2\sqrt{\pi}}\int_0^\infty \beta^{-\frac{3}{2}} e^{-\alpha^2/4\beta} e^{-\beta r^2} d\beta, \quad (30)$$

requires Gaussian functions with an infinite number of different exponents. However, in the FC method, it always generates the term $re^{-\beta r^2}$, so that it has the potential to describe the cusp value well, even if we start from the Gaussian function.

Similar to the Slater case, if we apply the condition that the local energy should be equal to the exact energy even at the nuclear-electron singularity point, i.e., Eq. (24), together with the cusp condition, we obtain the relation:

$$\left.\frac{c_2}{c_0}\right|_{\text{at exact}} = \left.\frac{c_{2,1}}{c_{0,3}}\right|_{\text{at exact}} = \frac{1}{3}(Z^2 - E) + \beta, \quad (31)$$

for the Gaussian case, where Z is the nuclear charge.

It is interesting to use the cusp condition and also the local energy condition at the nucleus as the constraints to the trial wave function, but in the present FC calculations, we performed free variation without using any constraints at all. When we perform the FC calculations to essentially infinite order, these two calculations should give the same results, i.e., the exact wave function and energy.

We summarize in Table III the various quantities calculated from the FC wave function starting from the Gaussian initial function. The first column shows the order n and the second shows the number of complement functions M_n in each order of the FC calculation. The third column is the variational upper bound energy. It converges from above to the exact value of -0.5 au. The number of

TABLE III

The convergence of the energy, coefficients, wave function error, H-square error, average local energy near the nucleus, and the cusp value of the FC wave function starting from the Gaussian initial function.

n^a	$M_n{}^b$	Energy (a.u.)	c_1/c_0	c_2/c_0	Wave function error	H-square error	*L.E.*	Cusp
0	1	−0.305			5.024×10^{-1}	7.177×10^{-2}	−149.812	0.000
1	3	−0.427	−0.279		7.134×10^{-2}	1.458×10^{-1}	−107.932	−0.279
2	6	**−0.49**835	−0.813	0.288	7.356×10^{-4}	1.688×10^{-2}	−28.096	−0.813
3	9	**−0.4999**8908	**−0.9**724	**0.**4985	4.342×10^{-6}	2.445×10^{-4}	−4.496	**−0.9**724
4	12	**−0.4999999**559	**−0.99**723	**0.5**533	1.597×10^{-8}	1.677×10^{-6}	−0.893	**−0.99**723
5	15	**−0.499999999**8718	**−0.999**784	**0.56**1547	4.129×10^{-11}	7.439×10^{-9}	**−0.5**299	**−0.999**784
10	30	**−0.4999999999999999999**580	**−0.99999999**636	**0.5624999**603	4.735×10^{-20}	8.937×10^{-19}	**−0.500000**441	**−0.99999999**636
15	45	**−0.49999999999999999999999**899	**−1.0000000000**324	**0.562500000**641	1.103×10^{-24}	3.788×10^{-23}	**−0.49999999**674	**−1.0000000000**324
20	60	**−0.499999999999999999999999999**888	**−0.999999999999**468	**0.5624999999**838	1.213×10^{-28}	6.543×10^{-27}	**−0.5000000000**419	**−0.999999999999**468
25	75	**−0.4999999999999999999999999999999**655	**−1.0000000000000**131	**0.562500000000**552	3.699×10^{-32}	2.823×10^{-30}	**−0.499999999999**233	**−1.0000000000000**131
30	90	**−0.4999999999999999999999999999999999**778	**−0.999999999999999**562	**0.5624999999999**757	2.356×10^{-35}	2.385×10^{-33}	**−0.5000000000000**176	**−0.999999999999999**562
35	105	**−0.4999999999999999999999999999999999999**750	**−1.0000000000000000**185	**0.56250000000000**129	2.641×10^{-38}	3.392×10^{-36}	**−0.499999999999999**533	**−1.0000000000000000**185
40	120	**−0.499999999999999999999999999999999999999**761	**−0.999999999999999999**608	**0.5624999999999999**767	4.650×10^{-41}	7.335×10^{-39}	**−0.5000000000000000**129	**−0.999999999999999999**608
45	135	**−0.49999999999999999999999999999999999999999**782	**−0.999999999999999999**761	**0.5624999999999999**813	1.187×10^{-43}	2.243×10^{-41}	**−0.50000000000000000**430	**−0.999999999999999999**761
50	150	**−0.4999999999999999999999999999999999999999999**648	**−1.0000000000000000000**312	**0.56250000000000000**249	4.141×10^{-46}	9.202×10^{-44}	**−0.499999999999999999**480	**−1.0000000000000000000**312
Exact		**−0.5**	**−1**	**0.5625**	**0**	**0**	**−0.5**	**−1**

[a] Order.

[b] Number of complement functions at order *n*.

correct digits in energy is 10, 19, 28, 34, 39, and 43 for $n = 5$, 10, 20, 30, 40, and 50, respectively. Because the number of Gaussian functions at each order is three times larger than that for the Slater case, the energy is relatively good for small orders, but, at $n = 50$, the result for the Slater function with 51 complement functions is better than that for Gaussians with 150 complement functions. Although these results are also dependent on the values of the exponents, α and β, we may conclude that the Slater function is a better function, as expected, for describing the hydrogen atom using the FC method.

The fourth and fifth columns show the coefficient ratios c_1/c_0 and c_2/c_0, which must be -1 and $9/16 = 0.5625$, respectively, for the exact wave function. These values were estimated from Eqs. (29) and (31). As a feature of the variation calculation, the coefficients converge more slowly than the energy. The number of correct digits of c_1/c_0 are 3, 8, 13, 15, 18, and 19 and those for c_2/c_0 are 2, 7, 10, 13, 16, and 17, respectively, for $n = 5$, 10, 20, 30, 40, and 50. These numbers are less than half those for energy. The coefficient c_2/c_0 is always less accurate than c_1/c_0 for similar reasons to those for the Slater case. These coefficients oscillate while converging to the exact value.

The sixth and seventh columns show the wave function error and the H-square error. They converge very rapidly to the exact value, zero. The accuracy of these values at each order in the present Gaussian case is similar to that in the previous Slater case, although the number of functions, M_n is three times larger than in the Slater case. Again, the numbers of correct digits of the H-square error, 9, 19, 27, 33, 39, and 44 are almost the same as the numbers of correct digits of the calculated energy, 10, 19, 28, 34, 39, and 43 for $n = 5$, 10, 20, 30, 40, and 50, respectively. This again supports the estimation in the FC method about the number of correct digits of the calculated energy from the accuracy of the calculated H-square error.

Finally, the last two columns show the local energy near the nucleus and the cusp value. The cusp value starts from zero in the present Gaussian case and gradually approaches the correct value. This shows that even starting from the Gaussian function, the FC method finally gives the correct cusp value. This is necessary for the FC method to give the exact wave function at convergence, because the exact wave function must satisfy the cusp condition. The local energy is very low for lower orders, because this quantity reflects the singularity of the attractive nuclear potential at the nuclear origin, but gradually approaches the correct value from about order 5 and becomes more and more correct as the order increases.

Thus, even starting from the Gaussian function, all the quantities shown in Table III converge well to their exact values. This should be so, because in our theoretical proof of the exactness of the free ICI theory, we did not assume any restriction on the initial wave function, except that it should have an overlap with the exact wave function to be calculated. Therefore, the Gaussian function can safely be used as the initial function of the FC method. This may be particularly so in molecular calculations. From the computational point of view, any function can be used if the integrations in the variation calculations or the sampling in the LSE calculations are easy. A rapid convergence, i.e., a correctness of the calculated wave function versus the number of complement functions M_n used, is an important criterion in the choice of the initial function. In this sense, the Slater function is much better than the Gaussian function. In the present case, about three times more functions were used for the Gaussian functions than for the Slater functions. In both variation and LSE calculations, the smaller number of functions in the Slater case is definitely a merit.

Electron–Nucleus and Electron–Electron Cusp Conditions for the Helium Atom and the r_{12} Terms

For more than two particle systems, there is a chance where particles 1 and 2 with the coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ approach each other within a very small distance r ($r = |\mathbf{r}_1 - \mathbf{r}_2|$), and all the other particles 3, 4, … are well separated from particles 1 and 2, i.e., $r' > r$, where r' represents the particle–particle distances between $\mathbf{r}_i$ and $\mathbf{r}_j$ ($i = 1$ or 2 and $j = 3$, 4, …). Kato [33] rigorously proved the cusp condition for such a many-electron system as:

$$\left.\frac{\partial \bar{\psi}}{\partial r}\right|_{r=0} = \lambda \psi(r = 0), \tag{32}$$

where $\bar{\psi}$ represents the spherically averaged wave function around $r = 0$. The value λ should be $-Z$ (the nuclear charge) for electron–nucleus coalescence, and 1/2 for electron–electron singlet pair coalescence. Pack and Byers Brown [35] derived the explicit formulations of the coalescence conditions without spherical averaging and for identical particles. The spatial wave function at the coalescence point of the identical particles should be symmetric or antisymmetric to the interchange of the particles. The Pauli principle requires that the spatial wave function of the singlet pair must be symmetric and that of the triplet pair should be antisymmetric and, therefore, the triplet-pair wave function becomes $\psi = 0$ at $r = 0$.

For many-electron systems, the wave function may be expanded (and spherically averaged) around $r_{12} \approx 0$ as:

$$\bar{\psi} = c_0 + c_1 r_{12} + c_2 r_{12}^2 + \ \ldots, \tag{33}$$

where r_{12} is an electron–electron distance. Eq. (33) implies the importance of including the r_{12} term explicitly in the wave function. In 1929 [36], Hylleraas first introduced the explicit r_{12} dependence in his wave function of the helium atom and obtained the energy accurate to within mH with only three terms in the wave function. To achieve the same accuracy with the ordinary orbital expansion method, many functions would become necessary. So, it is important to describe well the behaviors of the wave function around the region near $r_{12} \approx 0$. If the first two coefficients in Eq. (33) satisfy the relation:

$$c_1 = \frac{1}{2} c_0, \tag{34}$$

then the electron–electron cusp condition given in Eq. (32) is satisfied.

In the FC method, such explicit r_{12} dependence is automatically generated in the ICI step and, therefore, the FC wave function shows quite excellent convergence to the exact wave function. This has actually been shown previously for the helium atom, giving highly accurate energy, wave function, and properties [19, 21, 23, 24]. More recently [25], we have further examined the local energy, H-square error, and energy upper and lower bounds using the FC wave function of the helium atom and shown the highly accurate nature of the FC wave function. Here, we rigorously examine the electron–nucleus and electron–electron coalescence properties using the same wave function of the helium atom [19].

The electron–nucleus and electron–electron cusp conditions for the nth-order FC wave function of the helium atom $\psi_{(n)}$ are expressed, similarly to Eq. (21), as:

$$\mathrm{Cusp}_{(n)}(\mathbf{r}') = \frac{1}{\psi_{(n)}(r=0)} \cdot \left. \frac{\partial \psi_{(n)}}{\partial r} \right|_{r=0}, \tag{35}$$

where $r = |\mathbf{r}_1 - \mathbf{r}_2|$. The difference from Eq. (21) is that the cusp value of Eq. (35) depends on the other coordinate $\mathbf{r}' = \mathbf{r}_3 - \mathbf{r}_1$. Without any spherical average, if particles 1 and 2 approach each other perpendicularly to $\mathbf{r}'$, i.e., $\mathbf{r} \cdot \mathbf{r}' = 0$, then the cusp value, $\mathrm{Cusp}_{(n)}(\mathbf{r}')$ depends on the distance r' ($\mathrm{Cusp}_{(n)}(r')$) but, at any r', it should converge to $-Z$ for the electron–nucleus case and $1/2$ for the electron–electron singlet-pair case as the order n increases.

Tables IV and V show the convergence behaviors of the cusp values, $\mathrm{Cusp}_{(n)}(r')$ given by Eq. (35), for the electron–nucleus and electron–electron coalescences, respectively, with the condition $\mathbf{r} \cdot \mathbf{r}' = 0$, i.e., $\theta' = \pi/2$. Because such cusp values are still a function of r', we tested three cases with $r' = 0.03$, 1.0, and 5.0 (a.u.). Although the FC wave function [19] was calculated without any constraint on the cusp properties, the electron–nucleus and electron–electron cusp values of the FC wave functions converge to the correct values as the order n increases, even for different values of r'. When $r' = 0.03$, the third particle is very close to the coalescence point, and therefore, the convergence is slightly worse than in the two other cases. However, these cusp values with $r' = 0.03$ attain the correct precision of almost 19 digits at the order $n = 27$ for both the electron–nucleus and electron–electron cases; they have almost the same or slightly better accuracy as the accuracy of the wave function estimated from the H-square error [25]. This indicates that the FC wave function was calculated correctly even in the region very close to the electron–nucleus and electron–electron coalescence regions.

If r' approaches much closer to 0, i.e., if all three particles collide, then our assumption of $\mathbf{r} \cdot \mathbf{r}' = 0$ is not satisfied and we must consider the three-particle coalescence condition explicitly. Several authors have studied the three-particle coalescence condition extensively [37–39]. The logarithmic weak singularity is very important to represent this condition well, and we introduced such a logarithmic singularity into our FC wave function [19]. We have also shown that the exponential integral (Ei) function can also describe the same weak singularity property even better than the logarithm function [24].

Conclusions

We have shown how the FC method improves the wave function starting from a given initial wave

TABLE IV

Electron–nucleus cusp values of the FC wave functions of helium atom published in [19].

		$\mathrm{Cusp}_{(n)}^{N-e}(r',\theta' = \pi/2)$ (a.u.)		
n[a]	M_n[b]	$r' = 0.03$	$r' = 1.0$	$r' = 5.0$
0	2	15.800818910489975718562	–1.714691761867488968865309	–1.81050235465118582747250
1	10	5.7656200348575955966519	**–2.0**37695302738053451073425	**–1.9**3885007205207453085670
2	34	–2.004006089500033721060	**–2.00**2504052234478500223599	**–2.00**492083097179888665935
3	77	–0.6907654637216551659013	**–2.0000**95337681210167679009	**–1.999**71747640800371454340
4	146	**–2.0**84238608631479552328	**–1.9999**60751001985481002999	**–2.000**15420324811064257670
5	247	**–2.00**8980415080118959667	**–2.00000**4034901946326124536	**–1.99999**304204835715978318
6	386	**–1.999**071200433179942111	**–2.000000**252006472327502965	**–2.00000**100131988011343124
7	569	**–1.9999**52965873027058359	**–1.99999999**0139523025500075	**–1.999999**47142251626522246
8	802	**–2.00000**5321742295295912	**–2.00000000**1732245168503244	**–2.000000**11212220909873839
9	1,091	**–2.00000**1471632546928489	**–1.9999999999**54741231937599	**–1.9999999**7932798968526278
10	1,442	**–1.999999**861472086577460	**–2.0000000000**28992139510927	**–2.00000000**344673723392008
11	1,861	**–2.000000000**505346833941	**–1.99999999999**4506214502899	**–1.999999999**46760042302302
12	2,354	**–1.999999999**266341600055	**–2.000000000000**770317391674	**–2.0000000000**9025112007165
13	2,927	**–2.000000000**124129877163	**–1.9999999999999**18885202492	**–1.9999999999**8436694386263
14	3,586	**–1.9999999999**86243251568	**–2.00000000000000**7641057691	**–2.00000000000**265742947846
15	4,337	**–2.000000000000**994338045	**–1.99999999999999**8856501484	**–1.999999999999**55448364436
16	5,186	**–2.000000000000**242424477	**–2.000000000000000**172175707	**–2.0000000000000**7306734972
17	6,139	**–2.0000000000000**55805156	**–1.9999999999999999**68175846	**–1.9999999999999**8812436025
18	7,202	**–2.00000000000000**2702633	**–2.00000000000000000**6492680	**–2.00000000000000**192795141
19	8,381	**–1.99999999999999**8362005	**–1.99999999999999999**8818275	**–1.999999999999999**68668361
20	9,682	**–1.999999999999999**858871	**–2.000000000000000000**112782	**–2.0000000000000000**5084416
21	11,111	**–2.0000000000000000**82375	**–1.9999999999999999999**73697	**–1.99999999999999999**177068
22	12,674	**–2.0000000000000000**13560	**–2.0000000000000000000**16585	**–2.00000000000000000**132618
23	14,377	**–1.9999999999999999**75596	**–1.99999999999999999999**7746	**–1.999999999999999999**78670
24	16,226	**–1.9999999999999999**83930	**–1.99999999999999999999**8202	**–2.0000000000000000000**3546
25	18,227	**–1.99999999999999999**6283	**–2.000000000000000000000**911	**–1.99999999999999999999**279
26	20,386	**–2.000000000000000000**600	**–1.999999999999999999999**660	**–2.00000000000000000000**249
27	22,709	**–2.000000000000000000**286	**–2.000000000000000000000**175	**–1.99999999999999999999**858
Exact		**–2.0**	**–2.0**	**–2.0**

[a] Order.

[b] Number of the complement functions at order *n*.

function, taking the hydrogen atom as an example. We have shown two versions of this process, starting from the Slater function and the Gaussian function. The accuracy of the wave function in the course of the FC calculations was checked by examining the wave function itself, using c_0, c_1, and c_2, and several other quantities: the energy, wave function error, H-square error, average local energy near the nucleus, and the cusp value. All these quantities converged well to the exact values, irrespective of the type of initial function used. It was shown numerically that the FC method certainly gives the exact wave function at convergence.

Between the Slater and Gaussian functions, the accuracy was similar at each order. However, the number of complement functions was three times larger in the Gaussian case than in the Slater case, and therefore, practically speaking, the Slater function is superior to the Gaussian function. Although the starting Gaussian function did not have a cusp, the FC method improves this property as well and finally the cusp value becomes essentially the exact value. The same was true for the Slater case: although the initial cusp was wrong, it became almost exact at a high order of the FC calculations.

As an example of many-electron cases, the electron–nucleus and electron–electron cusp conditions were examined for the FC wave function of the helium atom published in an earlier paper [19]. The FC method automatically generates the complement functions including the r_{12} prefactors explicitly. Therefore, the FC method improves not only

TABLE V

Electron–electron cusp values of the FC wave functions of helium atom published in [19].

		$\mathrm{Cusp}^{e-e}_{(n)}(r',\theta' = \pi/2)$ (a.u.) (a.u.)		
n[a]	M_n[b]	$r' = 0.03$	$r' = 1.0$	$r' = 5.0$
0	2	17.62781891048997571856	0.1123082381325110311346903	0.01649764534881417252
1	10	1.521183587259717985953	**0.5**388261133165970364082007	–0.6950777030756195274
2	34	0.4195059827128190888337	**0.49**31913843555658894128673	0.47555759694327787520
3	77	0.4472420070136433186987	**0.499**3133049214858311939703	**0.5**1698967972633002260
4	146	**0.49**18106859386469962874	**0.4999**264052122836846890241	**0.5**2409383946851068709
5	247	**0.499**1219280690646784698	**0.4999**888812723545347905886	**0.49**804725181170437244
6	386	**0.499**8962297672840088628	**0.499999**3481518041394710234	**0.500**52694828961996437
7	569	**0.4999**858546938728264001	**0.499999**8678901444684668622	**0.499**80575942518210534
8	802	**0.49999**84110237687228715	**0.4999999**843747191143208148	**0.5000**2302305744417569
9	1,091	**0.499999**8217707126010523	**0.499999999**1854449195682342	**0.500000**31282247268772
10	1,442	**0.4999999**768427751319411	**0.4999999999**520485964408054	**0.499999**71075033927096
11	1,861	**0.49999999**70286532070810	**0.49999999999**68561359042406	**0.50000000**817826573147
12	2,354	**0.499999999**6797557610061	**0.5000000000000**789589242552	**0.50000000**547016285966
13	2,927	**0.4999999999**754541501899	**0.5000000000000**750757147237	**0.499999999**61124819570
14	3,586	**0.500000000000**1468808388	**0.5000000000000**128229900478	**0.499999999**87322976784
15	4,337	**0.500000000000**5768766807	**0.500000000000000**8582572593	**0.5000000000**2420671618
16	5,186	**0.500000000000**1588292557	**0.4999999999999999**293406817	**0.500000000000**42879920
17	6,139	**0.5000000000000**325241130	**0.4999999999999999**740766894	**0.499999999999**59385888
18	7,202	**0.50000000000000**57792613	**0.49999999999999999**57258457	**0.49999999999999**721270
19	8,381	**0.500000000000000**9199944	**0.499999999999999999**6645368	**0.5000000000000**1142711
20	9,682	**0.500000000000000**1310736	**0.5000000000000000000**124903	**0.50000000000000**106670
21	11,111	**0.5000000000000000**184315	**0.4999999999999999999**850833	**0.499999999999999**34857
22	12,674	**0.50000000000000000**40081	**0.50000000000000000000**87634	**0.500000000000000**21335
23	14,377	**0.50000000000000000**14014	**0.49999999999999999999**89519	**0.500000000000000000**82
24	16,226	**0.500000000000000000**3737	**0.499999999999999999999**5815	**0.4999999999999999**8970
25	18,227	**0.4999999999999999999**724	**0.500000000000000000000**5676	**0.5000000000000000**1608
26	20,386	**0.4999999999999999999**135	**0.499999999999999999999**7157	**0.49999999999999999**432
27	22,709	**0.4999999999999999999**579	**0.5000000000000000000000**691	**0.50000000000000000**231
Exact		**0.5**	**0.5**	**0.5**

[a] Order.
[b] Number of the complement functions at order n.

the r_i dependence (electron–nucleus) of the wave function, but also the r_{ij} dependence (electron–electron) of the wave function, and so makes the wave function essentially exact at high orders. This was supported here from the cusp values, as well as many other properties examined in an earlier article [25].

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