



Research paper

Inverse Hamiltonian method assisted by the complex scaling technique for solving the Dirac-Coulomb equation: Helium isoelectronic atoms

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ABSTRACT

The free complement (FC) theory, proposed for solving the Schrödinger equations of atoms and molecules, was previously extended to solving the relativistic Dirac-Coulomb equations (DCE) [H. Nakatsuji and H. Nakashima, *Phys. Rev. Lett.* **95**, 050,407 (2005)]. In this letter, the inverse Hamiltonian method assisted by the complex scaling technique is further introduced to solve two problems associated with the many-electron DCE, the unbound problem of the Dirac-Coulomb Hamiltonian and the continuum dissolution problem. The proposed accurate FC theory is applied to the calculations of the ground and low-lying excited states of helium isoelectronic atoms: He, Th^{88+} , and Nh^{111+} .

1. Introduction

The Dirac equation (DE) is essential for the studies of the relativistic effects in one-electron atoms and molecules [1–7]. However, the many-electron versions of the DE with the algebraic generalizations of the classical Coulomb potential, called Dirac-Coulomb equation (DCE), are not perfect since they do not satisfy the Lorentzian transformation [3,4]. Two problems associated with these versions are (1) the unbound problem of the Dirac-Coulomb (DC) Hamiltonian, the so-called variational collapse problem, and (2) the continuum dissolution problem, the so-called Brown-Ravenhall disease [8]. They consist of the computational obstacles that must be solved in the variational treatments of the DCE for many electron atoms and molecules.

Several approximate methods were proposed to address these problems, such as the lower-order balance condition [9,10], the no-pair approximation [4,11], etc. However, the approximate characters within these methods seem to destroy the essential relativistic natures themselves [12–15]. For example, Savukov et al. [12] pointed out that the negative energy states are important to reproduce the experimental results of the magnetic-dipole transitions of the alkali-metal atoms. Pestka, Watanabe, and Bylicki et al. [13–15] investigated the correlation energies of the helium isoelectronic atoms with and without the no-pair approximation. They found that, when the no-pair approximation was employed, the correlation energies were overestimated especially for the atoms of large nuclear charges. Thus, in order to correctly solve the DCE without affecting the essential relativistic natures, a new reliable methodology seems to be necessary.

In our previous study [16], the free complement (FC) theory,

proposed for solving the nonrelativistic Schrödinger equation (SE) of atoms and molecules [17], was extended to solving the relativistic Dirac equation. There, we reported two significant methodologies: the FC balance and the inverse Hamiltonian method to resolve (1) the unbound problem of the DC Hamiltonian. The FC theory generates the analytical complement functions (cf's), using the scaling function and the Hamiltonian applied to the initial wave functions of the system. This feature leads to the FC balance [16,20] that the exact wave function of the DCE must satisfy [18,19]. The inverse Hamiltonian method was introduced by Hill and Krauthausser for the one-electron DE to recover the Ritz variational property [21]. Similar method was also invented by one of the present authors to overcome the Coulomb singularity problem in solving the SE [22]. This method was also used for solving the two-electron DCE in our previous work [16]. We applied these methodologies to several simple systems and confirmed that the accurate solutions were stably obtained without the variational collapse [16,20,23,24].

Then, the remaining problem is (2) the continuum dissolution problem for the DCE. The continuum states, Brown-Ravenhall continuum, appear almost always in the energy spectra. In a two-electron system, that occurs because

$$E [\text{1st electron: Positive continuum}] + E [\text{2nd electron: Negative continuum}] = [\text{Any value}]. \quad (1)$$

The electronic bound states are embedded in the continuum states and they are considered as resonance states in a strict sense. Thus, we need to solve the many-electron DCE with resonance characters although this arose from the fact that the many-electron DCE is not a

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perfect relativistic equation [3,4,8]. For that purpose, the complex scaling (CS) technique was introduced [25,26]. Pestka et al. and Al-haidari applied the CS technique to the Hylleraas-CI calculations of helium isoelectronic atoms with the ordinary (regular) Dirac Hamiltonian [27–30]. Their studies were impressive and considerably improved the accuracies and stabilities from their previous works. However, the unphysical solutions from the problem (1) still exist near the electronic bound states though they may be distinguishable by the CS technique.

In order to solve both (1) the unbound problem of the DC Hamiltonian and (2) the continuum dissolution problem, simultaneously, we introduce the inverse Hamiltonian method combined with the CS technique. With this method, most of the unbound solutions are first shifted to the negative energy region by the inverse Hamiltonian method. Then, we just have to treat the remaining Brown-Ravenhall continuum by the CS technique. In the present paper, we examine this method with the higher-order FC calculations of the ground and low-lying excited states of helium isoelectronic atoms: Helium (He ($Z = 2$)), Thorium (Th⁸⁸⁺ ($Z = 90$)), and Nihonium (Nh¹¹¹⁺ ($Z = 113$)) [31], where Z denotes nuclear charge. “Nihonium” is a new element named officially in 2016: “Nihon” means “Japan” in Japanese.

Note that the purpose here is not to reproduce the experimental data, but to develop a method for accurately solving the DCE. The present model employs the fixed nucleus approximation with the central field potentials around the nucleus and the classical electron-repulsion Coulomb potential. The present model does not consider the finite mass of the nucleus, size of the nucleus, nucleus recoil, Breit interaction, QED corrections, etc. These effects can be included perturbatively if one can accurately solve the DCE of the present model.

2. Inverse Hamiltonian method assisted by the complex scaling technique

In the inverse Hamiltonian method [16,21,22], the variational parameters in ψ are optimized through the inverse energy $E_w^{-1} = \langle \psi | H_w^{-1} | \psi \rangle / \langle \psi | \psi \rangle$ being variationally maximized. w is a shift parameter and $E_w (= E + w)$ and H_w are the shifted energy and Hamiltonian, respectively. One should set w for the electronic bound states to have the lowest positive energies. The Ritz variational property recovers with the variational principle $E_w^{-1} \leq E_{\text{exact}}^{(w)-1}$ [21], where $E_{\text{exact}}^{(w)-1} = (E_{\text{exact}} + w)^{-1}$ is the shifted exact energy of the target state. This is rigorously valid at least for the one-electron DE. Although we do not know an explicit form of H_w^{-1} , E_w^{-1} can be alternatively evaluated by

$$E_w^{-1} = \frac{\langle \varphi | H_w | \varphi \rangle}{\langle \varphi | H_w^2 | \varphi \rangle} \quad (2)$$

with a clever trick of $\psi = H_w \varphi$ [16,21]. It is obvious that, if φ is exact, then ψ is also exact. The variational optimization, therefore, can be applied to the parameters in φ .

The CS technique is one of the established methods to study resonance states [25,26]. The regular DCE with the complex coordinate rotation $\mathbf{r} \rightarrow \mathbf{r}e^{i\theta}$ is given by

$$H(\theta)\psi(\theta) = E(\theta)\psi(\theta), \quad (3)$$

where θ is a rotation angle on the complex plane. $H(\theta)$ is the rotated Hamiltonian and $\psi(\theta)$ and $E(\theta)$ are respectively the corresponding wave function and energy eigenvalue. Similarly, the inverse DCE with the complex coordinate rotation is given by

$$H_w(\theta)^{-1}\psi(\theta) = E_w(\theta)^{-1}\psi(\theta). \quad (4)$$

Introducing the same trick in Eq. (2): $\psi(\theta) = H_w(\theta)\varphi(\theta)$, the complex inverse energy is given by

$$E_w(\theta)^{-1} = \frac{\langle H_w(\theta)\varphi(\theta) | \varphi(\theta) \rangle}{\langle H_w(\theta)\varphi(\theta) | H_w(\theta)\varphi(\theta) \rangle}. \quad (5)$$

Eq. (5) is also derived from Eq. (4) capped by $H_w(\theta)\varphi(\theta)$ from bra

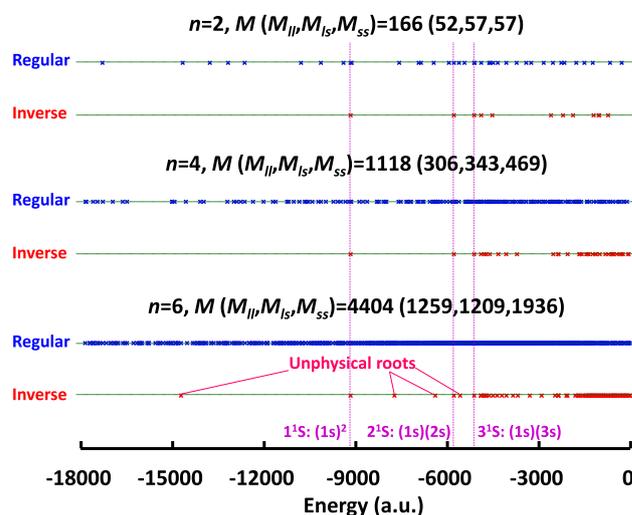


Fig. 1. Energy eigenvalue distributions obtained by the regular and inverse Hamiltonian methods without complex scaling for Th⁸⁸⁺ ($Z = 90$). The blue and red points show the distributions of the RR- and II-energies, respectively, at the FC orders: $n = 2, 4$, and 6 . The pink vertical lines indicate the positions of the $1^1S: (1s)^2$, $2^1S: (1s)(2s)$, and $3^1S: (1s)(3s)$ states. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

side. $E_w(\theta)^{-1}$ and $\varphi(\theta)$ are calculated by solving the complex inverse secular equation with the $H_w(\theta)$ and $H_w(\theta)^2$ matrices. In the DCE, $H_w(\theta)$ is represented by $H_w(\theta) = e^{-i\theta}H_w - [e^{-i\theta} - 1]\beta$ with the no-scaling H_w and the constant diagonal matrix β . Note that $H_w(\theta)$ of the DCE does not contain any second order $e^{-2i\theta}$ terms whereas that of the SE includes them from the kinetic energy operator.

In the CS technique [25,26], if the basis set is complete, the exact energies of the bound states are real and independent on θ . The energies of the resonance or antiresonance states are complex but they are still independent on θ . In contrast, the energies of the continuum states are strongly dependent on θ , i.e. they rotate on the complex plane proportional to θ . Thus, the physical bound and/or resonance electronic states can be distinguished from the continuum states by the CS technique.

We want to emphasize that the inverse Hamiltonian method is still important even in the CS technique. In a two-electron system, the electronic bound states locate around $E \approx 2c^2$; both electrons have the electronic rest energy c^2 , where c is the speed of light in atomic units. By Eq. (1), the continuum states around $E \approx 2c^2$ emerge when one particle has a positive energy near $3c^2$ and the other particle has a negative energy near $-c^2$. Since $3c^2$ is third times as the ordinary rest energy c^2 , such an ultra-relativistic continuum state rarely gives obstacles in the variational calculations. On the other hand, the critical configuration that causes problems is that one particle is an ordinary electronic state around c^2 and the other particle is a positron state around $-c^2$. The total energy of this configuration is $c^2 + (-c^2) \approx 0$ which is far away from $2c^2$. In the regular Hamiltonian, however, these roots seep into the region of the electronic bound states as increasing the basis space. These roots may unphysically couple with the continuum states near the electronic bound states. In contrast, in the inverse Hamiltonian method, most of these roots around $c^2 + (-c^2) \approx 0$ are driven into the negative energy region with a sufficiently large energy shift. Therefore, the CS technique is only needed to address the continuum dissolution problem.

We classify the three-type energies [22,23]; II (Inverse-Inverse), IR (Inverse-Regular), and RR (Regular-Regular) energies, denoted by E_{II} , E_{IR} , and E_{RR} , respectively. The II and RR energies correspond to the eigenvalues of the secular equations with the inverse and regular Hamiltonian, respectively. The IR energy is the energy expectation value

Table 1

Energy convergences of the FC theory for Th^{88+} ($Z = 90$) with the regular and inverse Hamiltonian methods assisted by the CS technique. RR-, II-, and IR-energies of the ground and excited states are summarized at each order of the FC theory with $w = c^2$ and $\theta = 0.05$. $|\Delta E_{II-IR}|$ at each order and ΔE_{Ref} and ΔE_{Nonrel} at $n = 6$ are also given. All data represented in atomic units (a.u.).

n^a	$M (M_{ll}, M_{ls}, M_{ss})^b$	Regular		Inverse		$ \Delta E_{II-IR} ^c$		
		$\text{Re}(E_{RR}(\theta))$	$\text{Im}(E_{RR}(\theta))$	$\text{Re}(E_{II}(\theta))$	$\text{Im}(E_{II}(\theta))$	$\text{Re}(E_{IR}(\theta))$	$\text{Im}(E_{IR}(\theta))$	
Ground state: $1^1\text{S}(1\text{s})^2$								
1	48 (16,16,16)	-9167.007 04	4.066×10^{-2}	-9166.649 36	1.408×10^{-2}	-9166.920 28	1.408×10^{-2}	0.270 9
2	166 (52,57,57)	-9166.964 96	2.262×10^{-2}	-9166.738 94	-1.208×10^{-2}	-9166.930 68	-1.208×10^{-2}	0.191 7
3	492 (127,157,208)	-9166.929 43	2.217×10^{-2}	-9166.812 71	-8.396×10^{-3}	-9166.929 74	-8.396×10^{-3}	0.117 0
4	1118 (306,343,469)	-9166.932 48	-1.587×10^{-3}	-9166.846 88	-6.080×10^{-3}	-9166.929 21	-6.080×10^{-3}	0.082 3
5	2400 (666,684,1050)	-9166.927 34	-6.992×10^{-4}	-9166.867 62	-4.438×10^{-3}	-9166.926 80	-4.438×10^{-3}	0.059 2
6	4404 (1259,1209,1936)	-9166.927 63	-6.551×10^{-4}	-9166.878 92	-3.552×10^{-3}	-9166.927 88	-3.552×10^{-3}	0.049 0
	Ref. [35] ^d	-9166.927 2		-9166.927 2		-9166.927 2		
	Ref. [28] ^d	-9166.927 29		-9166.927 29		-9166.927 29		
	Nonrelativistic	-8043.907 56		-8043.907 56		-8043.907 56		
	ΔE_{Ref}^e	-0.000 34		0.048 37		-0.000 59		
	ΔE_{Nonrel}^f	-1123.020 07		-1122.971 35		-1123.020 31		
First excited state: $2^1\text{S}(1\text{s})(2\text{s})$								
1	48 (16,16,16)	-5783.275 88	-1.043×10^0	-5783.146 94	6.919×10^{-1}	-5784.457 44	6.918×10^{-1}	1.310 5
2	166 (52,57,57)	-5782.777 44	8.194×10^{-3}	-5782.690 47	1.823×10^{-3}	-5782.740 14	1.823×10^{-3}	0.049 7
3	492 (127,157,208)	-5782.740 40	3.364×10^{-3}	-5782.712 68	-4.722×10^{-4}	-5782.736 21	-4.722×10^{-4}	0.023 5
4	1118 (306,343,469)	-5782.737 57	-3.295×10^{-4}	-5782.719 41	-3.600×10^{-4}	-5782.736 02	-3.600×10^{-4}	0.016 6
5	2400 (666,684,1050)	-5782.735 74	-3.431×10^{-4}	-5782.723 57	-2.456×10^{-4}	-5782.735 85	-2.456×10^{-4}	0.012 3
6	4404 (1259,1209,1936)	-5782.735 72	-9.669×10^{-4}	-5782.725 84	-6.551×10^{-5}	-5782.734 33	-6.551×10^{-5}	0.008 5
	Nonrelativistic	-5041.750 20		-5041.750 20		-5041.750 20		
	ΔE_{Nonrel}^f	-740.985 52		-740.975 63		-740.984 13		
Second excited state: $3^1\text{S}(1\text{s})(3\text{s})$								
1	48 (16,16,16)	-5118.706 59	-2.555×10^0	-5114.305 20	3.718×10^0	-5120.206 34	3.717×10^0	5.901 1
2	166 (52,57,57)	-5118.206 74	1.486×10^{-2}	-5118.197 11	-2.449×10^{-2}	-5118.388 16	-2.449×10^{-2}	0.191 1
3	492 (127,157,208)	-5118.226 17	1.651×10^{-3}	-5118.217 60	-4.567×10^{-4}	-5118.224 35	-4.567×10^{-4}	0.006 7
4	1118 (306,343,469)	-5118.224 00	1.344×10^{-4}	-5118.219 01	-8.023×10^{-5}	-5118.223 50	-8.023×10^{-5}	0.004 5
5	2400 (666,684,1050)	-5118.223 50	-5.303×10^{-5}	-5118.220 14	-4.707×10^{-5}	-5118.223 37	-4.707×10^{-5}	0.003 2
6	4404 (1259,1209,1936)	-5118.223 40	-6.649×10^{-5}	-5118.220 71	-2.837×10^{-5}	-5118.223 17	-2.837×10^{-5}	0.002 5
	Nonrelativistic	-4490.576 16		-4490.576 16		-4490.576 16		
	ΔE_{Nonrel}^f	-627.647 25		-627.644 56		-627.647 02		

^a The order of the FC theory.

^b M is the total dimension of the FC theory and M_{ll} , M_{ls} , and M_{ss} are the dimensions of ll , ls , and ss components, respectively.

^c $\Delta E_{II-IR} = \text{Re}(E_{II}(\theta)) - \text{Re}(E_{IR}(\theta))$.

^d Value of parameter c is different from the present calculations.

^e Energy differences (real parts) between $E_{IR}(\theta)$ of the FC theory at $n = 6$ and those of the Ref. [28].

^f Energy differences (real parts) between $E_{IR}(\theta)$ of the FC theory at $n = 6$ and nonrelativistic energies calculated for this paper.

of the regular Hamiltonian using the wave function obtained by the inverse Hamiltonian method. Note that, if $|\text{Re}(\langle \varphi(\theta) | H_w(\theta)^\dagger | \varphi(\theta) \rangle)| \gg |\text{Im}(\langle \varphi(\theta) | H_w(\theta)^\dagger | \varphi(\theta) \rangle)|$ and $|\langle \varphi(\theta) | H_w(\theta) | \varphi(\theta) \rangle|^2 \approx \langle H_w(\theta) \varphi(\theta) | H_w(\theta) \varphi(\theta) \rangle$ are roughly satisfied, then the imaginary parts of II- and IR-energies become almost same values.

In the inverse Hamiltonian method, since the r.h.s. of Eq. (5) includes the H^2 (H -square) integrations, the complex-scaling H -square quantity

$$\sigma^2 = \langle H_w(\theta) \varphi(\theta) | H_w(\theta) \varphi(\theta) \rangle - |\langle \varphi(\theta) | H_w(\theta) | \varphi(\theta) \rangle|^2 \quad (6)$$

is simultaneously evaluated, where $\varphi(\theta)$ is assumed to be normalized. σ^2 is known as one of the stringent quantities to judge the exactness; σ^2 is always positive for approximate $\varphi(\theta)$ and zero only for the exact $\varphi(\theta)$ [32]. This is valid for the unbound DCE. This σ^2 can be reformed to

$$\sigma^2 = E_{IR}^\dagger \cdot \Delta E_{II-IR}, \quad (7)$$

where $\Delta E_{II-IR} = E_{II} - E_{IR}$. If the solution is exact, $\sigma^2 = 0$, then $|\Delta E_{II-IR}| = 0$ and E_{II} , and E_{IR} converge to the same exact energies. Therefore, $|\Delta E_{II-IR}|$ is also one of the intelligible quantities to assess the exactness.

3. Applications to He ($Z = 2$), Th^{88+} ($Z = 90$), and Nh^{111+} ($Z = 113$)

3.1. Free complement calculations

We applied the present method to the helium isoelectronic atoms: He ($Z = 2$), Th^{88+} ($Z = 90$), and Nh^{111+} ($Z = 113$). The wave functions are represented by $\varphi = (\varphi^{ll}, \varphi^{ls}, \varphi^{sl}, \varphi^{ss})^\dagger$, where l and s denote positive-energy (large) and negative-energy (small) components. ll means both electrons occupy positive-energy (large) components and similar notations for ls , sl , and ss . Each component composes of a 4-dimensional vector and φ is a $4^2 = 16$ dimensional spinor.

We constructed the FC wave functions with the same manner as the previous case [16]. We employed the g function $g = 1 + r_1 + r_2 + r_{12}$ to eliminate the Coulomb singularity in the DC Hamiltonian. We also used the same-form initial function ψ_0 as the previous case [16], but here employed the three sets of Slater functions with the exponents, $(\alpha_1, \alpha_2) = (Z, Z)$, $(Z, Z/2)$, and $(Z, Z/4)$ for electrons 1 and 2, to represent the ground and a few low-lying excited states. The FC calculations were performed up to order $n = 6$ without expanding the spin-angular parts. The dimension M consists of M_{ll} , M_{ls} , and M_{ss} for the ll , ls , and ss components, respectively, where φ^{ls} and φ^{sl} are not independent: $\varphi^{ls} = -\varphi^{sl}$. Due to the symmetry of the spin-angular parts, we can calculate the states corresponding to the singlet states of the nonrelativistic case. Thus, we targeted the ground, first, and second excited states, 1^1S :

Table 2
 Energies by the FC theory at $n = 6$ with $M (M_{ll}, M_{ls}, M_{ss}) = 4404 (1.259, 1209, 1936)$ for He ($Z = 2$), Th⁸⁸⁺ ($Z = 90$), and Nh¹¹¹⁺ ($Z = 113$) with the regular and inverse Hamiltonian methods assisted by the CS technique. RR-, II-, and IR-energies of the ground and excited states are summarized with $w = c^2$ and $\theta = 0.05$ for He and Th⁸⁸⁺ and $\theta = 0.01$ for Nh¹¹¹⁺. $|\Delta E_{II-IR}|$, ΔE_{Ref} , and ΔE_{Nonrel} are also given. All data represented in atomic units (a.u.).

State	Regular		Inverse		$ \Delta E_{II-IR} ^a$	ΔE_{Ref}^b	ΔE_{Nonrel}^c	Ref. [28] ^d	Nonrelativistic
	$\text{Re}(E_{RR}(\theta))$	$\text{Im}(E_{RR}(\theta))$	$\text{Re}(E_{II}(\theta))$	$\text{Im}(E_{II}(\theta))$					
He ($Z = 2$)									
1 ¹ S:(1s) ²	-2.904 074 85	2.556×10 ⁻⁶	-2.903 803 38	-1.329×10 ⁻⁵	-2.903 867 34	-1.329×10 ⁻⁵	-0.000 143	-2.903 856 84	-2.903 724 37
2 ¹ S:(1s)(2s)	-2.146 102 74	-9.108×10 ⁻⁷	-2.146 080 70	-1.114×10 ⁻⁶	-2.146 086 10	-1.114×10 ⁻⁶	-0.000 112	-2.145 974 04	-2.145 974 04
3 ¹ S:(1s)(3s)	-2.061 385 12	-1.796×10 ⁻⁷	-2.061 378 74	-2.434×10 ⁻⁷	-2.061 380 02	-2.434×10 ⁻⁷	-0.000 108	-2.061 271 98	-2.061 271 98
Th⁸⁸⁺ ($Z = 90$)									
1 ¹ S:(1s) ²	-9166.927 63	-6.551×10 ⁻⁴	-9166.878 92	-3.552×10 ⁻³	-9166.927 88	-3.552×10 ⁻³	-1123.020 31	-9166.927 29	-8043.907 56
2 ¹ S:(1s)(2s)	-5782.735 72	-9.669×10 ⁻⁴	-5782.725 84	-6.551×10 ⁻⁵	-5782.734 33	-6.551×10 ⁻⁵	-740.984 13	-5041.750 20	-5041.750 20
3 ¹ S:(1s)(3s)	-5118.223 40	-6.649×10 ⁻⁵	-5118.220 71	-2.837×10 ⁻⁵	-5118.223 17	-2.837×10 ⁻⁵	-627.647 02	-4490.576 16	-4490.576 16
Nh¹¹¹⁺ ($Z = 113$)									
1 ¹ S:(1s) ²	-16206.507 0	-1.831×10 ⁻³	-16205.928 6	-3.085×10 ⁻³	-16206.510 6	-3.085×10 ⁻³	-3507.978 1	-16206.508 8	-12698.532 5
2 ¹ S:(1s)(2s)	-10274.821 1	-9.143×10 ⁻⁴	-10274.757 1	3.029×10 ⁻³	-10274.821 6	3.029×10 ⁻³	-2320.278 3	-7954.543 26	-7954.543 26
3 ¹ S:(1s)(3s)	-9038.126 00	-6.010×10 ⁻⁵	-9038.109 92	7.025×10 ⁻⁴	-9038.126 01	7.025×10 ⁻⁴	-1956.081 8	-7082.044 17	-7082.044 17

^a $\Delta E_{II-IR} = \text{Re}(E_{II}(\theta)) - \text{Re}(E_{IR}(\theta))$.

^b Energy differences (real parts) between $E_{IR}(\theta)$ of the FC theory and those of the Ref. [28].

^c Energy differences (real parts) between $E_{IR}(\theta)$ of the FC theory (E_{IR}) and nonrelativistic energies: Ref. [36] for $Z = 2$ and the values for $Z = 90$ and 113 were calculated for this paper.

^d Value of parameter c is different from the present calculations.

(1s)², 2¹S:(1s)(2s), and 3¹S:(1s)(3s), in the present work.

We used the value $c = 137.035\,999\,679$ [33]. In all the tables and figures, the origin of the total energies is set to $2c^2 + w$ without notification. We employed the energy shift $w = c^2$ for all the calculations of the inverse Hamiltonian method.

3.2. Energy distributions by the regular and inverse Hamiltonian methods without complex scaling

We first applied the regular and inverse Hamiltonian methods without complex scaling. Fig. 1 plots all the eigenvalues of the regular (RR-) and inverse (II-) energies with the energy range: $-18,000$ to 0 a.u. for Th⁸⁸⁺ at FC orders $n = 2, 4$, and 6 , where c^2 is 18778.865 a.u.

In the regular Hamiltonian method, the unphysical roots appeared at $n = 2$ and they grew rapidly as increasing the FC orders. However, the physical solutions surely exist in the energy spectra due to satisfying the FC balance [16]. However, one must distinguish the physical solutions embedded in the unphysical roots. This task is not generally easy especially in higher order FC calculations.

In contrast, in the inverse Hamiltonian method, no unphysical roots existed around the target electronic states at $n = 2$ and 4 . However, at $n = 6$, a few unphysical roots were observed among 1¹S:(1s)², 2¹S:(1s)(2s), and 3¹S:(1s)(3s) states and also below the ground state. Thus, unphysical roots may emerge even in the inverse Hamiltonian method especially when a small energy shift w is employed and/or a large number of complement (basis) functions are used. This would be due to the continuum dissolution problem rather than the unbound problem of the DC Hamiltonian. To eliminate such unphysical roots, one way is to employ a larger energy shift w in the inverse Hamiltonian method without complex scaling. This way is practically important. However, the CS technique combined the inverse Hamiltonian method is more straightforwardly useful to address this problem.

3.3. Convergence of the FC theory with the regular and inverse Hamiltonian methods assisted by the complex scaling technique

First, we examined the convergences of the FC calculations with the regular and inverse Hamiltonian methods assisted by the CS technique. Table 1 summarizes the RR-, II-, and IR-energies of the FC calculations at $n = 1$ to 6 for 1¹S:(1s)², 2¹S:(1s)(2s), and 3¹S:(1s)(3s) states of Th⁸⁸⁺ with the rotation angle $\theta = 0.05$. The reference ground-state energies [28,34,35] and the nonrelativistic energies [36] were also given for comparison.

In the regular Hamiltonian method, the real parts of the RR-energies approached to their correct energies as increasing the FC orders for all three states. However, they did not always approach from above, i.e. the Ritz variational property does not always hold. The imaginary parts were 10^{-4} – 10^{-5} a.u., which were quite small compared to their real parts 10^3 – 10^4 a.u. However, their amplitudes cannot be ignored since they are the same order as chemical accuracy, i.e. 1 kcal/mol $\approx 1.6 \times 10^{-3}$ a.u.

In the inverse Hamiltonian method, the real parts of the II-energies always satisfied the Ritz variational property, i.e. they converged to the exact values from above though this feature is not theoretically guaranteed due to the non-Hermite complex Hamiltonian. On the other hand, the real parts of the IR-energies were not always approaching to the exact values from above but their values were more accurate than those of the II-energies. Those IR-energies were $-9166.927\,88$ – $0.000\,55$ i , $-5782.734\,33$ – $0.000\,07$ i , and $-5118.223\,17$ – $0.000\,03$ i a.u. for the 1¹S:(1s)², 2¹S:(1s)(2s), and 3¹S:(1s)(3s) states at $n = 6$, respectively. Similar to the RR-energies, the imaginary part of the ground state was 10^{-3} order and those of the excited states were 10^{-5} order.

Table 1 also summarizes $|\Delta E_{II-IR}| = |E_{II} - E_{IR}|$ at each FC order. For all three states, $\text{Re}(\Delta E_{II-IR})$ were always positive, i.e. $\text{Re}(E_{II}) \geq \text{Re}(E_{IR})$, and $|\Delta E_{II-IR}|$ monotonically converged to zero as increasing the FC orders. $|\Delta E_{II-IR}|$ for the excited states were better than those of the ground

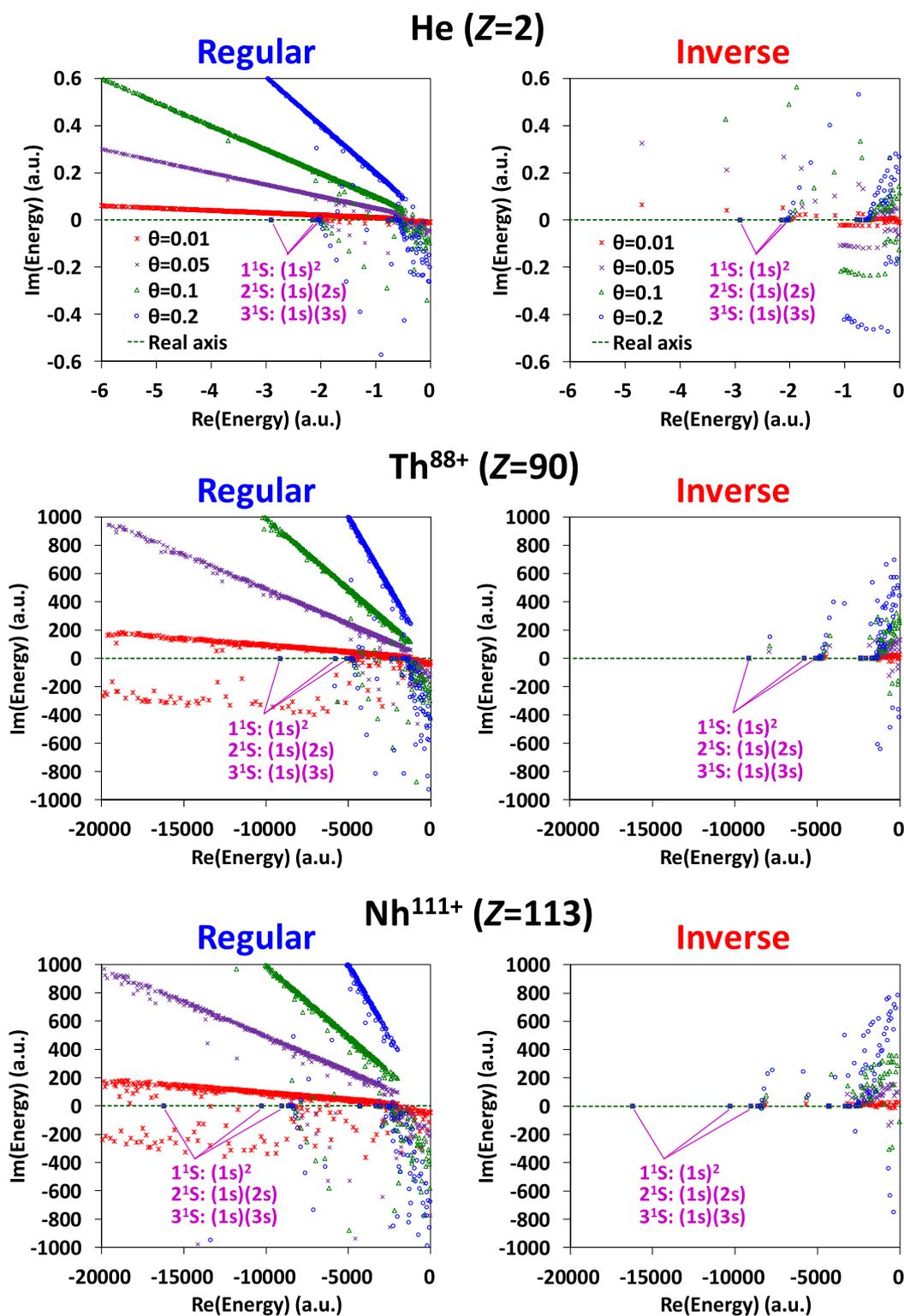


Fig. 2. Complex energy eigenvalue distributions obtained with the regular and inverse Hamiltonian methods assisted by the CS technique for He ($Z = 2$), Th⁸⁸⁺ ($Z = 90$), and Nh¹¹¹⁺ ($Z = 113$). The left and right figures show the distributions of the RR- and II-energies, respectively, at the FC order: $n = 6$ with M (M_{II} , M_{IS} , M_{SS}) = 4404 (1259,1209,1936) with the rotation angle $\theta = 0.01, 0.05, 0.1$, and 0.2 . The horizontal and vertical axes represent the real and imaginary parts of the complex energy, respectively. The points indicated by the pink lines show the $1^1S: (1s)^2$, $2^1S: (1s)(2s)$, and $3^1S: (1s)(3s)$ states. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

states. It implies that both II- and IR-energies approached to the exact energies at high FC orders and the excited states were more accurately calculated than the ground state.

3.4. FC calculations with the regular and inverse Hamiltonian methods assisted by the complex scaling technique for He, Th⁸⁸⁺, and Nh¹¹¹⁺

We next applied the FC theory to He and Nh¹¹¹⁺ in the same way as Th⁸⁸⁺ with the regular and inverse Hamiltonian methods assisted by the CS technique. Table 2 summarizes the RR-, II-, and IR-energies of the FC calculations at $n = 6$ for 1¹S:(1s)², 2¹S:(1s)(2s), and 3¹S:(1s)(3s) states. We employed the rotation angle $\theta = 0.05$ for He and Th⁸⁸⁺ and $\theta = 0.01$ for Nh¹¹¹⁺. For heavy elements, a small rotation angle may be enough in the inverse Hamiltonian method with a large energy shift since their electronic states become isolated from the unbound roots.

The real parts of the IR-energies were $-2.903\ 867\ 34$, $-9166.927\ 88$, and $-16206.510\ 6$ a.u. and the energy differences from Ref. [28] $\Delta E_{Ref.}$ were $-0.000\ 010\ 5$, $-0.000\ 59$, and $-0.001\ 80$ a.u. for the ground states of He, Th⁸⁸⁺, and Nh¹¹¹⁺, respectively. Thus, the absolute total energies were slightly lower and better than those of Ref. [28] in variational sense. $|\Delta E_{II-IR}|$ were $0.000\ 064\ 0$, $0.000\ 005\ 4$, and $0.000\ 001\ 3$ a.u. for the 1¹S:(1s)², 2¹S:(1s)(2s), and 3¹S:(1s)(3s) states of He, respectively. Those for Th⁸⁸⁺ were $0.049\ 0$, $0.008\ 5$, and $0.002\ 5$ a.u. and those for Nh¹¹¹⁺ were $0.582\ 0$, $0.064\ 5$, and $0.016\ 1$ a.u., respectively. Thus, all for three atoms, the solutions of the excited states converged to their exact solutions more rapidly than those of the ground states. The relativistic effects of the excited states are generally smaller than those of the ground states. Since the Rydberg 2s, 3s, ... electrons of the excited states are far apart from the nucleus, their relativistic kinetic energies are small in comparison with that of the 1s electron. The solutions of the excited states, therefore, would be more easily calculated than that of the ground state. The energy differences $\Delta E_{Nonrel.}$ between the relativistic and nonrelativistic energies were less than 1 mH for the ground state of He; only 0.01% to the total energy. It was $-1123.020\ 31$ a.u. for Th⁸⁸⁺; 12.3% to the total energy. For Nh¹¹¹⁺, it reached $-3507.978\ 1$ a.u.; 21.6% to the total energy.

Fig. 2 shows the distributions of the complex energy eigenvalues of the regular (RR-) and inverse (II-) energies at $n = 6$ with $\theta = 0.01$, 0.05 , 0.1 , and 0.2 for He, Th⁸⁸⁺, and Nh¹¹¹⁺. In the regular Hamiltonian method, the physical solutions almost located on the real axis independent on θ although many unphysical roots existed around the electronic bound states. As increasing the FC orders, the number of such unphysical roots increased and they formed spectra lines proportional to θ . Thus, the physical solutions are distinguishable from the unphysical roots even in the regular Hamiltonian method. However, this task may become difficult for the calculations at higher FC order and/or for more general complicated systems. On the other hand, since the inverse Hamiltonian method is free from the unbound problem, the continuum dissolution problem just remains in the complex plane. A small rotation angle, therefore, might be enough compared to the regular case. As shown in Fig. 2, there were no or only a few unphysical roots around the ground and low-lying excited states. Their physical electronic states were clearly distinguishable. Their solutions were obtained more accurately and stably than those of the regular Hamiltonian case.

Note that we did not discuss the definite values of the imaginary parts in details since their values are artifact and physically meaningless. To determine the resonance energies (especially imaginary parts) more precisely, it would be efficient to draw the θ trajectories and find stationary points. However, this process is beyond the present purpose. Even without such a process, the energies converged to the correct solutions as increasing the FC orders almost independent on θ .

4. Concluding remarks

In this paper, we introduced the complex scaling technique in the inverse Hamiltonian method that was used in our previous paper [16] to correctly solve the many-electron DCE with the free complement (FC) theory. This method could resolve both (1) the unbound problem of the DC Hamiltonian and (2) the continuum dissolution problem existed in the method of solving the DCE. The inverse Hamiltonian method pushed the most of unbound solutions into the negative energy region with a sufficiently large energy shift. Further, combining with the CS technique, the physical bound solutions could be clearly distinguished in the continuum sea. The electronic bound states could be more stably and accurately computed than the regular case due to a weak coupling with the continuum.

We examined this method for the ground and low-lying excited states of the helium isoelectronic atoms: He, Th⁸⁸⁺, and Nh¹¹¹⁺. In the present calculations, the best real absolute energies of the 1¹S:(1s)², 2¹S:(1s)(2s), and 3¹S:(1s)(3s) states were calculated, respectively, to be $-2.903\ 867\ 34$, $-2.146\ 086\ 10$, and $-2.061\ 380\ 02$ a.u. for He, $-9166.927\ 88$, $-5782.734\ 33$, and $-5118.223\ 17$ a.u. for Th⁸⁸⁺, and $-16206.510\ 6$, $-10274.821\ 6$, and $-9038.126\ 01$ a.u. for Nh¹¹¹⁺. The present new methodology would be useful for more complex many-electron systems.

CRedit authorship contribution statement

Hiroyuki Nakashima: Conceptualization, Methodology, Software, Validation, Formal analysis, Writing - original draft, Writing - review & editing, Visualization. **Hiroshi Nakatsuji:** Conceptualization, Methodology, Software, Validation, Formal analysis, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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