Solving the Schrödinger equation of helium and its isoelectronic ions with the exponential integral (Ei) function in the free iterative complement interaction method†

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We introduce here the exponential integral (Ei) function for variationally solving the Schrödinger equation of helium and its isoelectronic ions with the free iterative complement interaction (ICI) method. In our previous study [*J. Chem. Phys.*, 2007, **127**, 224104], we could calculate very accurate energies of these atoms by using the logarithmic function as the starting function of the free ICI calculation. The Ei function has a weak singularity at the origin, similarly to the logarithmic function, which is important for accurately describing the three-particle coalescence region. The logarithmic function, however, has a node and a maximum along the radial coordinate which may be physically meaningless. In contrast, the Ei function does not have such unphysical behaviors and so would provide an improvement over the logarithmic function. Actually, using the Ei function, instead of the logarithmic function, we obtained the energy, $E = -$**2.903 724 377 034 119 598 311 159 245 194 404 446 696 924**865 a.u. for the helium ground state with 21 035 functions, which is a slight improvement over our previous result (the bold face shows the digits that are believed to have converged). This result supports the suggestion that the Ei function is better than the logarithmic function for describing the three-particle coalescence region.

1. Introduction

As Dirac noted in 1929,[1] the Schrödinger equation (SE),

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

provides a governing principle of chemistry. Therefore, if a general solution of the SE were possible, very accurate prediction of chemical phenomena would become possible. However, it was simply a dream for over 80 years.

Helium atom was the simplest realistic unsolved system and many studies have been done to obtain essentially exact solutions of the SE. The first important achievement was by Hylleraas[2] as early as 1929. He employed a function of the form

$$\psi_{\text{Hylleraas}} = \sum_{(abc)}^{6\text{ terms}} C_{abc} \exp(-\alpha s) s^a t^b u^c, \tag{2}$$

where $s \equiv r_1 + r_2$, $t \equiv r_1 - r_2$ and $u \equiv r_{12}$. The indices a, b and c are all nonnegative integers and α is a nonlinear parameter. The coefficients C_{abc} were determined by the variational principle and the calculated energy was $E = -$**2.903**329 354 a.u., which was different from the essentially exact solution now available by less than 1 kcal mol^{-1}. Kinoshita[3] improved the Hylleraas wave function by introducing negative powers of s in eqn (2). Thakkar and Koga[4] even introduced real numbers for a, b and c and obtained the energy of $E = -$**2.903 724 377 034**03 a.u. with only 100 basis functions.

Several studies pointed out the importance of the logarithmic functions for describing the boundary condition at the three-particle coalescence region.[5–7] Frankowski and Pekeris performed the variational calculations using the logarithmic functions and showed a good convergence of the energies of the two-electron atoms as a support to the existence of the logarithmic terms in the exact wave function.[8] Freund *et al.* applied the logarithm basis to the helium isoelectronic ions and obtained quite accurate energies.[9] They concluded the importance of using the basis functions that have the same analytic structure as the exact wave function. More recently, Schwartz[10] performed quite extensive variational calculations based on the wave functions written as

$$\psi_{\text{Schwartz}} = \sum_{(abcd)}^{10\,259\text{ terms}} C_{abcd} \exp(-\alpha s)[\ln(s)]^d s^a t^b u^c, \tag{3}$$

where d is 0 or 1, and obtained a very accurate energy correct up to 36 digits. There are many other important studies on the helium and isoelectronic ions[11–17] and one may refer to our recent paper.[16]

In our laboratory, since 2000 we have studied the structure of the exact wave function and investigated the general method of solving the SE.[18] Overcoming the singularity problem caused by the Coulomb potentials of atomic and

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molecular Hamiltonians, we could have established the general method of solving the SE and proposed the free ICI (iterative complement interaction) method.[19] It was proved that the ICI wave function becomes exact at convergence.[18–20] Several applications have been reported since then.[21–23] In particular, we have applied the free ICI method to helium and its isoelectronic ions.[16] We have shown that the free ICI method generates a wave function of the form,

$$\psi = \sum_{(abcd)}^{22\,709\ \text{terms}} C_{abcd} \exp(-\alpha s)[\ln(s+u)]^d s^a t^b u^c, \qquad (4)$$

when we start from the initial wave function of the logarithmic form, $\exp(-\alpha s)\ln(s + u)$. We have shown that the use of the logarithmic function as the initial function of the free ICI formalism gives fast convergence, and obtained the energy $E =$ **−2.903 724 377 034 119 598 311 159 245 194 404 446 696 9**05 37 a.u. that is correct to over 40 digits, which was the world's best within the published literature. Similar accuracy was also obtained with the calculations that include the effect of nuclear motion as well as the electronic ones.[24] Excited states of the two-electron atoms were also calculated quite accurately with the free ICI formalism.[25] These data may be regarded as a numerical proof of the fact that one can obtain the energy and the wave function to any desired accuracy by using the free ICI methodology.

Let us examine several functions that were used to describe the wave function. Fig. 1 shows the plots of the Slater-type function, $\exp(-s)$, Kinoshita function, $\exp(-s)s^{-1}$, and the logarithmic function, $-\exp(-s)\ln(s)$. At the limit of $s = 0$, the Slater-type function has a finite cusp value but the Kinoshita function and the logarithmic function become infinite. These divergences are the essential behaviors from the three-particle coalescence boundary conditions.[5–7] However, the logarithmic function has the following two strange behaviors: a node at $s = 1$ and a maximum (minimum with minus sign) around $s = 1.763$, as shown in Fig. 1. These properties look unphysical for the ground state of the helium atom because the 1s orbital smoothly decreases to zero as $s \to \infty$ with neither a node nor a maximum. Therefore, the logarithmic functions must be improved, at least, for these unphysical behaviors.

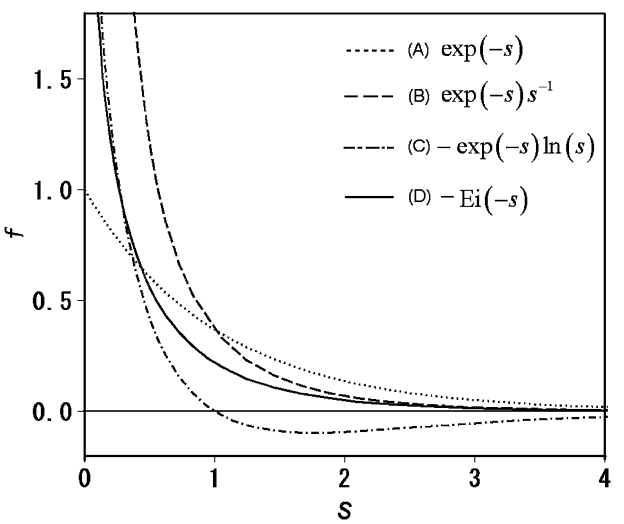

Fig. 1 Graphs of (A) Slater-type (dot line), (B) Kinoshita-type (dashed line), (C) logarithm-type (dash and dot line) and (D) Ei-type (solid line) functions. The logarithm-type function has a node at $s = 1$ and a maximum (minimum with minus sign) at $s = 1.763\ldots$.

In the present paper, we introduce the exponential integral (Ei) function as a new type of function that improves these behaviors of the logarithmic function. In the next section, we summarize the properties of the Ei function and in section 3 the free ICI method is briefly explained. In section 4, the applications of the free ICI method starting from the Ei function are described for helium and its isoelectronic ions and the concluding remarks are given in the last section.

2. The exponential integral function, Ei

In this section, the mathematical definition and some formulas about the Ei function are summarized very briefly. For more details, one may refer to mathematical books.[26–28]

The Ei function is defined for real x by an integral form as

$$\mathrm{Ei}(-x) \equiv \int_{-\infty}^{-x} \frac{\exp(t)}{t}\mathrm{d}t. \qquad (5)$$

We treat only positive x in the present study, and so the evaluation of the Ei function is straightforward. In the region of x being negative, which does not occur in our case, eqn (5) must be evaluated in terms of the Cauchy principal value. The plot of the Ei function is shown in Fig. 1. It is similar to the logarithmic function, but does not have the strange behaviors of the logarithmic function as described in the introduction. The Ei function can be generalized and extended to an entire complex plane as

$$\mathrm{Ei}(m,z) \equiv \int_1^{\infty} \frac{\exp(-zt)}{t^m}\mathrm{d}t, \qquad (6)$$

where m is an integer and z is a complex number. This function is named the m-argument Ei function. In the case of $x > 0$ and $m = 1$, eqn (6) is related to eqn (5) by

$$\mathrm{Ei}(-x) = -\mathrm{Ei}(1,x). \qquad (7)$$

The Ei functions with $m = 2, 3, \ldots$ have finite values at $x = 0$. Since their behaviors are very similar to the exponential function, we do not treat them in the present study. Hereafter we deal with the Ei function given by eqn (5) alone.

The Ei function is expandable in a power series as

$$\mathrm{Ei}(-x) = \gamma + \ln(x) - \exp(-x)\sum_{n=1}^{\infty} C_n x^n \qquad (8)$$

with

$$C_n = \frac{1}{n!}\left(\sum_{r=1}^{n}\frac{1}{r}\right), \qquad (9)$$

where $\gamma = 0.5772\ldots$ is the Gamma constant.[28] Eqn (8) is called Bessel's expansion formula. According to eqn (8), $\mathrm{Ei}(-x)$ contains $\ln(x)$, which becomes dominant at the region of x being very small. $\mathrm{Ei}(-x)$ diverges at $x = 0$ to minus infinity:

$$\lim_{x\to+0} \mathrm{Ei}(-x) = -\infty, \qquad (10)$$

but the following integrals exist:

$$\int_0^\infty \mathrm{Ei}(-x)\mathrm{d}x = -1, \tag{11}$$

$$\int_0^\infty \mathrm{Ei}(-x)^2\mathrm{d}x = 2\ln(2). \tag{12}$$

Further, the difference between the two Ei functions at $x = 0$ is finite as

$$\lim_{x\to+0}[\mathrm{Ei}(-\alpha x) - \mathrm{Ei}(-\beta x)] = \ln(\alpha) - \ln(\beta), \tag{13}$$

where $\alpha > 0$ and $\beta > 0$. Similarly, the difference between the Ei function and the logarithmic function at $x = 0$ is finite as

$$\lim_{x\to+0}[\mathrm{Ei}(-\alpha x) - \exp(-\alpha x)\ln(\beta x)] = \gamma + \ln\left(\frac{\alpha}{\beta}\right). \tag{14}$$

The differentiation of both sides of eqn (14) leads to

$$\lim_{x\to+0}\left[\frac{\mathrm{d}}{\mathrm{d}x}\mathrm{Ei}(-\alpha x)\right] = \lim_{x\to+0}\left[\frac{\mathrm{d}}{\mathrm{d}x}\exp(-\alpha x)\ln(\beta x)\right], \tag{15}$$

which indicates that the derivatives of the Ei and the logarithmic functions at $x = 0$ are identical. On the other hand, the limit of $\mathrm{Ei}(-x)$ at $x = \infty$ is zero:

$$\lim_{x\to\infty}\mathrm{Ei}(-x) = 0. \tag{16}$$

The differentials of the Ei function are possible as follows:

$$\frac{\mathrm{d}}{\mathrm{d}x}\mathrm{Ei}(-x) = \frac{\exp(-x)}{x} \tag{17}$$

and

$$\frac{\mathrm{d}^2}{\mathrm{d}x^2}\mathrm{Ei}(-x) = -\frac{\exp(-x)}{x} - \frac{\exp(-x)}{x^2}. \tag{18}$$

Eqn (17) is confirmed from eqn (5). Since the first derivative of $\mathrm{Ei}(-x)$ is always positive and becomes zero at $x = \infty$, it has no maximum and no nodes. These are the differences from the logarithmic function, $\ln(x)\exp(-x)$, as seen from Fig. 1. The indefinite integral of $\mathrm{Ei}(-x)$ is derived from eqn (5) by integration by parts as:

$$\int \mathrm{Ei}(-x)\mathrm{d}x = x\mathrm{Ei}(-x) + \exp(-x). \tag{19}$$

3. Free ICI (iterative complement interaction) method

In this section, we briefly explain the free ICI method[19,20] which is pertinent to the present study. The simplest form of the ICI wave function is defined by the recursion formula given by

$$\psi_{n+1} = [1 + C_n g(H - E_n)]\psi_n, \tag{20}$$

where n is an iteration number, C_n the variational parameter, and E_n the energy defined by

$$E_n \equiv \frac{\langle\psi_n|H|\psi_n\rangle}{\langle\psi_n|\psi_n\rangle}. \tag{21}$$

The g function is the scaling function that was introduced to eliminate the singularity problem caused by the integrals of the higher powers of the Hamiltonian including Coulomb singularities.[19,20] The initial function ψ_0 can be chosen freely if it satisfies the given conditions such as the spatial symmetry, spin multiplicity *etc*. Once g and ψ_0 are given, the ICI calculations proceed automatically and the wave function is improved systematically toward the exact wave function.

The free ICI method was proposed[19,20] to accelerate the convergence to the exact solution and to increase the freedom of the ICI calculations. The r.h.s. of eqn (20) consists of a sum of the analytical functions. We gather from them all the independent functions as $\{\phi_i^{(n)}\}$, $(i = 1,2,\ldots M_n)$ and make up our wave function by a linear combination of them as

$$\psi_{n+1} = \sum_{i=1}^{M_n} c_i^{(n)}\phi_i^{(n)}, \tag{22}$$

where $c_i^{(n)}$ is the variational parameter assigned to $\phi_i^{(n)}$. This is the free ICI wave function. Because of the increased freedom, the free ICI wave function converges faster than the original ICI wave function to the exact one. The variational parameters, $c_i^{(n)}$, are determined by solving the generalized eigenvalue problem:

$$\boldsymbol{H}^{(n)}\boldsymbol{C}^{(n)} = E_n\boldsymbol{S}^{(n)}\boldsymbol{C}^{(n)} \tag{23}$$

where $\boldsymbol{H}^{(n)}$ and $\boldsymbol{S}^{(n)}$ are the Hamiltonian and the overlap matrices, respectively, given by $\boldsymbol{H}_{ij}^{(n)} \equiv \langle\phi_i^{(n)}|H|\phi_j^{(n)}\rangle$ and $\boldsymbol{S}_{ij}^{(n)} \equiv \langle\phi_i^{(n)}|\phi_j^{(n)}\rangle$. In the free ICI method, we call n "order" instead of "iteration number", since ψ_n does not depend on the former coefficients $\{c_i^{(n-1)}\}$ *etc*. The key point of the ICI formalism is that the exact wave function of a system is constructed by the Hamiltonian itself of the system, *i.e.* $\psi = f(H)\psi_0$, and eqn (20) or (22) gives an expression of this equation in an analytical expansion form.

4. Applications to helium and its isoelectronic ions

4.1 Free ICI formalism

Our goal is to solve the SE of the ground state of the helium atom and its isoelectronic ions with the free ICI method. The Hamiltonian is represented in the Hylleraas coordinate as

$$\hat{H} = -\left(\frac{\partial^2}{\partial s^2} + \frac{\partial^2}{\partial t^2} + \frac{\partial^2}{\partial u^2}\right) - 2\frac{s(u^2-t^2)}{u(s^2-t^2)}\frac{\partial^2}{\partial s\partial u} - 2\frac{t(s^2-u^2)}{u(s^2-t^2)}\frac{\partial^2}{\partial u\partial t} - \frac{4s}{s^2-t^2}\frac{\partial}{\partial s} - \frac{2}{u}\frac{\partial}{\partial u} + \frac{4t}{s^2-t^2}\frac{\partial}{\partial t} - \frac{4sZ}{s^2-t^2} + \frac{1}{u}, \tag{24}$$

where Z is the nuclear charge. As the g function, we used

$$g = 1 + \frac{s^2-t^2}{s} + u, \tag{25}$$

which showed the best performance in our previous study.[16] The choice of the initial function ψ_0 is important since it determines the functional form of the free ICI wave function and this is our major concern in the present paper. First, we propose here to choose the Ei function, *i.e.*

$$\psi_0 = \mathrm{Ei}(-\alpha s), \tag{26}$$

where α is a kind of screening parameter. Our second choice is

$$\psi_0 = \mathrm{Ei}(-\alpha s)[1 + \ln(u)], \quad (27)$$

which includes the $\ln(u)$ function as an explicitly correlated factor that was introduced to accelerate the convergence. The $\ln(u)$ function was first introduced in our previous paper[16] and showed very good performance in spite of its simplicity. To compare the performance of the Ei function, we referred to the four different types of calculations that were taken from the previous paper:[16] (i) starting from the standard Slater-type function given by

$$\psi_0 = \exp(-\alpha s), \quad (28)$$

(ii) starting from the logarithmic function of the s coordinate with exponential function,

$$\psi_0 = \exp(-\alpha s)[1 + \ln(s)], \quad (29)$$

(iii) starting from the logarithmic function of s and correlated u coordinates with exponential function,

$$\psi_0 = \exp(-\alpha s)[1 + \ln(s) + \ln(u)], \quad (30)$$

and (iv) finally, starting from the function that includes s and u coordinates in the same logarithm function as

$$\psi_0 = \exp(-\alpha s)[1 + \ln(s + u)]. \quad (31)$$

The last one produced the best energy in our previous study.[16]

The wave functions that are generated by the free ICI formalism using the above g and the Ei-type initial functions ψ_0 [eqn (26) and (27)] are represented by

$$\psi = \sum_{(\mu\nu lmn)} C_{\mu\nu lmn}[\nu \exp(-\alpha s) + (1-\nu)\mathrm{Ei}(-\alpha s)][\ln(u)]^{\mu} s^a t^b u^c, \quad (32)$$

where ν, μ, a, b and c are integers, ν and μ take either 0 or 1. For the ψ_0 of eqn (26), μ is always zero. As seen from eqn (17), the exponential-type function is automatically generated from the differentiation of the Ei function. On the other hand, when one performs the free ICI calculations with the usual exponential and logarithmic ψ_0 given by eqn (28), (29) and (30), one obtains the wave functions that are represented by

$$\psi = \sum_{(\mu\nu lmn)} C_{\mu\nu lmn} \exp(-\alpha s)[\ln(u)]^{\mu}[\ln(s)]^{\nu} s^a t^b u^c, \quad (33)$$

where ν, μ, a, b and c are integers and the quantity $\nu + \mu$ takes the value 0 or 1. The wave function generated with ψ_0 of eqn (31) was already given in eqn (4). The Ei part of eqn (32) can be expanded using the Bessel's expansion formula given by eqn (8), and then the wave function given by eqn (33) can be reformulated into the same forms as eqn (32), though the details are different at finite order of the free ICI. When the order reaches infinity, the quantities ν, μ, a, b and c take all the patterns in both cases of eqn (32) and (33), and therefore these two wave functions will become identical. The Kinoshita-type terms (including negative powers of s) are also automatically generated in both types of the wave functions.[19,20] In Fig. 2, we summarized the function generation schemes of the free ICI method starting from different initial functions ψ_0.

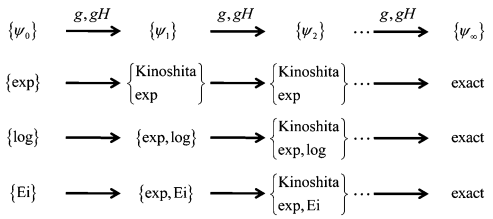

Fig. 2 Schemes of the basis function generations in the ICI method starting from different types of $\{\psi_0\}$. {exp}-type basis function represents $\exp(-\alpha s)s^a t^b u^c$ with a being positive or zero; {Kinoshita}-type basis function represents $\exp(-\alpha s)s^a t^b u^c$ with a being negative; {log}-type basis function represents $\exp(-\alpha s)\ln(s)s^a t^b u^c$; and {Ei}-type basis function represents $\mathrm{Ei}(-\alpha s)s^a t^b u^c$.

4.2 Computational details

The generations of the free ICI functions and the evaluations of the matrix elements for eqn (23) were performed with an algebraic mathematical package, *Maple 10*.[29] The diagonalization of the secular equation represented by eqn (23) was performed by our original solver using the GMP library.[30] Both enabled us to perform the calculations to any precision. In most calculations, we set the precision of the calculations to be 60 digits. However, in section 4.6 we will perform extensive calculations to a very large order n of the free ICI and there we set the precision to be 160 digits to avoid numerical instability.

4.3 Lower-order calculations of the helium atom starting from the Ei function

The energy of the initial function of eqn (26) with $\alpha = 1.6$ is $E_0 = -\mathbf{2}.425\,758\,617\,410\,142\,390$ a.u. This value was improved toward the exact one in the subsequent increased order n, as shown in Table 1. We performed the same calculations with $\alpha = 1.5$ and 1.7 and estimated the optimal α value as shown in Table 1. We also calculated approximately the derivatives $\partial E/\partial\alpha$ and $\partial^2 E/\partial\alpha^2$, which indicate the sensitivity of the energy with respect to the parameter α. From these quantities, we calculated the estimated best values of α, though all the calculations were done with the fixed value of $\alpha = 1.6$. For comparison, Table 2 shows the energies of the free ICI calculations starting from the ordinary Slater-type function of eqn (28) and from the one including the logarithmic function of eqn (29): these data are taken from our previous paper, ref. 16. Note that the screening parameter, α, in Table 2 was optimized at each order.

At order 9 ($n = 9$), 919 complement functions were generated from the Ei-type initial function given by eqn (26) and the corresponding energy was $E_9 = -\mathbf{2.903\,724\,377\,034\,119}\,147$ a.u., which has 16 digits accuracy. On the other hand, at $n = 9$, 541 functions were generated from the initial function of eqn (28) and 9 digits' accuracy was obtained: almost the same accuracy was obtained already at $n = 5$ ($M_5 = 188$) with the Ei case. In comparison with the calculations using the logarithmic initial function of eqn (29), the energy of the Ei case was almost the same at each order but the number of the complement functions was always smaller in the Ei case than in the logarithmic case. As seen in Table 1, the energy derivatives with respect to the screening parameter α approached zero as the order increases, and therefore at large

Table 1 Energy of helium atom calculated by the free ICI method with the initial function $\psi_0 = \exp(-\alpha s)$ (eqn (26)), the first and second derivatives of the energy with respect to the parameter α and the best estimated value of α

n^a	$M_n{}^b$	α	Energy E/a.u.	$E - E_{best}$/a.u.	$\partial E/\partial\alpha^d$	$\partial^2 E/\partial\alpha^{2e}$	Best α^f
0	1	1.6	**−2.**425 758 617 410 142 390	4.78×10^{-1}	1.74×10^{0}	2.04×10^{0}	1.172
1	7	1.6	**−2.90**0 008 689 031 112 995	3.72×10^{-3}	1.01×10^{-3}	8.55×10^{-2}	1.594
2	22	1.6	**−2.903** 376 336 198 933 179	3.48×10^{-4}	2.05×10^{-3}	4.24×10^{-3}	1.359
3	61	1.6	**−2.903 72**3 729 740 132 823	6.47×10^{-7}	1.06×10^{-6}	1.20×10^{-5}	1.556
4	111	1.6	**−2.903 724 3**58 079 515 735	1.90×10^{-8}	1.34×10^{-8}	1.33×10^{-7}	1.550
5	188	1.6	**−2.903 724 37**6 475 282 897	5.59×10^{-10}	1.23×10^{-10}	1.48×10^{-9}	1.559
6	310	1.6	**−2.903 724 377 0**17 385 340	1.67×10^{-11}	7.49×10^{-13}	1.03×10^{-11}	1.564
7	505	1.6	**−2.903 724 377 03**3 617 731	5.02×10^{-13}	7.52×10^{-15}	7.80×10^{-14}	1.552
8	697	1.6	**−2.903 724 377 034 1**04 549	1.50×10^{-14}	6.54×10^{-17}	6.35×10^{-16}	1.548
9	919	1.6	**−2.903 724 377 034 119** 147	4.51×10^{-16}	5.37×10^{-19}	5.53×10^{-18}	1.551
$E_{best}{}^c$			**−2.903 724 377 034 119 598**				

[a] Order of the free ICI. [b] Number of the complement functions. [c] Ref. 16. [d] The approximate first derivative at $\alpha = 1.6$ calculated from the quadratic interpolation of the energies at $\alpha = 1.5$, 1.6 and 1.7. [e] The approximate second derivative at $\alpha = 1.6$ calculated from quadratic interpolation of the energies at $\alpha = 1.5$, 1.6 and 1.7. [f] Variationally best α estimated from the interpolated quadratic curve.

Table 2 Energy of helium atom calculated by the free ICI method with the initial function $\psi_0 = \exp(-\alpha s)$ (eqn (28)) and $\psi_0 = \exp(-\alpha)[1 + \ln(s)]$ (eqn (29)). This table is taken from ref. 16

n^a	$\psi_0 = \exp(-\alpha s)$			$\psi_0 = \exp(-\alpha s)[1 + \ln(s)]$		
	$M_n{}^b$	α	Energy E/a.u.	$M_n{}^b$	α	Energy E/a.u.
0	1	1.688	**−2.**847 656 250 00	2	1.687	**−2.**847 656 242 128 24
1	4	1.689	**−2.90**1 337 956 94	10	1.550	**−2.90**2 964 172 868 10
2	16	1.736	**−2.903** 642 984 26	34	1.561	**−2.903** 702 734 675 68
3	37	1.779	**−2.903 72**0 264 20	77	1.619	**−2.903 72**3 749 601 90
4	71	1.837	**−2.903 724** 018 70	146	1.638	**−2.903 724 3**58 395 41
5	121	1.92	**−2.903 724 3**23 45	247	1.641	**−2.903 724 37**6 476 31
6	190	1.995	**−2.903 724 36**4 00	386	1.651	**−2.903 724 377** 01 739
7	281	2.083	**−2.903 724 37**3 59	569	1.670	**−2.903 724 377 03**3 61
8	397	2.161	**−2.903 724 37**5 90	802	1.683	**−2.903 724 377 034 1**04 549
9	541	2.251	**−2.903 724 37**6 66	1091	1.696	**−2.903 724 377 034 119** 147
	$E_{best}{}^c$		**−2.903 724 377 034**			

[a] Order of the free ICI. [b] Number of the complement functions. [c] Ref. 16.

n a small change in α influenced the energy very little. The estimated best value of α seemed to converge to the constant around 1.55. This suggests that only linear parameters must be optimized as variational parameters and that the scaling parameter α may not really be the variational parameter but a quantity related to a physical property like ionization energy.[31] In principle, the free ICI formalism does not require the optimization of the nonlinear parameters.[19,20] On the other hand, the optimal α of the exponential-type function [eqn (28)] shown in Table 2 increased as the order increased and did not yet show a sign of the convergence.

At first order, seven complement functions were generated and they are listed in Table 3 together with their optimized coefficients. There, the function, $\phi_1^{(1)} = \exp(-\alpha s)$, that is identical to eqn (28), is included. Therefore, afterwards the free ICI method generates from this function the same series of complement functions as those that are generated from the starting function of eqn (28). This implies that the difference between the nth order result of Table 1 and the $(n - 1)$th order result of Table 2 are the improvement due to the Ei-type functions.

As shown above, the Slater-type function is generated from the Ei function by applying the Hamiltonian operator according to eqn (20). This suggests that conversely the Ei function is generated by applying the inverse operator, H^{-1}, to the Slater-type function. In Fig. 2, the inverse operation corresponds to generating functions from right to left. According to the linear algebraic formalism, quadratic convergence may be obtained with the inverse iteration method. Previously, one of the authors[32] applied the inverse Hamiltonian method to solve the SE of hydrogen atom and obtained a faster convergence than the regular Hamiltonian case. If we regard the Ei functions and the logarithmic functions to be generated by applying the inverse Hamiltonian operator to the exponential function, we may be able to understand an aspect of the origin of their fast convergence.

Table 4 shows the free ICI energy starting from the Ei function with the explicitly correlated term given by eqn (27) with $\alpha = 1.6$. We performed the same calculation with $\alpha = 1.5$ and $\alpha = 1.7$ and calculated the approximate first and second derivatives of the energy with respect to the screening parameter α and the best estimated α, which are also shown in Table 4.

Fig. 3 shows the convergence speeds of the free ICI calculations starting from the four types of the initial functions given by eqn (26), (27), (28) and (30). The logarithms of the energy differences from the so-far best value, $E = -2.903\,724\,377\,034\,119\,598\,311\,159\,245\,194\,404\,446\,696\,9$ a.u.,[16] were plotted there. The convergence speed of the free ICI calculations starting from the Ei-type function, given by eqn (27), was poor in the initial stage, but as the order increases, it became similar to that of eqn (30). The energy

Table 3 The free ICI wave function at first order starting from the initial function, $\psi_0 = \mathrm{Ei}(-\alpha s)$ (eqn (26)), ($n = 1$, $M_1 = 7$ and $\alpha = 1.6$)[a]

Coefficient	Complement function	Coefficient	Complement function
1.000000000	$\exp(-\alpha s)$	−0.5860458840	$\mathrm{Ei}(-\alpha s)s$
−0.1312519886	$\exp(-\alpha s)s^{-1}u$	0.0992782326	$\mathrm{Ei}(-\alpha s)s^{-1}t^2$
−0.0697537604	$\exp(-\alpha s)s^{-2}t^2$	0.2737850022	$\mathrm{Ei}(-\alpha s)u$
−0.0368809315	$\mathrm{Ei}(-\alpha s)s^{-2}t^2$		

[a] Each complement function is normalized to unity but the total wave function is not normalized. The coefficients are the relative values to the one of $\exp(-\alpha s)$.

Table 4 Energy of helium atom calculated by the free ICI method with the initial function $\psi_0 = \mathrm{Ei}(-\alpha s)[1 + \ln(u)]$ (eqn (27)), the derivatives with respect to α, and the best estimated α

n[a]	M_n[b]	α	Energy E/a.u.	$E - E_{\mathrm{best}}$/a.u.	$\partial E/\partial\alpha$[d]	$\partial^2 E/\partial\alpha^2$[e]	Best α[f]
0	2	1.6	**−2.**666 888 282 498 509 506	2.37×10^{-1}	1.06×10^{0}	1.57×10^{0}	1.262
1	14	1.6	**−2.90**2 295 055 973 125 945	1.43×10^{-3}	2.67×10^{-3}	1.97×10^{-2}	1.532
2	44	1.6	**−2.903** 640 326 345 850 979	8.41×10^{-5}	8.06×10^{-4}	2.46×10^{-3}	1.436
3	122	1.6	**−2.903 724 37**6 098 371 470	9.36×10^{-10}	1.52×10^{-8}	1.95×10^{-7}	1.561
4	222	1.6	**−2.903 724 377 0**21 228 247	1.29×10^{-11}	3.19×10^{-10}	3.35×10^{-9}	1.552
5	376	1.6	**−2.903 724 377 034** 097 813	2.18×10^{-14}	1.67×10^{-12}	1.72×10^{-11}	1.551
6	620	1.6	**−2.903 724 377 034 119** 430	1.68×10^{-16}	2.14×10^{-16}	3.65×10^{-15}	1.571
7	1010	1.6	**−2.903 724 377 034 119 59**5	2.65×10^{-18}	-3.82×10^{-20}	1.73×10^{-18}	1.611
	E_{best}[c]		**−2.903 724 377 034 119 598**				

[a] Order of the free ICI. [b] Number of the complement functions. [c] Ref. 16. [d] The approximate first derivative at $\alpha = 1.6$ calculated from the quadratic interpolation of the energies at $\alpha = 1.5$, 1.6 and 1.7. [e] The approximate second derivative at $\alpha = 1.6$ calculated from quadratic interpolation of the energies at $\alpha = 1.5$, 1.6 and 1.7. [f] Variationally best α estimated from the interpolated quadratic curve.

derivatives with respect to α approached zero as the order increased, but the best estimated value slightly increased in a oscillating manner. Similar behavior was also seen for the case starting from eqn (30).

We will give below the extensive calculations of helium atom starting from the Ei function of eqn (26) up to the order $n = 27$, but before that we give the results for the helium isoelectronic ions.

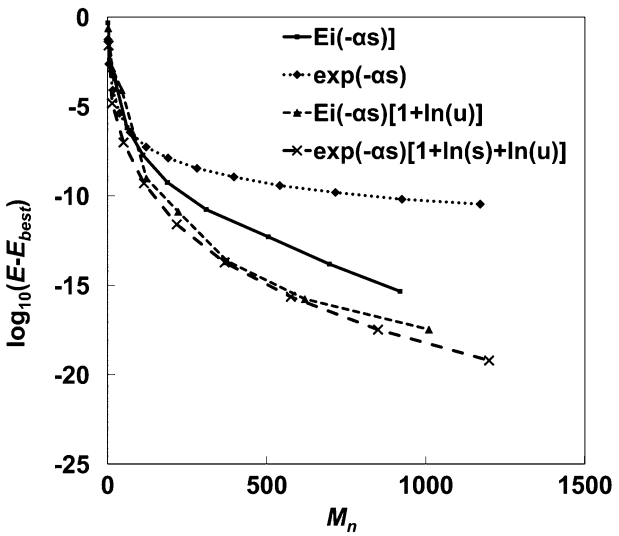

Fig. 3 Energy convergence of the free ICI calculations with different types of initial functions: $\psi_0 = \mathrm{Ei}(-\alpha s)$ (solid line) (eqn (26)), $\psi_0 = \exp(-\alpha s)$ (dotted line) (eqn (28)), $\psi_0 = \mathrm{Ei}(-\alpha s)[1 + \ln(u)]$ (short dashed line) (eqn (27)), and $\psi_0 = \exp(-\alpha s)[1 + \ln(s) + \ln(u)]$ (long dashed line) (eqn (30)). E_{best} is estimated to be the so-far best value, $E = -2.903\,724\,377\,034\,119\,598\,311\,159\,245\,194\,404\,446\,696\,9$ a.u. obtained in ref. 16.

4.4 Application to helium isoelectronic ions

Here, we show briefly the results for the helium isoelectronic ions, represented as $\mathrm{M}^{(Z-2)+}$ ($Z = 1,2,3,\ldots,10$), starting from the Ei function with the explicitly correlated term given by eqn (27). The free ICI was done only up to order four ($n = 4$, $M_4 = 222$) and the value of α was optimized for each ion. The results are shown in Table 5, where the energies calculated by Freund *et al.*[9] using 230 logarithmic basis functions are also shown. We could obtain more than 11 digits accuracy for all ions except for the hydride ion H^-. More accurate energies of these ions were published in our previous paper.[16]

As Freund *et al.*[9] noted, electrons of the hydride ion exist rather far from the nucleus; however, the logarithmic functions are suited for describing electrons near the nucleus. Therefore, it would be difficult to describe such electrons to high accuracy by using the logarithmic functions. This consideration holds true also for the Ei-type wave functions of the present study.

The optimal α of each ion and the nuclear charge Z have a linear relation represented by $\alpha_{\mathrm{opt}} = aZ - b$, where a and b were calculated, by least-squares fitting, to be 0.9254 and 0.2583 respectively. This result is in accordance with the interpretation of α as the screening parameter that is related to the ionization potential.

4.5 Fully extensive calculations of the helium atom starting from the Ei function

Finally, let us report the result of the fully extensive free ICI calculations of the helium atom with the Ei function given by eqn (26). Table 6 shows the converging series of energies up to $n = 27$ and the convergence indicator Δ_n at order n, that is the logarithm of the energy difference from the best energy value, for which we adopted the best energy we obtained here at $n =$

Table 5 Energy of the helium isoelectronic ions calculated by the free ICI method with the initial function $\psi_0 = \mathrm{Ei}(-\alpha s)[1 + \ln(u)]$ (eqn (27)) and a comparison with the energy obtained by Freund *et al.*[c] using the logarithm-type functions

Character	Z	Free ICI results with Ei-type function[a]		Logarithm-type function[c]	
		α[b]	Energy/a.u.	α[b]	Energy/a.u.
H	1	0.4477	−0.527 750 970 358 127	0.390	−0.527 751 015 3
He	2	1.550	−2.903 724 377 026 498	1.600	−2.903 724 377 034 0
Li	3	2.520	−7.279 913 412 662 821	2.820	−7.279 913 412 669 2
Be	4	3.493	−13.655 566 238 414 004	3.840	−13.655 566 238 423 5
B	5	4.365	−22.030 971 580 230 969	4.850	−22.030 971 580 242 7
C	6	5.300	−32.406 246 601 884 841	5.880	−32.406 246 601 898 4
N	7	6.288	−44.781 445 148 757 529	6.930	−44.781 445 148 772 6
O	8	7.162	−59.156 595 122 741 245	8.000	−59.156 595 122 757 8
F	9	7.852	−75.531 712 363 926 577	9.000	−75.531 712 363 959 4
Ne	10	9.116	−93.906 806 515 019 002	10.00	−93.906 806 515 037 4

[a] The order is four, the number of the complement function is 222, and the initial function is $\psi_0 = \mathrm{Ei}(-\alpha s)[1 + \ln(u)]$ (eqn (27)). [b] The screening parameter optimized at each ion. [c] The results of Freund *et al.*, taken from ref. 9. The wave function has the form of $\psi = \sum_{(abc)}^{230\ \mathrm{terms}} C_{abc} \exp(-\alpha s) \ln(s) s^a t^b u^c$.

27. The energy at $n = 27$ ($M_{27} = 21\,035$) was $E_{27} =$ **−2.903 724 377 034 119 598 311 159 245 194 404 446 696 924** 865 a.u. which has 43 digits accuracy and variationally improves the best energy of our previous paper[16] by about 2–3 digits in spite of the smaller dimensions in the present case. The α value was fully optimized until $n = 16$ but the change became small and so from $n = 17$, α was fixed to 1.6.

Fig. 4 shows the energy convergence behaviors of the free ICI energies with ψ_0 given by eqn (26), (29) and (31): it is a plot of Δ_n against M_n. When we compare the calculations with ψ_0 values of eqn (26) and (29), one notices that the two energies at the same order n are almost same, though the number of the generated functions M_n is slightly smaller in the Ei case than in the logarithmic case. It suggests that the free ICI functional spaces generated from these two sets are almost the same but the Ei case is slightly more efficient because of the smaller dimension. It also becomes a numerical proof that the three-particle coalescence behavior is also satisfactory with the Ei function because the Ei function includes the logarithm property.

Comparing the Ei case to the calculation with ψ_0 given by eqn (31), the convergence of the latter case is better than the Ei case at small dimensions until about $M_n = 14\,000$. The speed

Table 6 Energy of helium atom calculated with $\psi_0 = \mathrm{Ei}(-\alpha s)$ (eqn (26)). Δ_n shows the convergent digits defined as $\Delta_n = \log_{10}(E_n - E_{\mathrm{exact}})$

n	M_n	α	Energy/a.u.	Δ_n
0	1	1.173	−**2.**797 959	−0.98
1	7	1.612	−**2.90**0 021	−2.43
2	22	1.363	−**2.903** 607	−3.93
3	61	1.562	−**2.903 72**3 737	−6.19
4	111	1.547	−**2.903 724** 358 271	−7.73
5	188	1.607	−**2.903 724 37**6 475	−9.25
6	310	1.599	−**2.903 724 377 0**17 385	−10.8
7	505	1.578	−**2.903 724 377 03**3 617	−12.3
8	697	1.576	−**2.903 724 377 034 1**04 549	−13.8
9	919	1.585	−**2.903 724 377 034 119** 147	−15.3
10	1206	1.585	−**2.903 724 377 034 119 5**84 790	−16.9
11	1589	1.591	−**2.903 724 377 034 119 59**7 905	−18.4
12	2027	1.586	−**2.903 724 377 034 119 598** 298 978	−19.9
13	2572	1.595	−**2.903 724 377 034 119 598 31**0 792	−21.4
14	3236	1.588	−**2.903 724 377 034 119 598 311 1**48 179	−23.0
15	4081	1.612	−**2.903 724 377 034 119 598 311 15**8 909	−24.5
16	4845	1.636	−**2.903 724 377 034 119 598 311 159 2**34 996	−26.0
17	5647	(1.6)	−**2.903 724 377 034 119 598 311 159 24**4 882	−27.5
18	6546	(1.6)	−**2.903 724 377 034 119 598 311 159 245 1**84 832	−29.0
19	7573	(1.6)	−**2.903 724 377 034 119 598 311 159 245 194** 108	−30.5
20	8679	(1.6)	−**2.903 724 377 034 119 598 311 159 245 194** 395 279	−32.0
21	9912	(1.6)	−**2.903 724 377 034 119 598 311 159 245 194 404** 160	−33.5
22	11 326	(1.6)	−**2.903 724 377 034 119 598 311 159 245 194 404 4**37 749	−35.0
23	12 994	(1.6)	−**2.903 724 377 034 119 598 311 159 245 194 404 446** 415	−36.6
24	14 699	(1.6)	−**2.903 724 377 034 119 598 311 159 245 194 404 446 6**88 045	−38.1
25	16 552	(1.6)	−**2.903 724 377 034 119 598 311 159 245 194 404 446 696** 642	−39.5
26	18 646	(1.6)	−**2.903 724 377 034 119 598 311 159 245 194 404 446 696 9**15 844	−41.0
27	21 035	(1.6)	−**2.903 724 377 034 119 598 311 159 245 194 404 446 696 924** 865	(−42.5)[a]
Ref. 16	22 709		−**2.903 724 377 034 119 598 311 159 245 194 404 446 696 9**05 34	−40.7

[a] The value presumed from the convergent behavior.

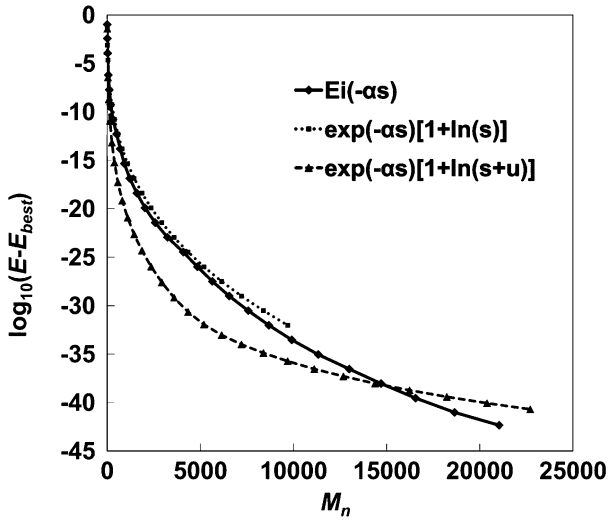

Fig. 4 Energy convergence of the free ICI calculations with different types of initial functions: $\psi_0 = \mathrm{Ei}(-\alpha s)$ (solid line) (eqn (26)), $\psi_0 = \exp(-\alpha s)[1 + \ln(s)]$ (dotted line) (eqn (29)), and $\psi_0 = \exp(-\alpha s)$-$[1 + \ln(s + u)]$ (dashed line) (eqn (31)). E_{best} is estimated here to be the best value calculated here, $E = -$**2.903 724 377 - 034 119 598 311 159 245 194 404 446 696 924** 865 a.u., which is lower (better) than the value obtained in ref. 16.

of convergence of the latter case becomes slowed down after exceeding that dimension; the two cases become almost equivalent at $M_n = 14\,000$ and the Ei case becomes faster at $M_n > 14\,000$. The speed of the convergence does not become worse in the Ei case even at a very large dimension over $M_n = 20\,000$ and its plot of Δ_n in Fig. 4 is almost linear (slightly downward convex). Thus, although the most rapid convergence in $M_n < 14\,000$ is obtained with ψ_0 given in eqn (31), *i.e.* the logarithmic form, the fastest convergence at very high dimension is obtained with the ψ_0 of the Ei function, eqn (26). This nice property would be due to the better behaviors of the Ei function over the logarithmic function as shown in Fig. 1.

5. Conclusion

We introduced the Ei function as a new type of function that has a physical meaning similar to the logarithmic function, and yet does not show the unphysical behaviors that the logarithmic function shows. We have used here the Ei functions as the starting functions of the free ICI formalism to calculate the accurate wave functions and energies of the helium and its isoelectronic ions. The free ICI wave functions generated from the Ei function showed very good convergence and the speed of the convergence was almost the same as that with the logarithmic function. Further, when we perform highly extensive calculations, the free ICI wave function starting from the Ei function gave a better performance than the one starting from the logarithmic function, reflecting the good behavior of the Ei function in comparison with the logarithmic function. For this reason, we could improve the variational energy of helium atom: correct up to about 43 digits.

The natures of these two types of functions are considered to be very similar and with the free ICI formalism both functions produce an identical set of complement functions at infinite orders. The logarithmic function has a node and a maximum, which seems to be unphysical for the ground state of the present system, while the Ei function has neither a node nor a maximum and decreases smoothly to zero. The Ei functions are considered to be suited for describing the electrons near the nucleus like those of inner-shell region. The Ei function may also be understood as the function generated by operating the inverse Hamiltonian to the ordinary exponential function and this may be a reason why the Ei functions lead to a fast convergence. The more general functions widely used in the correlated methods, like the Gaussian function with the Jastrow functions[33,34] are also automatically generated from the Ei-type function, such as $\psi_0 = \exp(-\alpha r^2)\mathrm{Ei}(ar/(r + b))$ or $\psi_0 = \mathrm{Ei}(-ar^2)\exp(ar/(r + b))$. They would be of some value for general atomic and molecular calculations.

These results may be considered to support the suggestion that the Ei function is better than the logarithmic function for describing the three-particle coalescence region.

The use of the Ei functions for larger atoms and molecules is also very interesting for accurate descriptions of atomic and molecular electronic structures in which the wave function must have the freedom that the exact wave function has in the three-particle coalescence region. Though we used the variation principle (VP) to calculate the variables in the free ICI wave function, we have published a method of using the Schrödinger equation directly instead of the variation principle.[35] This local Schrödinger equation (LSE) method is applicable to wider classes of many-electron atoms and molecules than is the variation principle.

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