Free Complement Method for Solving the Schrödinger Equation: How Accurately Can We Solve the Schrödinger Equation

H. Nakatsuji and H. Nakashima

Abstract Free complement (FC) method provides a general and systematic method of solving the Schrödinger equation. In this method, the Hamiltonian of the system modified for the singularity of the potential is used to generate the FC functions that span the exact wave function of the system. Thus, by applying the variation principle to the sum of the complement functions, which we call FC wave function, we can calculate the essentially exact wave function and energy for the ground and excited states of the system. We here show that the Schrödinger equation can be solved to an arbitrary accuracy with the FC method by examining the upper and lower bounds of the energy, local energy, H-square error, cusp condition, and so on, for the helium atom.

Keywords: Solving the Schrödinger equation · Free complement method · Cusp condition · Upper and lower bounds

1 Introduction

This chapter summarizes briefly the lecture of Nakatsuji given on July 10, 2008, at the QSCP-13 workshop at Lansing organized by Prof. Piotr Piecuch of the Michigan State University. Let us first celebrate our exciting memories of this workshop for its high-quality science and good performance, and nice organization, all of which were due to the careful coordination and organization of the workshop by Profs. P. Piecuch and J. Maruani. So, let us first deeply thank Profs. Piotr Piecuch and Jean Maruani for all of this.

The Schrödinger equation has long been believed to be insoluble for over 80 years, since it was discovered by Prof. Erwin Schrödinger in 1926 [1], though it was believed to govern all of chemistry and most of physics [2]. For this reason, all we could have done in quantum science was to formulate "approximate" theories to "understand" or "interpret" the main features of chemical phenomena [2]. Thus,

H. Nakatsuji (✉) and H. Nakashima
Quantum Chemistry Research Institute, JST, CREST, Nishikyo-ku, Kyoto 615-8245, Japan,
e-mail: h.nakatsuji@qcri.or.jp

quantum chemistry has long been characterized as an approximate science that can never predict phenomena in full accuracy. However, recently, we have found simple, general, and accurate methods of solving the Schrödinger equation [3–13]. We referred to them as iterative complement (configuration) interaction (ICI) method [3, 4] and the free ICI [6] or free complement (FC) method [12], the latter two being the same.

The FC method is completely different from the conventional quantum chemistry. In the state-of-the-art quantum chemistry, one first defines Hartree–Fock orbitals based on the initially chosen basis set and then expands many-electron correlated wave functions by means of the Hartree–Fock orbitals. In this approach, any theory lies between the Hartree–Fock and the full CI and so, the full CI is a goal of this type of the theory. However, the full CI cannot be the exact solution of the Schrödinger equation because of the incompleteness of the basis set first introduced. When we use numerical Hartree–Fock that is free from the basis set, the full CI becomes infinite expansion that cannot be handled in principle.

Explicitly correlated wave function theory [14] is another important approach in quantum chemistry. One introduces inter-electron distances together with the nuclear–electron distances and set up some presumably accurate wave function and applies the variation principle. The Hylleraas wave function reported in 1929 [15] was the first of this theory and gave accurate results for the helium atom. Many important studies have been published since then even when we limit ourselves to the helium atom [16–28]. They clarified the natures and important aspects of very accurate wave functions. However, the explicitly correlated wave function theory has not been very popularly used in the studies of chemical problems in comparison with the Hartree–Fock and electron correlation approach. One reason was that it was generally difficult to formulate very accurate wave functions of general molecules with intuitions alone and another reason was that this approach was rather computationally demanding.

Thus, quantum chemistry has long been a science mainly for understanding and interpretation. It was difficult for quantum chemists to become truly confident on the calculated results. One reason was the approximate nature of the theory and another reason was an incompleteness of the basis set. For example, many people might have experienced the feeling of "maybe, my basis set was not good enough." In the author's opinion, quantitative reliability is a key of the theory. Otherwise, one cannot do "confident prediction." For getting truly quantitative reliability in theoretical quantum science, there is no other way than solving the Schrödinger equation and the Dirac–Coulomb equation accurately.

2 Free Complement Method

In 1999, one of the authors got an inspiration that the Schrödinger equation might be able to be solved. He clarified the structure of the exact wave function and showed a method of obtaining the exact wave function by introducing the ICI method and its variants [3, 4]. However, there still existed a big obstacle, called

singularity problem [6]. Namely, the integrals involved in the formulation diverge to infinity when the Hamiltonian involves Coulomb potential, as it does for atoms and molecules. However, a simple idea came. Instead of solving the original Schrödinger equation,

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

one may solve an equivalent equation, called scaled Schrödinger equation [6].

$$g(H - E)\psi = 0. \tag{2}$$

The factor g is called scaling function. It is always positive but can become zero only at the singular points. Even there, the g function must satisfy

$$\lim_{r \to 0} gH \neq 0 < \infty, \tag{3}$$

for not to erase the information of the Hamiltonian at the singular regions. Then, we can formulate the simplest ICI (SICI) method based on the scaled Schrödinger equation as

$$\psi_{n+1} = [1 + C_n g(H - E_n)]\,\psi_n, \tag{4}$$

where E_n is defined by $\langle \psi_n | g(H - E_n) | \psi_n \rangle = 0$. This SICI was also proved to become exact at convergence, and for the existence of the g-function, we do not encounter the singularity problem in the course of the iterative calculations.

When we do the SICI calculations to n-th iteration, the right-hand side of Eq. (4) becomes a sum of the analytical functions multiplied with the coefficients C_i. Now, we reformulate it as follows. 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 again our wave function as

$$\psi_{(n+1)} = \sum_i^{M_n} c_i \phi_i. \tag{5}$$

We referred to this wave function as the free ICI wave function. It converges faster to the exact wave function than the original SICI one, because of the increased freedom. In the SICI scheme, the $(n + 1)$-th result, ψ_{n+1}, depends on all the former results, ψ_m and $C_m (m = 0 \ldots n)$, 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 naming, the free ICI method may be confusing. So, hereafter we use 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.

The FC formalism for the exact wave function may be summarized as follows.

1. The Hamiltonian defines the system.
2. The Hamiltonian paves the way toward its exact wave functions in the analytical expansion form starting from a given initial function ψ_0: Eq. (4) in the SICI case or Eq. (5) in the FC formalism.
3. This formalism is applicable for any system when its Hamiltonian is defined unambiguously.
4. We have no basis set nightmare: the complement functions, which may correspond to the basis set, are generated by the Hamiltonian of the system and so should be a best possible functions for the system.

A general method for calculating the unknown coefficients in the FC wave function given by Eq. (5) is the variation principle. Applying the variation principle to the FC wave function, we obtain the secular equation

$$(\mathbf{H} - E\mathbf{S})\mathbf{C} = 0, \tag{6}$$

where the Hamiltonian and overlap matrices are defined by

$$\mathbf{H} = \begin{pmatrix} \cdot & \cdot & \cdot \\ \cdot & \int \phi_i H \phi_j \, d\tau & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix}, \mathbf{S} = \begin{pmatrix} \cdot & \cdot & \cdot \\ \cdot & \int \phi_i \phi_j \, d\tau & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix}. \tag{7}$$

For simple few-electron atoms and molecules, these matrix elements are easily calculated. We apply here our FC formalism only to such systems. Then, starting from the initial wave function ψ_0 and using some appropriate scaling function g, we can calculate the solution of the Schrödinger equation in an analytical expansion form. The accuracy of the calculated results would depend on the choices of ψ_0, g, and the expansion order n. We show here that, in principle, we can get the solution of the Schrödinger equation to any desired accuracy in this formalism.

3 Super-Accurate FC Calculation of Helium Atom

Helium atom is the simplest case for which the Schrödinger equation cannot be solved in a closed form. There have been many attempts to solve the Schrödinger equation of the helium atom accurately, starting from the famous study by Hylleraas [15–28]. These studies have produced a lot of important insights about the nature of the accurate wave functions of atoms and molecules. We applied the FC method described above to the helium atom immediately after this method was discovered [6]. It gave a strong support that the FC method was correct and useful. We have given more extended accurate calculations [9, 10] and examined the accuracy of the calculated wave functions by studying several properties that are the stringent test of the exactness of the wave functions [12, 13]. We have further studied the effect of nuclear motion [29] and the excited states with and without considering the effect of nuclear motion [30].

Here we overview our applications to the helium atom ground state. In the Hylleraas coordinate defined by

$$s = r_1 + r_2, \quad t = r_1 - r_2, \quad u = r_{12}, \tag{8}$$

the Hamiltonian in the fixed nucleus approximation is given by

$$H = -\left(\frac{\partial^2}{\partial s^2} + \frac{\partial^2}{\partial t^2} + \frac{\partial^2}{\partial u^2}\right) - 2\frac{s(u^2 - t^2)}{u(s^2 - t^2)}\frac{\partial^2}{\partial s \partial u} - 2\frac{t(s^2 - u^2)}{u(s^2 - t^2)}\frac{\partial^2}{\partial u \partial t},$$
$$- \frac{4s}{s^2 - t^2}\frac{\partial}{\partial s} - \frac{2}{u}\frac{\partial}{\partial u} + \frac{4t}{s^2 - t^2}\frac{\partial}{\partial t} - \frac{4sZ}{s^2 - t^2} + \frac{1}{u}, \tag{9}$$

where the last two terms represent the nuclear–electron attraction potential (Z is nuclear charge) and the electron–electron repulsion potential. The other terms originate from the kinetic operator. Using these potentials, we chose the g-function as

$$g = \frac{1}{V_{Ne}} + \frac{1}{V_{ee}}. \tag{10}$$

The initial function ψ_0 was chosen as

$$\psi_0 = [1 + \ln(s + u)]\exp(-\alpha s), \tag{11}$$

where the exponent α was dealt with as a variation parameter. The logarithmic dependence on s and u was introduced to describe well the three-particle coalescence region [16, 18, 20]. Then, the FC calculations are automatic and its wave function is guaranteed to become essentially exact at convergence. The FC wave function in this case is written as

$$\psi = \sum_i c_i\, s^{l_i} t^{m_i} u^{n_i} [\ln(s + u)]^{j_i} \exp(-\alpha s), \tag{12}$$

where l_i runs both positive and negative [9, 19] integers, $\{m_i, n_i\}$ run non-negative integers (m_i is even integers) and j_i is 0 or 1.

Table 1 shows the convergence of the variational energy [9]. The bold face implies that the figure is confidently reliable. A landmark calculation of the helium atom with the explicitly correlated wave function approach was done by Schwartz [28], who obtained the energy correct to 37 digits by applying the variation principle to his intuitively generated trial wave function. This was a surprising result. In the FC method, all we have to do is to fix ψ_0 and g function. Then, the FC formalism automatically generates a series of analytical functions in the form of Eq. (5). It is generated by the successive applications of the Hamiltonian and the g-function of the system to the starting wave function ψ_0 as expressed by Eq. (4). So, no severe intuition is necessary. Because this FC algorithm is automatic, we could continue the calculations up to the order n of 27 and obtained the energy correct to 41 digits.

Table 1 Ground-state energies of the helium atom calculated with the g function given by Eq. (10) and the initial function ψ_0 given by Eq. (11)[a]

n[a]	M_n[b]	Optimal α	Energy (a.u.)[c]
0	2	1.827	−**2.865** 370 819 026 71
1	10	1.475	−**2.903** 536 812 281 53
2	34	1.627	−**2.903 724** 007 321 45
3	77	1.679	−**2.903 724 3**75 094 16
4	146	1.683	−**2.903 724 377** 022 34
5	247	1.679	−**2.903 724 377 034** 05
6	386	1.693	−**2.903 724 377 034 119** 011 25
7	569	1.704	−**2.903 724 377 034 119 59**2 84
8	802	1.707	−**2.903 724 377 034 119 598** 24
9	1091	1.713	−**2.903 724 377 034 119 598 3**09 973 48
10	1442	1.724	−**2.903 724 377 034 119 598 311** 136 32
11	1861	1.738	−**2.903 724 377 034 119 598 311 15**8 76
12	2354	1.757	−**2.903 724 377 034 119 598 311 159** 23
13	2927	1.779	−**2.903 724 377 034 119 598 311 159 24**4 938 53
14	3586	1.806	−**2.903 724 377 034 119 598 311 159 245** 187 71
15	4337	1.837	−**2.903 724 377 034 119 598 311 159 245 194** 18
16	5186	1.866	−**2.903 724 377 034 119 598 311 159 245 194** 39
17	6139	1.899	−**2.903 724 377 034 119 598 311 159 245 194 40**3 526 60
18	7202	(1.93)	−**2.903 724 377 034 119 598 311 159 245 194 404** 346 36
19	8381	(1.96)	−**2.903 724 377 034 119 598 311 159 245 194 404 4**33 80
20	9682	(1.99)	−**2.903 724 377 034 119 598 311 159 245 194 404 44**4 83
21	11111	(2.02)	−**2.903 724 377 034 119 598 311 159 245 194 404 446** 40
22	12674	(2.05)	−**2.903 724 377 034 119 598 311 159 245 194 404 446 6**46 839 61
23	14377	(2.08)	−**2.903 724 377 034 119 598 311 159 245 194 404 446 68**7 685 92
24	16226	(2.11)	−**2.903 724 377 034 119 598 311 159 245 194 404 446 695** 101 79
25	18227	(2.14)	−**2.903 724 377 034 119 598 311 159 245 194 404 446 696** 542 44
26	20386	(2.17)	−**2.903 724 377 034 119 598 311 159 245 194 404 446 696 8**40 21
27	22709	(2.20)	−**2.903 724 377 034 119 598 311 159 245 194 404 446 696 90**5 37
Ref. 28	10259		−2.903 724 377 034 119 598 311 159 245 194 404 440 049 5

[a] Order of the FC wave function.
[b] Number of complement functions at order n.
[c] Surely correct digit is shown by the bold face.

The 37-digit accuracy was attained at order 20. There, the number of the complement analytical functions was 9682, which is a bit smaller than 10,256, the number of the analytical functions used by Schwartz.

More recently, we have found that the exponential integral (Ei) function describes the three-particle coalescence region better than the logarithmic function [10]. So, starting with the Ei function, we could obtain a better energy at the order $n = 27$ with smaller number of variables; the energy was correct up to 43 digits.

We have applied the same method as above to the helium iso-electronic ions with Z from 1 to 10. The resultant FC wave functions had exactly the same form as Eq. (12) with only one difference in the exponents α. We performed the calculations up to the order 20 and obtained the lowest variational energies ever obtained [9]. The calculations consisted of three steps: (1) complement function generation step

using MAPLE [31], (2) integral evaluation step, (3) diagonalization step in arbitrary accuracy. It took about 3 hours for the step (1), 2 days for the step (2), and 1.5 days for the step (3), with a single Intel(R) Core2 Duo 2.8 GHz workstation. We used MAPLE also in the second step, which means that this step can be substantially accelerated. Anyway, roughly 4 days were enough to get the world best energies and the analytical wave functions of the helium iso-electronic ions.

4 Properties Suitable for Checking the Exactness of the Calculated Wave Functions

To verify the exactness of the calculated results, the calculated energy alone is insufficient. We examine here several quantities that offer stringent test about the exactness of the calculated energy and wave function. Most of the properties shown here are useful only for the wave functions near the exact limit, otherwise, they show quite arbitrary numbers.

The Schrödinger equation is a local equation that must be satisfied at any local coordinate r. It is written as

$$\frac{H\psi(r)}{\psi(r)} = E(const.) \quad (^\forall r), \tag{13}$$

where $\psi(r)$ is the wave function at a coordinate, r. The left-hand side of Eq. (13) is called local energy, $E_L(r)$, as

$$E_L(r) = \frac{H\psi(r)}{\psi(r)}. \tag{14}$$

If ψ is not an exact wave function, then $E_L(r)$ may depend on r. If $E_L(r)$ is a constant at any point r, then Eq. (14) becomes Eq. (13), which is the Schrödinger equation. Therefore, the constancy of the local energy over the coordinate r is a straightforward test of how well the wave function ψ satisfies the Schrödinger equation.

In the formulation of the structure of the exact wave function, we introduced the H-square equation [3, 4],

$$\langle\psi|(H - E)^2|\psi\rangle = 0 \tag{15}$$

as the equation that is equivalent to the Schrödinger equation. When we define the left-hand side of Eq. (15) as

$$\sigma^2 = \langle\psi|(H - E)^2|\psi\rangle \tag{16}$$

for the normalized wave function and call it as H-square error, it is also the quantity that is very sensible to the exactness of the calculated wave function, because it is

an integral sum of the positive quantities over all the coordinates. $\sigma^2 = 0$ means that the corresponding wave function is exact. The H-square error is also related to the local energy by

$$\sigma^2 = \langle E_L^2 \rangle_{\psi^2} - \langle E_L \rangle_{\psi^2}^2,$$ (17)

where $\langle Q \rangle_{\psi^2}$ represents the expectation value of Q over the weight function $|\psi|^2$. Thus, σ^2 is the variance of the local energy weighted by $|\psi|^2$.

When we use the variation principle, the calculated energy is an upper bound to the exact energy, but as far as we do not know the exact energy, we cannot say how close the calculated energy is to the exact energy. A good theoretical way is to calculate the lower bound to the exact energy at the same time. If we can calculate both upper and lower bounds to the exact energy in high accuracy, we can predict the energy of the system with the error bars. The utility of such method lies entirely in the smallness of the error bars. As far as we use the variation principle, the upper bound of the exact energy is calculated twice more accurately than the accuracy of the wave function itself.

For the lower energy bound, Weinstein formulated the following expression [32],

$$E_{lower}^W = \langle \psi | H | \psi \rangle - \sqrt{\sigma^2}.$$ (18)

The Weinstein's lower bound is calculated for any state when its σ^2 and energy expectation value are known. However, a problem of this method is that the quality (accuracy) of this lower bound is not good enough: it is usually too low to be useful. Another method was proposed by Temple [33] for the ground state as

$$E_{lower}^T = \langle \psi | H | \psi \rangle - \frac{\sigma^2}{E_1 - \langle \psi | H | \psi \rangle},$$ (19)

which requires the energy expectation value, σ^2 and, furthermore, the exact energy E_1 of the first excited state having the same symmetry as the ground state. In general, the exact energy E_1 is not known and so we have to modify Eq. (19). If one replaces E_1 with its lower bound energy, then one obtains the energy that is lower than the Temple's lower bound energy given by Eq. (19). We used the Weinstein's formula, Eq. (18), for calculating the lower bound to the first excited state, $E_1^W = \langle \psi_1 | H | \psi_1 \rangle - \sqrt{\sigma_1^2}$, where ψ_1 and σ_1^2 are the quantities for the first excited state. Then, $E_1 \geq E_1^W$. When this further satisfies $E_1^W > \langle \psi | H | \psi \rangle$, then we can define the modified Temple's lower bound energy by

$$E_{lower}^{T'} \equiv \langle \psi | H | \psi \rangle - \frac{\sigma^2}{E_1^W - \langle \psi | H | \psi \rangle},$$ (20)

which satisfies

$$E_{exact} \geq E_{lower}^T \geq E_{lower}^{T'}.$$ (21)

The modified Temple's lower bound energy can be calculated only with the available theoretical quantities. Combining Eq. (21) with the result of the variation calculation, E_{upper}, we obtain

$$E_{upper} \geq E_{exact} \geq E_{lower}^{T'}. \tag{22}$$

When we calculate both the upper and lower bound of Eq. (22), we can say that the exact energy should lie in a definite region of the energy.

The cusp values of the wave function are also the necessary conditions of the exact wave function. Kato [34] rigorously derived the cusp conditions for many-electron systems as

$$\left. \frac{\partial \bar{\psi}}{\partial r} \right|_{r=0} = \lambda \psi(r = 0), \tag{23}$$

where $\bar{\psi}$ represents the spherically averaged wave function around the inter-particle coalescence region, $r = 0$. The value λ should be $-Z$ (nuclear charge) for the electron–nucleus coalescence and 1/2 for the electron–electron singlet-pair coalescence. We examine here the cusp values for the helium atom. The electron–nucleus and electron–electron cusp values for the helium wave function ψ are expressed, similarly to Eq. (23), as

$$Cusp(\mathbf{r}') = \frac{1}{\psi(r = 0)} \cdot \left. \frac{\partial \psi}{\partial r} \right|_{r=0}, \tag{24}$$

where $r = |\mathbf{r}_1 - \mathbf{r}_2|$ [13]. The difference from Eq. (23) is that the cusp value of Eq. (23) depends on the other coordinate $\mathbf{r}' = \mathbf{r}_3 - \mathbf{r}_1$ [35]. Without any spherical average, if the particles 1 and 2 approach each other perpendicularly to $\mathbf{r}'$, i.e., $\mathbf{r} \cdot \mathbf{r}' = 0$, then the cusp value still depends on the distance r' ($Cusp(r')$), but at any r', it should be $-Z$ for the electron–nucleus case and 1/2 for the electron–electron singlet-pair coalescence case.

5 Exactness Check of the Calculated Wave Functions

We examine the exactness of the helium wave function calculated by the FC method by calculating the quantities summarized in the above section.

Figure 1 shows the plots of the local energy at different orders up to $n = 27$ [12]. The helium nucleus is at the origin, one electron is located at $z = 0.5$ a.u. on the z-axis and the other electron moves along the z-axis from $z = -1.0$ to $+1.0$, experiencing the nuclear singularity at the origin and the electron singularity at $z = 0.5$. The vertical axis shows the relative value of the local energy, E_Y, which is scaled by the factor, ε, shown on the top of the vertical axis of each graph. Therefore, the local energy at each point, E_L, is calculated from the energy, E, shown on each
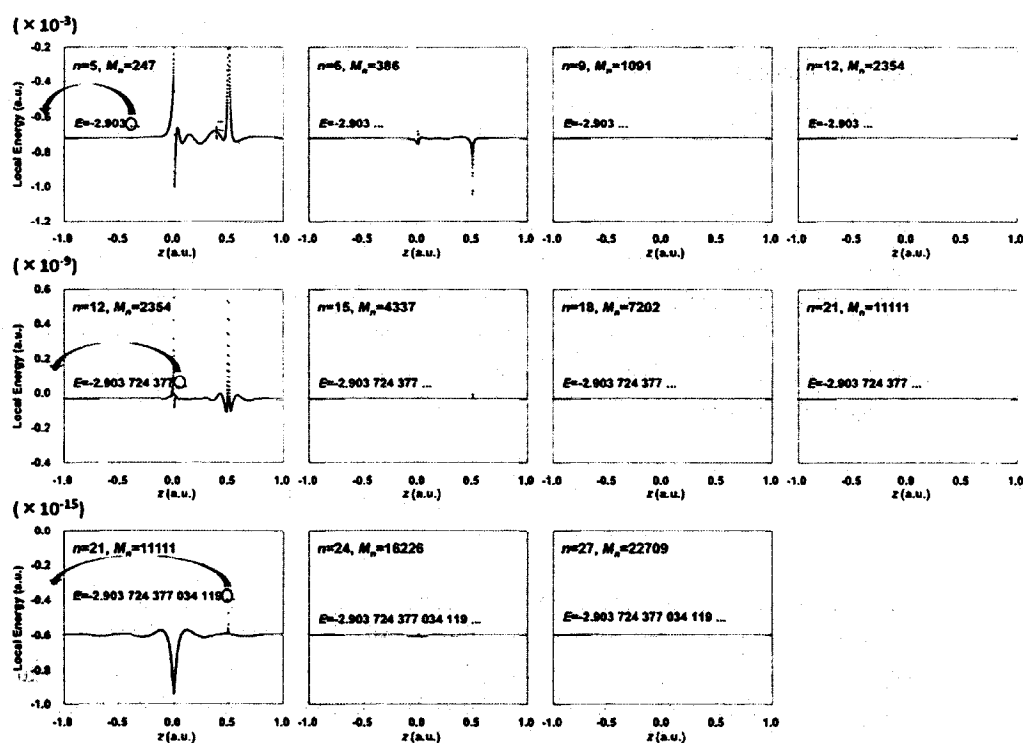
Fig. 1 Local energy plots of the FC wave functions for the orders n from 5 to 27. The *arrows* and *circles* in the *left-hand figures* show the digits of the total energy, in which the local energy is shown on the vertical axis changes

graph and the value of E_Y from $E_L = E + \varepsilon E_Y$. At the order $n = 5$, the local energy oscillates near the nucleus and another electron in the order of 10^{-3} a.u. However, at $n = 6$, the local energy becomes almost constant, except for the regions very close to the singularities. At $n = 9$ and $n = 12$, the local energy appears to be constant in the scale of 10^{-3} a.u. However, when we use a microscope and enlarge the figure by a scale of 10^6, we again see the fluctuations near the nuclear and electron singularities. Again, as we increase the order n from 12 to 15, 18, and 21, these fluctuations disappear and the local energy becomes completely flat. The same is true again in the last three figures in a finer scale.

In Fig. 2, we showed a very fine-detailed behavior of the local energy near the nuclear singularity and the electron singularity. Though there are fluctuations there, their half widths are very narrow, of the order of 10^{-5} a.u. and the heights of $0.5 - 1 \times 10^{-16}$ a.u. In all other regions of the space, the local energy is highly constant.

We next show in Table 2 the H-square error σ^2 and the energy lower bound calculated by the modified Temple equation. As the order n of the FC wave function increases, the H-square error gradually decreases and converges towards zero, the exact value. It is as small as 1.29×10^{-32} at $n = 27$. When the H-square error becomes zero, it means that the wave function becomes exact. So, this table means that, as the order n increases, the FC wave function approaches the exact wave
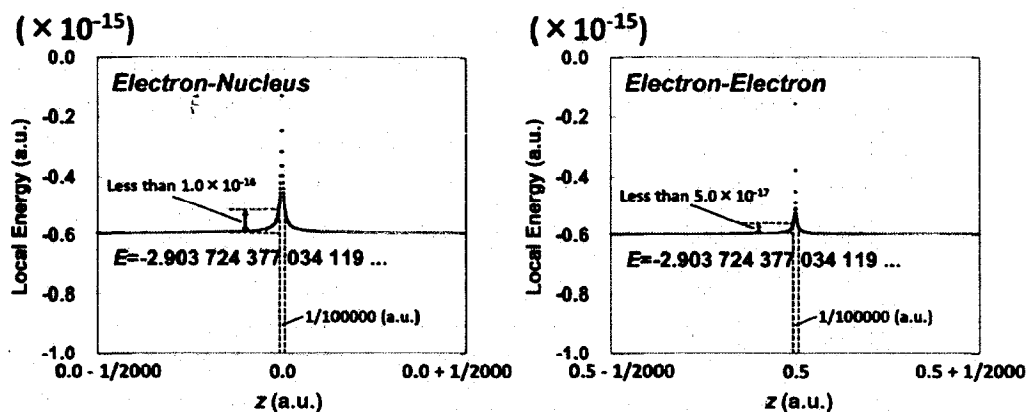
Fig. 2 Local energy plots at $n = 27$ ($M_n = 22709$) around the regions very close to the electron–nucleus ($z = 0$) and electron–electron ($z = 0.5$) singularities, where the local energy singularities are within 1.0×10^{-16} and 5.0×10^{-17} a.u., respectively, for an interval of $1/100000$ a.u.

Table 2 Convergence of the H-square error, σ^2, and the modified Temple's energy lower bound with increasing order n of the FC wave function

Order, n	M_n^{a}	H-square error, σ^2	Energy lower bound[b]
5	247	2.934869×10^{-9}	$-$**2.903 724 380** 97
6	386	4.782529×10^{-10}	$-$**2.903 724 377** 674
9	1091	1.095586×10^{-15}	$-$**2.903 724 377 034** 121 066
12	2354	5.007353×10^{-21}	$-$**2.903 724 377 034 119 598 317** 869
15	4337	1.835489×10^{-24}	$-$**2.903 724 377 034 119 598 311 161** 704
18	7202	5.372350×10^{-27}	$-$**2.903 724 377 034 119 598 311 159 252** 393
21	11111	4.000913×10^{-29}	$-$**2.903 724 377 034 119 598 311 159 245** 248
24	16226	5.665577×10^{-31}	$-$**2.903 724 377 034 119 598 311 159 245 195** 163
27	22709	1.293955×10^{-32}	$-$**2.903 724 377 034 119 598 311 159 245 194 421** 785

[a] Number of the complement functions for order n.
[b] Correct figure is expressed in bold face.

function, as shown clearly by the theoretical formulation [3, 4, 6]. This table confirms this numerically and further shows that the convergence speed is good.

As the order n of the FC wave function increases, the accuracy of the energy lower bound also increases. It approaches the exact value from below. This is in contrast to the variational energy shown in Table 1, which approaches the exact value from above. Using these lower and upper bounds to the exact energy, we can confidently predict that the exact energy should lie between the two bound energies, that is,

$$-2.903\,724\,377\,034\,119\,598\,311\,159\,245\,194\,421\,785 < E_{\text{exact}} <$$

$$-2.903\,724\,377\,034\,119\,598\,311\,159\,245\,194\,404\,446\,696\,905\,37, \qquad (25)$$

where the bold-face digits show that this number is confidently correct. Thus, we can predict in confidence that the exact non-relativistic energy of the helium atom in the fixed nucleus approximation is $-$**2.903 724 377 034 119 598 311 159 245 194 4** a.u.,

which is correct to 32 digits. From the experience of the variational calculations, we can estimate the correct digits of the exact energy in higher accuracy, as shown in the upper bound of the exact energy shown in the above formula (25). Though we are confident about the correctness of the bold-face digits, the most a priori estimate of the exact energy is due to the accurate calculations of both of the upper and lower bounds of the exact energy, as shown in the above formula (25).

Finally, we examine the cusp values for the helium atom. Table 3 shows the nuclear–electron and electron–electron cusp values at the distance $r' = 1.0$ a.u., which was explained below Eq. (24). Both nuclear–electron and electron–electron cusp values approach the exact values of -2.0 and 0.5, respectively, as the order n of the FC calculation increases. At $n = 27$, the cusp values are correct to 22 digits, which is about a half of the correct digits of the variational energy, 41 digits, given in Table 1. This result is natural from a theoretical point of view.

Table 3 Electron–nucleus and electron–electron cusp values of the FC wave functions of helium atom[a]

Order, n	M_n^b	$Cusp_{(n)}^{N-e}(r', \theta' = \pi/2)$ (a.u.) $r' = 1.0$	$Cusp_{(n)}^{e-e}(r', \theta' = \pi/2)$ (a.u.) $r' = 1.0$
0	2	−1.71469176186748896865309	0.11230823813251103311346903
1	10	−2.0376953027380534 51073425	0.5388261133165970364082007
2	34	−2.00250405223447 8500223599	0.4931913843555658894128673
3	77	−2.00009533768121016 7679009	0.4993133049214858311939703
4	146	−1.99996075100198548 1002999	0.4999264052122836846890241
5	247	−2.00000403490194 6326124536	0.4999888812723545347905886
6	386	−2.0000002520064723 27502965	0.4999993481518041394710234
7	569	−1.99999999013952302 5500075	0.4999998678901444684668622
8	802	−2.0000000017322451 68503244	0.4999999843747191143208148
9	1091	−1.9999999999547412 31937599	0.4999999991854449195682342
10	1442	−2.0000000000289921 39510927	0.4999999999520485964408054
11	1861	−1.9999999999994506 214502899	0.4999999999968561359042406
12	2354	−2.0000000000000770 317391674	0.5000000000000789589242552
13	2927	−1.99999999999999 18885202492	0.5000000000000750757147237
14	3586	−2.0000000000000007 641057691	0.5000000000000128229900478
15	4337	−1.9999999999999998 856501484	0.5000000000000008582572593
16	5186	−2.0000000000000000 172175707	0.4999999999999999293406817
17	6139	−1.99999999999999999 68175846	0.4999999999999999740766894
18	7202	−2.00000000000000000 06492680	0.4999999999999999957258457
19	8381	−1.99999999999999999 98818275	0.4999999999999999996645368
20	9682	−2.00000000000000000 00112782	0.5000000000000000000124903
21	11111	−1.99999999999999999 9973697	0.4999999999999999999850833
22	12674	−2.00000000000000000 0016585	0.5000000000000000000087634
23	14377	−1.99999999999999999 997746	0.4999999999999999999989519
24	16226	−1.99999999999999999 998202	0.4999999999999999999995815
25	18227	−2.00000000000000000 000911	0.5000000000000000000005676
26	20386	−1.99999999999999999 999660	0.4999999999999999999997157
27	22709	−2.00000000000000000 000175	0.5000000000000000000000691
Exact		**−2.0**	**0.5**

[a] Correct figure is expressed in bold face.
[b] Number of the complement functions at order n.

6 Concluding Remarks

We have shown here that the FC method for solving the Schrödinger equation gives a series of analytical complement functions that span the exact wave function. By increasing the number of the complement functions with increasing the order n, one can calculate the solutions of the Schrödinger equation as accurately as one desires. This was shown for the helium atom as an example. Not only the variational energy, which is an upper bound of the exact energy, but also the other properties like local energy, H-square error, lower energy bound, and nuclear–electron and electron–electron cusp values all approached the exact values as the order n of the FC method increased. Theoretically, the variational energy is always more accurate than the wave function itself and other properties. The present results constitute a numerical proof that with the FC method one can calculate the solution of the Schrödinger equation as accurately as one desires.

We could not show here the results of solving the relativistic Dirac–Coulomb equation. The FC method can be extended to the case of the Dirac–Coulomb equation with only a small modification [36]. It is important to use the inverse Dirac–Coulomb equation to circumvent the variational collapse problem which often appears in the relativistic calculations [37].

For complex atoms and molecules, the analytical integrations involved in Eqs. (6) or (7) are 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. (5) for large n. For more details, we refer to Ref. [11]. Using the LSE method, we can calculate the analytic wave function of atoms and molecules without doing the analytical integrations. This method is very general, since the integrations in Eq. (7) are difficult to perform for the complement functions of general atoms and molecules.

The programs for the variational calculations of the helium atom and its iso-electronic ions and the diagonalization program in arbitrary accuracy used for obtaining the data shown in this chapter can be obtained with charges. For details, please refer to the web site of our QCRI (www.qcri.or.jp).

References

1. E. Schrödinger, Phys. Rev. **28**, 1049 (1926)
2. P. A. M. Dirac, Proc. Roy. Soc. A **123**, 714 (1929)
3. H. Nakatsuji, J. Chem. Phys. **113**, 2949 (2000)
4. H. Nakatsuji, E. R. Davidson, J. Chem. Phys. **115**, 2000 (2001)
5. H. Nakatsuji, M. Ehara, J. Chem. Phys. **117**, 9 (2002); ibid. **122**, 194108 (2005)
6. H. Nakatsuji, Phys. Rev. Lett. **93**, 030403 (2004)
7. H. Nakatsuji, Phys. Rev. A **72**, 062110 (2005)
8. H. Nakatsuji, Bull. Chem. Soc. Jpn. **78**, 1705 (2005)
9. H. Nakashima, H. Nakatsuji, J. Chem. Phys. **127**, 224104 (2007)
10. Y. I. Kurokawa, H. Nakashima, H. Nakatsuji, Phys. Chem. Chem. Phys. **10**, 4486 (2008)
11. H. Nakatsuji, H. Nakashima, Y. Kurokawa, A. Ishikawa, Phys. Rev. Lett. **99**, 240402 (2007)

12. H. Nakashima, H. Nakatsuji, Phys. Rev. Lett. **101**, 240406 (2008)
13. H. Nakatsuji, H. Nakashima, Int. J. Quantum Chem., **109**, 2248 (2009)
14. *Explicitly Correlated Wave Functions in Chemistry and Physics – Theory and Applications,* ed. by J. Rychlewski (Kluwer, Dordrecht, 2003)
15. E. A. Hylleraas, Z. Phys. **54**, 347 (1929)
16. J. H. Bartlett, Jr., Phys. Rev. **51**, 661 (1937)
17. T. H. Gronwall, Phys. Rev. **51**, 655 (1937)
18. V. A. Fock, Izv. Akad. Nauk. SSSR, Ser. Fiz. **18**, 161 (1954)
19. T. Kinoshita, Phys. Rev. **105**, 1490 (1957)
20. K. Frankowski, C. L. Pekeris, Phys. Rev. **146**, 46 (1966)
21. A. J. Thakkar, T. Koga, Phys. Rev. A **50**, 854 (1994)
22. S. P. Goldman, Phys. Rev. A **57**, R677 (1998)
23. G. W. F. Drake, Phys. Scr. **T83**, 83 (1999)
24. G. W. F. Drake, M. M. Cassar, R. A. Nistor, Phys. Rev. A **65**, 054501 (2002)
25. J. S. Sims, S. A. Hagstrom, Int. J. Quantum Chem. **90**, 1600 (2002)
26. V. I. Korobov, Phys. Rev. A **66**, 024501 (2002)
27. A. J. Thakkar, T. Koga, Theor. Chem. Acc. **109**, 36 (2003)
28. C. Schwartz, Int. J. Mod. Phys. E **15**, 877 (2006)
29. H. Nakashima, H. Nakatsuji, J. Chem. Phys. **128**, 154107 (2008)
30. H. Nakashima, Y. Hijikata, H. Nakatsuji, J. Chem. Phys. **128**, 154108 (2008)
31. Computer code MAPLE, Waterloo Maple Inc., Waterloo, Ontario, Canada; see http://www.maplesoft.com
32. D. H. Weinstein, Proc. Natl. Acad. Sci. USA **20**, 529 (1934)
33. G. Temple, Proc. Roy. Soc. A **119**, 276 (1928)
34. T. Kato, Commun. Pure Appl. Math. **10**, 151 (1957)
35. V. A. Rassolov, D. M.Chipman, J. Chem. Phys. **104**, 9908 (1996)
36. H. Nakatsuji, H. Nakashima, Phys. Rev. Lett. **95**, 050407 (2005)
37. R. N. Hill, C. Krauthauser, Phys. Rev. Lett. **58**, 83 (1987)