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REGULAR ARTICLE

Relativistic free complement method for correctly solving the Dirac equation with the applications to hydrogen isoelectronic atoms

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Abstract The accuracy of the relativistic free complement (FC) method, which was previously reported for solving the Dirac–Coulomb equations of atoms and molecules, has been strictly examined with the applications to hydrogen isoelectronic atoms. The FC wave function grown up by the Hamiltonian automatically takes care of the correct relationship between large and small components, i.e., FC or ICI balance. Combining the FC method with the inverse Hamiltonian method can help to obtain correct solutions safely against to several obstacles characteristic to the Dirac–Coulomb equation. To ensure the exactness of the obtained wave function, we examined the total square deviation from the exact wave function, local energy constancy, H-square error, and energy upper and lower bounds for hydrogen-like atoms.

Keywords Dirac equation · Hydrogen isoelectronic atoms · Free complement method · Total square deviation from the exact wave function · Local energy · H-square error · Energy lower bound

Dedicated to Professor Pekka Pyykkö on the occasion of his 70th birthday and published as part of the Pyykkö Festschrift Issue.

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1 Introduction

As Dirac noted in 1929, the Schrödinger equation (SE) of atoms and molecules is a major quantum principal equation governing chemistry [1]. However, when atoms and molecules include heavy element or one wants to evaluate the fine physical effect beyond nonrelativistic limit, one cannot ignore relativistic effect. The Dirac–Coulomb equation (DCE) or Dirac–Coulomb-Breit equations are the relativistic quantum mechanical equations very often used for solving chemical problem [2]. Although one-electron Dirac equation (DE) is exactly invariant on the Lorentz transformation, many-electron DCE is not invariant due to the existence of classical electron-repulsion potential $1/r_{ij}$. It is well known; however, these equations can give accurate prediction for atomic and molecular systems. For more accurate description, we have to consider quantum electrodynamics (QED) but there is no closed form or Hamiltonian for addressing it except for a perturbative way [2].

In contrast to successful state-of-the-art quantum chemistry for nonrelativistic case, there are still several obstacles for solving the DE or DCE stably and accurately. One big problem is well-known variational collapse problem originating from the existence of the negative energy solutions that corresponds to the positive electron states [2]. Without any restriction of the variational parameters in the wave function, calculations may give incorrect answer. It is often called variational collapse problem. A kinetic balance condition is often adopted to avoid this problem [2], but it is nothing more than an approximation. The relativistic wave function for Coulomb system has weak singularities at particle coalescence points. This requires much more careful computational considerations than in the nonrelativistic case.

Many trials have been made for accurately and correctly solving these equations. Pestka and Karwowski et al. strictly investigated the balance conditions for Dirac spinor to avoid variational collapse [3–5]. They introduced rigorous balance condition or as its expanded form, atomic balance condition, but these conditions still have a practical problem. As an alternative way, a clever idea on the variational calculation using inverse Hamiltonian was proposed by Hill and Krauthauser [6]. If the energy is shifted correctly, then the inverse energy of the desired bound ground state moves to the maximum against complete vacuum. This can change the unbound variational problem of the normal Dirac Hamitonian to be a bound problem. Actually, one of the authors also introduced the inverse Schrödinger equation to overcome the singularity problem in the Hamiltonian [7], see the next paragraph for details.

Recently, one of the authors formulated a method that leads us to the exact solution of the SE [7–10] from the studies on the structure of the exact wave function, the iterative complement (IC) method (originally referred to as the ICI (iterative complement (or configuration) interaction) method) [8]. To overcome the singularity problem that leads to a divergence of the integrals involved, the inverse SE [7] and the scaled SE [9] were introduced. Among these, the latter was proved useful and, at the same time, the free complement (FC) method (originally called as free ICI method [9]) was proposed as a method of solving the SE. We have applied this methodology to many atoms and molecules and successfully obtained their very accurate energies and wave functions [11–13]. We are confident that this methodology certainly gives a route to obtain the exact solutions of the SE of atoms and molecules. One of the most important features of the IC and FC methods is that the Hamiltonian of the system produces the complete basis functions of their own wave functions. These basis functions are referred to as the complement functions as they are the elements of the complete functions that span the exact wave function of the system.

This feature of our theory should take much crucial role in the relativistic case, and we extended the IC and FC methods to the methods of solving the relativistic DE and DCE [14]. We reported that combining the FC method with the inverse Hamiltonian method is very important to stably obtain the solutions [6, 14]. To show this, we have applied this method to hydrogen and helium isoelectronic atoms [14] and later even in a strong magnetic field [15] and further to hydrogen molecular ion as a first application to molecular system [16]. The application to hydrogen atom in the strongest magnetic fields in the universe could provide very accurate fundamental data useful for astronomy [15].

The purpose of the present paper is to examine how correctly and accurately we can get the solutions of the DE using the relativistic FC method combined with the inverse Dirac Hamiltonian. In this paper, we will focus only on one-electron system, hydrogen isoelectronic atoms, and the analyses on two-electron helium isoelectronic atoms will be given in a future forthcoming paper. We perform the stringent theoretical tests of the exactness by calculating the total square deviation from the exact wave function, local energy, H-square error, and the upper and lower bounds of the exact energy for hydrogen isoelectronic atoms [17].

2 Relativistic free complement method

In this section, we briefly explain the relativistic free complement method for solving the Dirac equation [14]. One-electron DE is simply written as

$$H\psi = E\psi \tag{1}$$

with the Hamiltonian of the matrix form

$$H = \begin{pmatrix} (V + c^2)I_2 & c(\boldsymbol{\sigma}\cdot\mathbf{p}) \\ c(\boldsymbol{\sigma}\cdot\mathbf{p}) & (V - c^2)I_2 \end{pmatrix} \tag{2}$$

and the four-component spinor wave function ψ. We use atomic unit throughout the paper. $V_i = -\sum_A Z_A/r_{Ai}$ is the nuclear attraction potential with the summation over the central field potentials of nucleus A. c is the inverse of the fine structure constant, $c = 1/\alpha \approx 1/137$, which also corresponds to the velocity of light in atomic unit, and we used $c = 137.035999679$ [18]. I_2 is the two-dimensional unit matrix. $\boldsymbol{\sigma}$ is the Pauli matrix, and $\mathbf{p}$ is the momentum operator, $\mathbf{p} = -i\nabla$.

The free complement (FC) method was proposed to solve the SE of atoms and molecules very accurately [7–10]. Since the formulation is very general, we could straightforwardly extend the theory to the relativistic case [14]. The iterative complement (IC) wave function is defined by a recurrence formula given by

$$\psi^{(n+1)} = \left[1 + C^{(n)} g\left(H - E^{(n)}\right)\right]\psi^{(n)}, \tag{3}$$

where n is an iteration number, $\psi^{(n+1)}$ is a four-component spinor, $C^{(n)}$ is a diagonal matrix composed of the variational parameters, g is a scaling function that prevents the singularity problem caused by the singular Coulomb potential in the Hamiltonian [9], and $E^{(n)}$ is the energy expectation value of $\psi^{(n)}$. The IC wave function becomes exact at convergence [14]. After some iteration, the right hand side of Eq. 3 is actually a sum of analytical functions. We collect the independent functions $\left\{\phi_i^{(n)}\right\}$ and give independent coefficients $\left\{c_i^{(n)}\right\}$ to each and get the FC wave function written as

$$\psi^{(n+1)} = \sum_{i=1}^{M_n} c_i^{(n)} \phi_i^{(n)}. \tag{4}$$

Note that $\phi_i^{(n)}$ is a four-dimensional spinor. We calculate the unknown coefficients $\left\{c_i^{(n)}\right\}$ by applying the variation principle. Then, the FC wave function is not iterative, since we calculate $\left\{c_i^{(n)}\right\}$ at each n, and so we call n as "order n". The number of the independent functions involved in Eq. 4 is referred to as "dimension M_n".

In the solution spectra of the DE, the positron states lie below the bound electronic states. Therefore, when we use the ordinary regular Hamiltonian, the Ritz-type variational principle does not hold: the solutions are not bound from below. Each component of the spinor wave function is related to each other by the Dirac equation. Therefore, arbitrary basis sets that are not wide enough to permit this correct relationship between large and small components cause serious problems in the variational calculation. In the relativistic FC calculation, the exact relationship between the components of the spinor is automatically imposed because the FC wave function is generated in each step using the Dirac Hamiltonian. We call this balancing process as "ICI balance" [14] or, in new terminology, as "FC balance". This is a quite significant property for solving the multicomponent DE and DCE. This is also a reason of very stable computation process of our relativistic FC calculations of atoms and molecules [14–16]. We note that in early stage (order) of the FC calculations, the FC balancing may not be sufficient, but as the FC process proceeds, the balancing approaches the exact one.

Another important way to recover the Ritz variational property for the variational Dirac calculation was proposed by Hill and Krauthauser: they proposed to use the inverse Hamiltonian H_w^{-1} with an appropriate energy shift w ($H_w = H + w$) [6] instead of the regular Hamiltonian. A similar consideration for the nonrelativistic case was given by one of the authors in order to overcome the Coulomb singularity problem [7]. For one-electron system, the inverse energy of the lowest electronic state comes to highest against the complete vacuum, so that the expectation value E_w^{-1} ($E_w = E + w$) of the trial function ψ with respect to the inverse Hamiltonian should be always lower than the exact inverse energy $E_{\text{exact}}^{(w)-1}$ ($E_{\text{exact}}^{(w)-1} = (E_{\text{exact}} + w)^{-1}$) of the electronic ground state, namely,

$$E_w^{-1} = \frac{\langle\psi|H_w^{-1}|\psi\rangle}{\langle\psi \mid \psi\rangle} \leq E_{\text{exact}}^{(w)-1}. \tag{5}$$

Thus, the variational solutions become possible as long as we use the inverse Hamiltonian instead of the regular Hamiltonian in the variation process. Then, a problem is how to deal with the inverse Hamiltonian. Hill and Krauthauser [6] proposed a genius trick to circumvent this problem: they restricted the variation space of the trial wave function as

$$\psi = H_w \varphi, \tag{6}$$

where a free variation is done for φ. Then, the above-mentioned inverse energy can be rewritten as

$$E_w^{-1} = \frac{\langle\varphi|H_w|\varphi\rangle}{\langle\varphi|H_w^2|\varphi\rangle} \leq E_{\text{exact}}^{(w)-1}. \tag{7}$$

Then, we can calculate all the quantities appearing in Eq. 7. When we construct φ by the FC method, we know that our φ approaches to the exact wave function, and therefore, it is proved that $\psi = H_w\varphi$ also approaches to the exact wave function. Note that, in Eq. 7, we need to evaluate the expectation value of H_w^2. In the present paper, we call the variational method using the normal Hamiltonian as "regular Hamiltonian method" and the one using the inverse Hamiltonian as "inverse Hamiltonian method". We also define three types of energies, II (Inverse–Inverse), IR (Inverse–Regular), and RR (Regular–Regular) energies [16]. The IR energy is the energy expectation value of the regular Hamiltonian using the wave function obtained by the inverse Hamiltonian method. The II and RR energies are self-evident. In addition to the FC balance, the use of the inverse Hamiltonian in the variational calculation is important to calculate the solution of the Dirac equation in the relativistic Dirac and Dirac–Coulomb calculations.

3 Total square deviation from the exact wave function, local energy, H-square error, and energy upper and lower bounds

In this paper, we examine the accuracy of the relativistic FC wave function by calculating the above-mentioned stringent properties that test the exactness. We used these properties to test the exactness of our nonrelativistic FC wave function of the helium atom [17].

One straightforward quantity is the total square deviations between the trial wave function ψ and the exact wave function ψ_{exact} for each of the components. This quantity is available only when the exact wave function is known. We define its square root as

$$\Delta^{(k)} = \left[\int \left|\psi^{(k)} - \psi_{\text{exact}}^{(k)}\right|^2 d\tau\right]^{1/2}, \tag{8}$$

where k denotes the k-th component of the wave function ($k = 1, 2, 3, 4$ for one-electron system) and each of the components is normalized independently. Actually, $\Delta^{(k)}$ directly represents the wave function quality of each component independently but no information about the

Hamiltonian or energy properties and balancing of the multicomponent wave function. Due to the weak singularities of the wave function, the properties related to the Hamiltonian, which includes the first derivative of the wave function, would be quite sensitive in the relativistic case. Therefore, the following absolute properties related to the Hamiltonian would be very important to judge the exactness.

First of these quantities is the local energy that is formally defined by $E_{\text{local}}(\mathbf{x}) = H\psi/\psi$ at a local position $\mathbf{x}$. Since the relativistic wave function has multicomponents, we define the local energy $E^{(k)}_{\text{local}}(\mathbf{x})$ for each of the components as

$$E^{(k)}_{\text{local}}(\mathbf{x}) = \frac{[H\psi]^{(k)}}{\psi^{(k)}}, \tag{9}$$

where $\psi^{(k)}$ and $[H\psi]^{(k)}$ are the k-th components of ψ and $H\psi$, respectively. For the exact wave function, $E = E^{(1)}_{\text{local}}(\mathbf{x}) = E^{(2)}_{\text{local}}(\mathbf{x}) = E^{(3)}_{\text{local}}(\mathbf{x}) = E^{(4)}_{\text{local}}(\mathbf{x}) = \text{exact energy}$ at everywhere of $\mathbf{x}$. With this local energy, we can check the exactness of ψ at any local position $\mathbf{x}$.

Another quantity is the H-square error σ^2 defined by

$$\sigma^2 = \frac{\langle\psi|(H-E)^2|\psi\rangle}{\langle\psi \mid \psi\rangle}. \tag{10}$$

This quantity is especially important for the relativistic case to test the exactness, as will be seen below. The H-square error is always positive and becomes zero only for the exact wave function. The solutions of the DE or DCE are not variationally bound with respect to the regular Hamiltonian, but one can check their exactness using the bound H-square error. The H-square error is actually closely related to the inverse Hamiltonian method. For both cases, one needs to evaluate the expectation value of H^2 operator. This contains the integral of $1/r^2$ from Coulomb potential, and this requires more computational demands than the ordinary expectation value of H. However, this is indispensable to obtain the stable solutions and to ensure exactness in the relativistic case.

Next quantity is the energy lower bound, which is also related to the H-square error. The Weinstein's lower bound [19] is given by

$$E^{\text{Weinstein}}_{\text{lower}} = \frac{\langle\psi|H|\psi\rangle}{\langle\psi \mid \psi\rangle} - \sqrt{\sigma^2}. \tag{11}$$

This is very simple and general, but the result is not necessarily useful. Temple's lower bound [20] for the ground state is defined by

$$E^{\text{Temple}}_{\text{lower}} = \frac{\langle\psi|H|\psi\rangle}{\langle\psi \mid \psi\rangle} - \frac{\sigma^2}{E_1 - \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}}, \tag{12}$$

where the exact value of the excited state energy E_1 is necessary. Strictly speaking, the solution of the DE is not bound and the Kato's lower bound, which is a generalization of the Temple's lower bound, would be necessary in case the energy expectation value is lower than the exact energy [21, 22]. When we use the inverse Hamiltonian method, we can obtain the bound solutions and strictly evaluate the inverse lower bound (actually upper bound) with the inverse H-square error. If one knows the exact wave function ψ_{exact}, then one can evaluate the Weinhold's lower bound [23, 24] given by

$$E^{\text{Weinhold}}_{\text{lower}} = \frac{\langle\psi|H|\psi\rangle}{\langle\psi \mid \psi\rangle} - \sqrt{(S^{-2}-1)\sigma^2}, \tag{13}$$

where $S = \langle\psi \mid \psi_{\text{exact}}\rangle$ with normalized ψ and ψ_{exact}. This quantity is not useful, in general, because we never know the exact wave function. This is used only for the test of the theory applied to the system for which the exact solution is known. Actually, for hydrogen isoelectronic atoms, the exact relativistic solution is known [2].

4 Hydrogen isoelectronic atoms

We examine here the accuracy of our FC wave functions of the hydrogen isoelectronic atoms obtained with some different variational methods. The present system is the most typical and simplest one to examine the relativistic variational problems connected with the DE.

With the central field potential $V = -Z/r$, we can separate the radial part equation from the DE of the hydrogen isoelectronic atoms. The radial Hamiltonian (2 × 2 matrix form) is expressed as

$$H = \begin{pmatrix} c^2 - \frac{Z}{r} & c\left(-\frac{d}{dr} - \frac{1-k}{r}\right) \\ c\left(\frac{d}{dr} + \frac{1+k}{r}\right) & -c^2 - \frac{Z}{r} \end{pmatrix}, \tag{14}$$

where $k = \pm(j + 1/2)$ and $j = l \pm 1/2$ with j and l being the quantum numbers of the total and radial angular momentum, respectively. The exact energy of the ground state ($j = 1/2$, $k = -1$) is given by [2]

$$E_{\text{exact}} = c^2\gamma \tag{15}$$

with $\gamma = \sqrt{1-(Z/c)^2}$. The exact wave function of the ground state is given by

$$\begin{aligned} \psi^l_{\text{exact}} &= r^{\gamma-1}\exp(-Zr), \\ \psi^s_{\text{exact}} &= -\frac{Z}{c(\gamma+1)} r^{\gamma-1}\exp(-Zr), \end{aligned} \tag{16}$$

where ψ^l_{exact} and ψ^s_{exact} are the large and small components in two-dimensional spinor. The wave function contains the term $r^{\gamma-1}$, which represents a weak singularity of the wave function near the nucleus since $0 < \gamma < 1$ ($Z \le 137$).

The FC calculations of the present system we performed [14] are as follows. Since the Hamiltonian contains the Coulomb potential, we must introduce the g function based on the scaled DE to eliminate its Coulomb singularity [9, 10]. We also have to consider the weak singularity, special to the relativistic case, by means of either the g function or the initial function. We chose to consider it by means of the g function. So, our g function and the initial function are written as

$$g = 1 + r^{\delta}, \tag{17}$$

$$\psi_0^l = \psi_0^s = \exp(-\alpha r), \tag{18}$$

where δ is a noninteger number close to unity and $\delta < 1$. The superscripts l and s of ψ_n^l and ψ_n^s mean the large and small components, respectively, and the subscript n shows the order of the FC calculations. During the iteration process, different noninteger values, δ, δ^2, δ^3, etc., are introduced into the wave function to represent the weak singularity. We chose $\delta = 99/100$ simply by intuition in the present calculations. The g function of Eq. 17 contains unity in the first term. This ensures that the FC wave function ψ_{n+1} at order $n+1$ includes $c(\boldsymbol{\sigma}\cdot\mathbf{p})\psi_n^l$ in the small component and $c(\boldsymbol{\sigma}\cdot\mathbf{p})\psi_n^s$ in the large component. They represent a zero-th order balancing condition, i.e.,

Table 1 The II, IR, and RR energies (a.u.) of the hydrogen-like atoms (H, Fe^{25+}, and Th^{89+}) with the g and ψ_0 of Eqs. 17 and 18 with $\delta = 99/100$

n[a]	M (M_l, M_s)[b]	Energy (a.u.)		
		II	IR	RR
H ($Z = 1$)				
0	2 (1, 1)	**−0.**375 003 751 484 271	**−0.**375 033 703 275 011	**−0.**375 033 696 103 861
1	6 (3, 3)	**−0.4**92 424 139 698 409	**−0.4**93 033 366 249 320	**−0.**493 381 702 826 413
2	12 (6, 6)	**−0.499** 744 051 515 616	**−0.499** 766 508 702 579	**−0.499** 822 155 300 668
3	20 (10, 10)	**−0.500 00**2 351 421 181	**−0.500 002** 823 107 315	**−0.500 00**4 337 110 593
4	30 (15, 15)	**−0.500 006 6**20 862 788	**−0.500 006 6**25 279 992	**−0.500 006 6**41 669 787
5	42 (21, 21)	**−0.500 006 656** 430 976	**−0.500 006 656 4**52 913	**−0.500 006 656 5**42 068
6	56 (28, 28)	**−0.500 006 656 596** 037	**−0.500 006 656 596** 101	**−0.500 006 656 596 3**74
7	72 (36, 36)	**−0.500 006 656 596 494**	**−0.500 006 656 596 494**	**−0.500 006 656 596 494**
Exact		−0.500 006 656 596 494	−0.500 006 656 596 494	−0.500 006 656 596 494
Fe^{25+} ($Z = 26$)				
0	2 (1, 1)	**−2**56.766 187 595	**−2**69.563 439 847	**−2**68.305 482 321
1	6 (3, 3)	**−33**5.917 981 053	**−33**6.719 808 286	**−33**6.985 791 487
2	12 (6, 6)	**−340.**915 432 741	**−340.**950 298 879	**−340.**983 738 017
3	20 (10, 10)	**−341.09**4 864 967	**−341.09**5 518 357	**−341.09**6 419 261
4	30 (15, 15)	**−341.097 8**12 657	**−341.097 8**18 519	**−341.097 82**8 170
5	42 (21, 21)	**−341.097 837** 089	**−341.097 837** 118	**−341.097 837 1**70
6	56 (28, 28)	**−341.097 837 20**2	**−341.097 837 20**2	**−341.097 837 20**2
7	72 (36, 36)	**−341.097 837 203**	**−341.097 837 203**	**−341.097 837 203**
Exact		−341.097 837 203	−341.097 837 203	−341.097 837 203
Th^{89+} ($Z = 90$)				
0	2 (1, 1)	−3011.213 152 401	**−46***65.300 517 991*	**−45**68.087 584 490
1	6 (3, 3)	**−4**523.354 274 966	**−461**5.797 040 722	**−461**1.343 290 328
2	12 (6, 6)	**−461**3.225 656 098	**−4616.**746 249 132	**−4617.**258 363 353
3	20 (10, 10)	**−4617.6**54 504 266	**−4617.7**42 312 596	**−4617.75**2 849 185
4	30 (15, 15)	**−4617.75**6 164 268	**−4617.757 5***56 906*	**−4617.757 5**18 161
5	42 (21, 21)	**−4617.757 5**23 501	**−4617.757 542** *665*	**−4617.757 542 3**64
6	56 (28, 28)	**−4617.757 542** 229	**−4617.757 542 44**1	**−4617.757 542 444**
7	72 (36, 36)	**−4617.757 542 44**2	**−4617.757 542 444**	**−4617.757 542 444**
Exact		−4617.757 542 444	−4617.757 542 444	−4617.757 542 444

[a] The number of iteration or order

[b] The number of complement functions and their numbers for large and small components in the parenthesis

kinetic balance. Therefore, one should hold this unity in the g function for relativistic calculations [16]. Moreover, as the iteration proceeds, the higher-order functions for the exact relationship between large and small components are steadily generated mainly from the second term of the g function and therefore the FC wave function converges to the exact solution with true balancing.

We calculated the $s_{1/2}$ ground states ($j = 1/2$, $k = -1$) of H ($Z = 1$), Fe^{25+} ($Z = 26$) and Th^{89+} ($Z = 90$) [14]. We performed both the inverse and regular Hamiltonian methods. We employed the energy shift $w = 0$ since the electron states and positron states are well separated in the Hamiltonian of Eq. 14. Table 1 shows the energy convergences. We note that the II energies quickly converged to the exact ones from above for all three atoms even for the heaviest element. On the other hand, the IR and RR energies of Th^{89+} at order 0 and IR energy at order 4 showed the values lower than the exact energy. So, the IR and RR energies are not always guaranteed to be an upper bound of the exact energy. However, as iteration proceeds, both IR and RR energies also converged to the exact energies. This is true even with the regular Hamiltonian in the variation calculation process (the RR method). This indicates that the FC balance produces the correct wave function space for both large and small components.

To judge the exactness of the obtained wave function, we first showed the local energy plots of the wave function ψ_n^l and ψ_n^s ($n = 5$ and 7) of Th^{89+} obtained from the inverse Hamiltonian method in Fig. 1. Here, horizontal axis (radial distance) is scaled up by multiplying Z. At order 5, the local energies look oscillating around its energy expectation value. At order 7, however, the deviations are much improved and become almost constant, although very small deviations are still observed near the nucleus. Thus, the local energy constancies are very much improved with increasing the order n of the FC calculations.

Table 2 shows other quantities to check the exactness of the wave function of Th^{89+}. The square root of the total square deviations from the exact wave function, defined in Eq. 8, is denoted here by Δ^l and Δ^s for each of the large and small components. The H-square error and three energy lower bounds defined by Eqs. 10, 11, 12, and 13 are also shown in Table 2. In both the inverse and regular Hamiltonian methods, Δ^l and Δ^s showed very good convergence to zero as the order increases. Each of the wave function of large and small components looks correctly converges to the exact one. The convergences of σ^2, however, were very different between the inverse and regular Hamiltonian methods. In the inverse Hamiltonian method, σ^2 quickly converged to zero and the energies of the three lower bounds also quickly converged to the exact energy from below. In contrast, in the regular Hamiltonian method, the convergence of σ^2 is appreciably bad and the lower bound energy of the Temple's method showed quite slow convergence to the exact energy. This observation suggests that the wave function obtained by the regular Hamiltonian method is far from the exact one in some space, even though the energies and the differences $\Delta^{l,s}$ were very good.

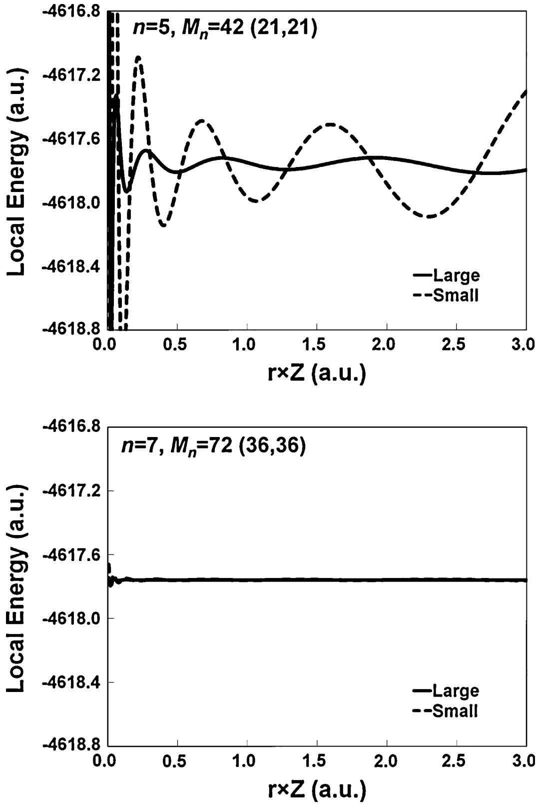

Fig. 1 Local energy plots of the wave function ψ_n^l (*large*: *solid line*) and ψ_n^s (*small*: *dashed line*) at $n = 5$ and 7 of Th^{89+} obtained from the inverse Hamiltonian method. Horizontal axis (radial distance) is scaled up by multiplying Z

This indicates that the density property of the wave function seems to be good, but the energy density would be bad in the regular Hamiltonian method. To analyze the reason more clearly, we investigated the reason why σ^2 convergence was so different between the two cases. We decomposed σ^2 in two distinct regions, one close to the nucleus, $\sigma^2|_{r=0,r_0}$ and the other far from the nucleus, $\sigma^2|_{r=r_0,\infty}$,

$$\begin{aligned} \sigma^2|_{r=0,r_0} &= \int_0^{r_0} 4\pi r_2 dr \cdot \psi^\dagger (H-E)^2 \psi \\ \sigma^2|_{r=r_0,\infty} &= \int_{r_0}^{\infty} 4\pi r_2 dr \cdot \psi^\dagger (H-E)^2 \psi, \end{aligned} \qquad (19)$$

Table 2 $\Delta^{l,s}$, H-square error, and energy lower bounds of Th^{89+} atom on both the inverse and regular Hamiltonian methods

n^{a}	M (M_l, M_s)^{b}	Δ^l	Δ^s	σ^2	Lower bounds		
					Weinstein	Temple	Weinhold
Inverse							
0	2 (1, 1)	1.97×10^{-1}	1.97×10^{-1}	2.33×10^{7}	−9496.974 041 441	−11387.152 818 006	−5633.063 635 609
1	6 (3, 3)	5.24×10^{-2}	5.37×10^{-2}	1.31×10^{6}	−5760.031 803 777	**−4**998.233 202 218	**−46**76.247 388 595
2	12 (6, 6)	1.50×10^{-2}	8.54×10^{-3}	4.99×10^{4}	**−4**840.037 667 122	**−46**31.305 946 276	**−461**9.965 731 525
3	20 (10, 10)	1.76×10^{-3}	9.23×10^{-4}	1.24×10^{3}	**−46**53.005 105 507	**−461**8.105 319 921	**−4617.**801 399 648
4	30 (15, 15)	7.20×10^{-5}	8.75×10^{-5}	1.97×10^{1}	**−46**22.198 424 652	**−4617.7**63 314 165	**−4617.757** 885 723
5	42 (21, 21)	3.32×10^{-6}	6.31×10^{-6}	2.71×10^{-1}	**−461**8.278 475 885	**−4617.757** 621 886	**−4617.757 54**4 653
6	56 (28, 28)	7.85×10^{-7}	3.19×10^{-7}	3.00×10^{-3}	**−4617.**812 300 236	**−4617.757 54**3 316	**−4617.757 542 4**81
7	72 (36, 36)	5.09×10^{-8}	2.39×10^{-8}	2.53×10^{-5}	**−4617.7**62 576 257	**−4617.757 542 4**51	**−4617.757 542 444**
Regular							
0	2 (1, 1)	1.97×10^{-1}	1.97×10^{-1}	2.90×10^{7}	−9953.860 751 916	−13160.589 093 085	−5657.862 956 433
1	6 (3, 3)	4.63×10^{-2}	3.97×10^{-2}	5.64×10^{6}	−6986.139 626 377	−6260.822 212 863	**−4**720.104 107 476
2	12 (6, 6)	8.68×10^{-3}	6.28×10^{-3}	2.69×10^{6}	−6257.161 140 488	−5402.457 002 923	**−46**31.083 272 305
3	20 (10, 10)	8.09×10^{-4}	5.95×10^{-4}	1.49×10^{6}	−5837.113 915 819	−5051.808 372 224	**−461**8.711 494 940
4	30 (15, 15)	5.70×10^{-5}	4.22×10^{-5}	7.64×10^{5}	−5491.865 248 272	**−4**840.811 493 700	**−4617.**805 959 228
5	42 (21, 21)	3.18×10^{-6}	2.36×10^{-6}	3.58×10^{5}	−5216.216 653 005	**−4**722.313 554 137	**−4617.75**9 394 511
6	56 (28, 28)	1.40×10^{-7}	1.04×10^{-7}	1.51×10^{5}	−5006.388 159 325	**−46**61.848 960 549	**−4617.757 5**95 360
7	72 (36, 36)	4.94×10^{-9}	3.66×10^{-9}	5.69×10^{4}	**−4**856.215 062 988	**−46**34.357 313 224	**−4617.757 54**3 590
Exact		0	0	0	−4617.757 542 444	−4617.757 542 444	−4617.757 542 444

[a] The number of iteration or order

[b] The number of complement functions and their numbers for large and small components in the parenthesis

Table 3 H-square error decomposition with Th^{89+} wave function at order 7 according to Eq. 19 with $r_0 = 1/Z$ and $r_0 = 1/(100Z)$

	$r_0 = 1/Z$		$r_0 = 1/(100Z)$	
	Inverse	Regular	Inverse	Regular
$\sigma^2\big\vert_{r=0,r_0}$	$2.486781620 \times 10^{-5}$	$5.686198910 \times 10^{4}$	$2.430815252 \times 10^{-5}$	$5.686198910 \times 10^{4}$
$\sigma^2\big\vert_{r=r_0,\infty}$	$4.714565234 \times 10^{-7}$	$2.774774423 \times 10^{-9}$	$1.031120204 \times 10^{-6}$	$4.209822907 \times 10^{-8}$
σ^2	$2.533927273 \times 10^{-5}$	$5.686198910 \times 10^{4}$	$2.533927273 \times 10^{-5}$	$5.686198910 \times 10^{4}$

where ψ is assumed to be normalized and $4\pi r_2$ is the Jacobian factor. These two quantities should be positive and always hold $\sigma^2 = \sigma^2\big|_{r=0,r_0} + \sigma^2\big|_{r=r_0,\infty}$. Table 3 shows these quantities from the inverse and regular Hamiltonian methods for the Th^{89+} order = 7 wave function with $r_0 = 1/Z$ and $r_0 = 1/(100Z)$. We see that the wrong behavior of the regular Hamiltonian method lies in the region very close to the nucleus. Even in the very small value of $r_0 = 1/(100Z)$, $\sigma^2\big|_{r=0,r_0}$ from the regular Hamiltonian method was quite large and almost the same as the value of $r_0 = 1/Z$. In contrast, $\sigma^2\big|_{r=0,r_0}$ from the inverse Hamiltonian method was very small. This analysis indicates that in the regular Hamiltonian method, the description of the weak singularity region causes a big problem; though the energy contributions from the large and small components may be canceled out each other, so that the energy expectation value looks good but the value of σ^2 is bad because no cancelation occurs in this quantity. Thus, the inverse Hamiltonian method would be more feasible than the regular Hamiltonian method to obtain the wave function stably and accurately in the relativistic case.

5 Conclusions

In the variational calculations of the DE and DCE solutions, some difficulties arise because of the existence of the positron states together with the electron states. The FC method is shown to avoid such difficulties mainly by two reasons. One by the FC or ICI balance between the components of the spinor wave function and the other is due to the use of the inverse variation method. Since the DE and DCE impose strict relations between the components of the spinor wave function, it is clear that the wave function constructed from poor variational space should cause a problem in the variational calculations. In the FC method, exact balancing is automatically made in the complement function generation step. The inverse variation principle based on the inverse Hamiltonian is useful because it guarantees the existence of the Ritz-type variation principle.

We have introduced several quantities to check the exactness of the calculated wave function. The quantities to examine the exactness are very important for the relativistic calculations because the solutions of the DE or DCE are not bound from below. As such quantities, we introduced the total square deviations from the exact wave function, local energy, H-square error, and the energy upper and lower bounds to check the exactness of the FC wave function of the hydrogen isoelectronic atoms calculated by some different variation methods. Especially, the H-square error is a very important quantity because it is always bound and takes always positive elements and zero only for the exact solution. In the regular Hamiltonian method, the energy looked like being successful but the wave function especially the energy density near the mild singularity region near the nucleus was far from the exact solution.

In conclusion, as a stable procedure to ensure the solution of the DE, we suggest first to make a correct wave function by the FC method that guarantees the FC or ICI balance and second to solve the DE with the inverse Hamiltonian method. The H-square error is a quite significant property to be able to guarantee the true solution. If we use the inverse Hamiltonian method, then σ^2 is simultaneously evaluated.

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