

How Accurately Does the Free Complement Wave Function of a Helium Atom Satisfy the Schrödinger Equation?

Hiroyuki Nakashima and Hiroshi Nakatsuji*

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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The local energy defined by $H\psi/\psi$ must be equal to the exact energy E at any coordinate of an atom or molecule, as long as the ψ under consideration is exact. The discrepancy from E of this quantity is a stringent test of the accuracy of the calculated wave function. The H -square error for a normalized ψ , defined by $\sigma^2 \equiv \langle \psi | (H - E)^2 | \psi \rangle$, is also a severe test of the accuracy. Using these quantities, we have examined the accuracy of our wave function of a helium atom calculated using the free complement method that was developed to solve the Schrödinger equation. Together with the variational upper bound, the lower bound of the exact energy calculated using a modified Temple's formula ensured the definitely correct value of the helium fixed-nucleus ground state energy to be **-2.903 724 377 034 119 598 311 159 245 194 4** a.u., which is correct to 32 digits.

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The formulation of a general method for solving the Schrödinger equation (SE) is one of the most important subjects in quantum chemistry, although many scientists believed this important task to be impossible [1]. Recently, we have proposed the free iterative complement interaction (ICI) method [2–4], which we refer to in short as the free complement (FC) method, for solving the SE accurately in an analytical expansion form, and using this method, we have obtained very accurate energies and wave functions with excellent convergence for various systems [5–8]. In this communication, we examine and prove the “exactness” or the “high accuracy” of the calculated results using stringent theoretical tests of how well the calculated wave functions satisfy the SE. For such tests, we have examined the local energy, H -square error, and the upper and lower bounds of the exact energy.

Exactness and accuracy of the wave function.—The SE, $H\psi = E\psi$, is a local equation that must be satisfied at any coordinate. It can also be written as

$$\frac{H\psi(\mathbf{r})}{\psi(\mathbf{r})} = E(\text{const}) \quad (\forall \mathbf{r}), \quad (1)$$

where H is the Hamiltonian and $\psi(\mathbf{r})$ is the wave function at a coordinate \mathbf{r} . The left-hand side of Eq. (1) is called local energy, $E_L(\mathbf{r})$, as

$$E_L(\mathbf{r}) \equiv \frac{H\psi(\mathbf{r})}{\psi(\mathbf{r})}. \quad (2)$$

If ψ is not an exact wave function, then $E_L(\mathbf{r})$ may depend on \mathbf{r} . If $E_L(\mathbf{r})$ is a constant at any point \mathbf{r} , then Eq. (2) corresponds to Eq. (1), which is the SE. Therefore, the constancy of the local energy at any coordinate \mathbf{r} is a straightforward test of how well the wave function ψ satisfies the SE.

Another quantity that is useful to assess the exactness of a wave function is the H -square error σ^2 , defined by

$$\sigma^2 \equiv \langle \psi | (H - E)^2 | \psi \rangle, \quad (3)$$

for a normalized ψ where $E = \langle \psi | H | \psi \rangle$. The H -square equation we have utilized previously [2] corresponds to $\sigma^2 = 0$, which is valid only for the exact wave function. The value of σ^2 is always positive and becomes zero only if ψ is exact. It is also related to the local energy by

$$\sigma^2 = \langle E_L^2 \rangle_{\psi^2} - \langle E_L \rangle_{\psi^2}^2, \quad (4)$$

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 $|\psi|^2$.

Information on both the upper and lower bounds, E_{upper} and E_{lower} , of the exact energy E_{exact} is very valuable to estimate the exact value of the energy. In this case, the exact energy is guaranteed to lie between $E_{\text{upper}} \geq E_{\text{exact}} \geq E_{\text{lower}}$. When we use the variation principle, the calculated energy is the upper bound of the exact energy.

There are several theories that produce the lower bound of the exact energy, and they are related to the H -square error σ^2 . One method is the Weinstein's lower bound energy E_{lower}^W , which is written as [9]

$$E_{\text{lower}}^W = \langle \psi | H | \psi \rangle - \sqrt{\sigma^2}. \quad (5)$$

This method is advantageous in that it only needs σ^2 and the energy expectation value. However, a problem of this method is that the quality (accuracy) of this lower bound is not good enough: it is too low usually to be useful.

Another method was proposed by Temple [10], and is written as

$$E_{\text{lower}}^T = \langle \psi | H | \psi \rangle - \frac{\sigma^2}{E_1 - \langle \psi | H | \psi \rangle}. \quad (6)$$

This method requires $\langle \psi | H | \psi \rangle$, σ^2 , and in addition, the exact energy E_1 of the first excited state having the same

symmetry as the ground state. In general, the exact excited state energy E_1 is unknown and so we have to modify Eq. (6). If one replaces the exact energy of the first excited state E_1 with its lower bound energy, then one can obtain the energy that is lower than the Temple's lower bound energy given by Eq. (6). We used the Weinstein's lower bound to the first excited state E_1^W as the lower bound energy to E_1 that is given by $E_1^W = \langle \psi_1 | H | \psi_1 \rangle - \sqrt{\sigma_1^2}$, where ψ_1 and σ_1 are the respective 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

$$E_{\text{lower}}^{T'} \equiv \langle \psi | H | \psi \rangle - \frac{\sigma^2}{E_1^W - \langle \psi | H | \psi \rangle}, \quad (7)$$

and we have the relationship $E_{\text{exact}} \geq E_{\text{lower}}^T \geq E_{\text{lower}}^{T'}$. Importantly, the modified Temple's lower bound energy can be calculated using our theory alone. Thus, both the upper and lower bounds can be calculated using our theory alone, and we have the inequality

$$E_{\text{upper}} \geq E_{\text{exact}} \geq E_{\text{lower}}^{T'}, \quad (8)$$

which is mathematically guaranteed. Therefore, strictly we

can say that the exact energy should lie in a definite region of the energy.

As shown below, the above quantities are important for examining the accuracy of a wave function. However, there have been few studies on these quantities [11,12]. A reason for this is that it is very difficult to obtain a wave function that shows a constancy in its local energy over a wide region of coordinates.

Free complement wave function of helium atom.—We calculated the above quantities using the free ICI or FC wave function of a helium atom, which was published in Ref. [5]. This wave function is written as

$$\psi = \sum_i c_i s^{l_i} t^{m_i} u^{n_i} [\ln(s + \beta u)]^{j_i} \exp(-\alpha s), \quad (9)$$

with the detailed definitions given in Ref. [5]. The logarithm function including $u = r_{12}$ was used to describe well the three-particle coalescence region. The energy for the different order n of the FC method is summarized in Table V in Ref. [5], and the best energy was correct over 41 digits at an order of $n = 27$ with a dimension of $M_n = 22\,709$. Recently, we have also performed FC calculations starting with the exponential integral function instead of the logarithmic function, and have obtained the energy

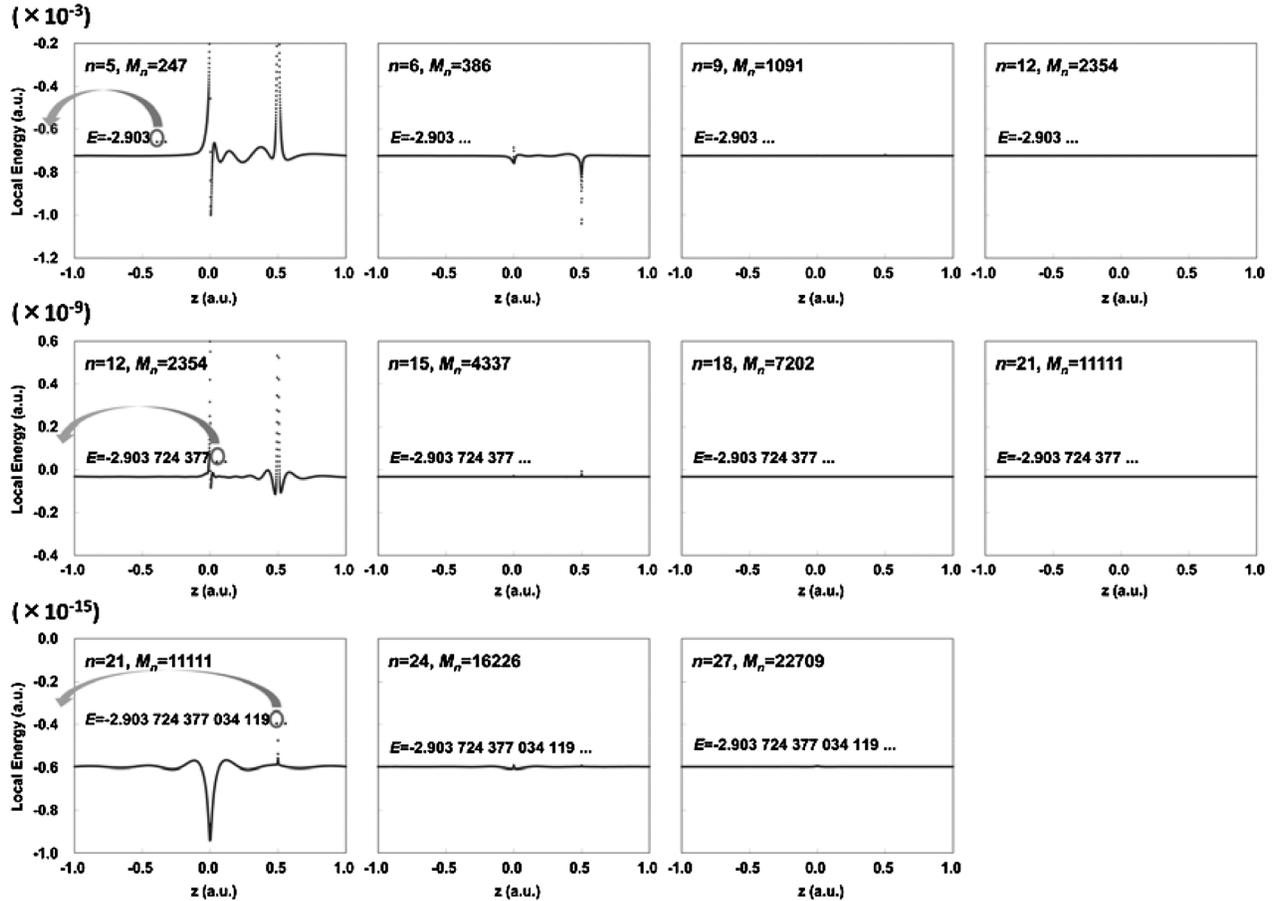


FIG. 1. Local energy plots of the FC wave functions for orders from $n = 5$ to 27. The arrows and circles in the left-hand figures show the digits of the total energy, in which the local energy shown on the vertical axis changes.

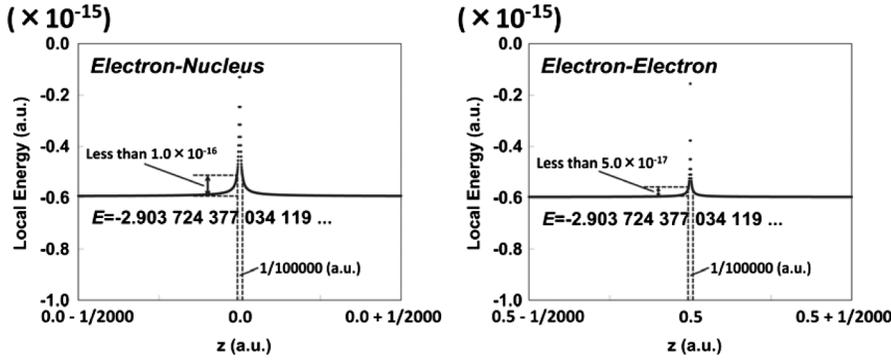


FIG. 2. Local energy plots at $n = 27$ ($M_n = 22709$) around the regions very close to the electron-nucleus ($z = 0$) and electron-electron ($z = 0.5$) singularities, where the local energy singularities are within 1.0×10^{-16} and 5.0×10^{-17} a.u., respectively, for an interval of $1/100\,000$ a.u.

correct to 43 digits at the order $n = 27$ with $M_n = 21\,035$ [6].

Local energy plots.—Let us first show the local energy plots of the FC wave function of Eq. (9). Figure 1 shows plots at different orders up to $n = 27$. In Fig. 1, the 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 dotted plots were evaluated at intervals of $1/2000$ a.u. 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 evaluated from the energy E shown on each graph and the value of E_Y from $E_L = E + \varepsilon E_Y$.

The top row in Fig. 1 shows plots for $n = 5$ – 12 with the factor $\varepsilon = 10^{-3}$. At $n = 5$, the local energy still oscillates in the order of 10^{-3} a.u. and appears not to be constant in the region $0.0 < z < 0.5$. At $n = 6$, the local energy becomes almost constant, except for the region very close to the singularities. At $n = 9$ and $n = 12$, the local energy appears to be constant for the factor of $\varepsilon = 10^{-3}$. The second row in Fig. 1 shows plots for $n = 12$ – 21 with $\varepsilon = 10^{-9}$; i.e., the graphs are scaled up by a factor of 10^6 from those in the previous row. Therefore, the vertical axis value E_Y shows the variation in the local energy below the tenth digit after the decimal point, i.e., less than

$-2.903\,724\,377$ a.u. The enlarged graph shown for $n = 12$ shows some deviations in the local energy at the singular points, but as the order increases to $n = 15$ and $n = 21$, these deviations disappear, and the local energy becomes near constant at orders $n = 18$ and $n = 21$. The lowest row shows a similar behavior for the local energy for a factor of $\varepsilon = 10^{-15}$. At $n = 27$, the local energy appears to be constant, even with a factor of 10^{-15} .

We further examined closely the behavior of the local energy in the region of the nuclear and electron singularities. Figure 2 shows these close examinations of the local energy at $n = 27$ with $\varepsilon = 10^{-15}$ in the very narrow nuclear singularity region from $z = 0.0 - 1/2000$ to $z = 0.0 + 1/2000$, and in the electron singularity region from $z = 0.5 - 1/2000$ to $z = 0.5 + 1/2000$. The plots were evaluated for intervals of $1/2\,000\,000$ a.u. As shown in Fig. 2, the local energy showed a high constancy, except for the very small regions of $z = 0.0 \pm 1/200\,000$ a.u. around the electron-nucleus singularity, and $z = 0.5 \pm 1/200\,000$ a.u. around the electron-electron singularity. Thus, we observed that the local energy calculated from the FC wave functions of the helium atom [5] shows a very high constancy when the order n is large.

H-square error and the energy lower bound.—First, we examined the H -square error σ^2 , defined by Eq. (3). Table I provides a summary of the values of σ^2 , which rapidly converge towards zero (exact value) with increasing order

TABLE I. Convergence of the H -square error σ^2 and the modified Temple's energy lower bound, defined in Eqs. (3) and (7), respectively, with increasing order of the FC wave function n .

Order n	M_n^a	H -square error σ^2	Energy lower bound ^b
5	247	$2.934\,869 \times 10^{-9}$	-2.903 724 380 97
6	386	$4.782\,529 \times 10^{-10}$	-2.903 724 377 674
9	1091	$1.095\,586 \times 10^{-15}$	-2.903 724 377 034 121 066
12	2354	$5.007\,353 \times 10^{-21}$	-2.903 724 377 034 119 598 317 869
15	4337	$1.835\,489 \times 10^{-24}$	-2.903 724 377 034 119 598 311 161 704
18	7202	$5.372\,350 \times 10^{-27}$	-2.903 724 377 034 119 598 311 159 252 393
21	11 111	$4.000\,913 \times 10^{-29}$	-2.903 724 377 034 119 598 311 159 245 248
24	16 226	$5.665\,577 \times 10^{-31}$	-2.903 724 377 034 119 598 311 159 245 195 163
27	22 709	$1.293\,955 \times 10^{-32}$	-2.903 724 377 034 119 598 311 159 245 194 421 785

^aNumber of independent functions for order n .

^bThe correct figure is expressed in bold face.

of the FC method. At $n = 27$, we obtained $\sigma^2 = 1.293955798978967642728022186398914855 \times 10^{-32}$. Because σ^2 is a variance (i.e., it is always positive or zero), and it cannot involve lucky cancellations, such as those seen in the energy expectation value, this small value indicates that the wave function itself is very accurate at each coordinate. In general, one can consider that the value of $\sqrt{\sigma^2}$ corresponds to the precision of the constancy of the local energy. Therefore, the scaling factor ε shown in Fig. 1 approximately corresponds to the value of $\sqrt{\sigma^2}$ for each order.

Using the value of the H -square error σ^2 one can calculate the energy lower bound. When we used Weinstein's formula given by Eq. (5), the lower bound energy E_{lower}^W was calculated to be **-2.903 724 377 034 119 712** a.u. for $n = 27$, which has an accuracy to only 16 digits. To obtain a more accurate lower bound energy without losing any mathematical strictness, we used the modified Temple's formula given by Eq. (7), where we needed the energy lower bound of the first excited state, E_1^{lower} , which was calculated by using Weinstein's formula. The wave function we used for the first excited state was the second solution of the diagonalization of the secular equation for $n = 27$. Because the FC calculations in Ref. [5] were designed to be appropriate only for the ground state, the description of the excited states obtained was poor: the calculated upper bound energy was **-2.145 974 046 053 596** a.u. and the calculated Weinstein's lower bound energy was $E_1^W = -2.157 464 627 324 812$ a.u. However, we note that the significant digit of E_{lower}^T is mostly determined by σ^2 , and so that even an approximate estimate of E_1^{lower} is acceptable.

The modified Temple's lower bound energy for the ground state was shown in the final column of Table I. It can be seen that this energy rapidly converges to the exact energy from below. The most accurate modified Temple's lower bound energy for $n = 27$ was **-2.903 724 377 034 119 598 311 159 245 194 421 785** a.u., while the upper bound energy for $n = 27$ was **-2.903 724 377 034 119 598 311 159 245 194 404 446 696 905 37** a.u. [5], where the bold faced characters denote the correct values judged from the convergence ratio of the neighboring order series of the FC calculations. Because our modified Temple's lower bound energy is mathematically correct, we can say that the exact ground state energy of the helium atom must be sandwiched in the region between these upper and lower bound energies. Thus, the mathematically guaranteed value for the fixed-nucleus nonrelativistic ground state energy of the helium atom was obtained as **-2.903 724 377 034 119 598 311 159 245 194 4** a.u., which is correct to 32 digits.

Conclusions.—In this Letter, we have examined the local energy properties of the FC wave function of the helium atom published in Ref. [5]. First, we showed that

the local energy calculated from the FC wave function was highly constant, and was very close to the ground state energy almost everywhere, except for the small regions around the Coulomb singularities. It is with no doubt true that the present FC wave function is highly accurate. This was also seen in the very small value of the calculated H -square error, $\sigma^2 = 1.294 \times 10^{-32}$ a.u. From our calculations of the strict upper and lower bound energies, the *exact* energy of the ground state of the helium atom in the nonrelativistic fixed-nucleus case was calculated to an accuracy within 32 digits. This result numerically supports that the FC method can provide the exact wave function and energy to any desired accuracy. This result also provides an excellent starting point for further studies on the remaining physical effects, such as relativistic [13] and quantum electrodynamic (QED) effects. An accurate theory of error bars is necessary for studies on atoms and molecules that do not have accurate reference data.

Recently, we have developed a local Schrödinger equation (LSE) method for solving the FC wave function without calculating the integrals of the complement functions [14]. This methodology is important, because the complement functions of the FC method of general atoms and molecules are not necessarily integratable to calculate the overlap and Hamiltonian matrix elements necessary for the variation calculations. The basic strategy of the LSE method lies in the constancy of the local energy for the potentially exact wave function. Therefore, the present proof of the high constancy of the local energy for the FC wave function of helium provides much credit for the FC LSE methodology in opening up a new route for accurately predictive quantum chemistry.

*Corresponding author.

h.nakatsuji@qcri.or.jp

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