Solving the electron-nuclear Schrödinger equation of helium atom and its isoelectronic ions with the free iterative-complement-interaction method

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Our previous paper [J. Chem. Phys. **127**, 224104 (2007)] revealed that the Schrödinger equation in the fixed-nucleus approximation could be very accurately solved for helium atom and its isoelectronic ions ($Z=1-10$) with the free iterative-complement-interaction (ICI) method combined with the variation principle. In this report, the quantum effect of nuclear motion has further been variationally considered by the free ICI formalism for the Hamiltonian including mass-polarization operator. We obtained **−2.903 304 557 729 580 294 733 816 943 892 697 752 659 27**3 965 a.u. for helium atom, which is over 40 digits in accuracy, similarly to the previous result for the fixed-nucleus level. Similar accuracy was also obtained for the helium isoelectronic ions. The present results may be regarded to be the nonrelativistic limits. We have further analyzed the physics of the free ICI wave function by applying it to an imaginary atom called "eneon," $[e^{-}e^{10+}e^{-}]^{8+}$, in which both of the quantum effect of nuclear motion and the three-particle collisions are differently important from the helium and its isoelectronic ions. This revealed the accurate physics automatically generated by the free ICI formalism. © *2008 American Institute of Physics*.
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I. INTRODUCTION

Schrödinger equation (SE) provides a governing principle for atomic and molecular quantum physics and chemistry, but it has long been thought not to be soluble except for some simple systems such as hydrogen atom. Two-electron helium atom is the next simplest atom and from Hylleraas' pioneering work in 1929,[1] many studies[2–10] have been devoted to solve its SE as accurately as possible. There the basic principle, was the variation principle and the wave function was constructed mostly with the intuitions. Recently, we have proposed the free iterative-complement-interaction (ICI) method,[11–18] which gives a series of analytical functions that describe the exact wave function at convergence. The variable parameters there were determined either by the variation principle or by the local SE (LSE) method.[18] We have applied the free ICI method to helium and obtained very accurate result: The energy was correct over 40 digits.[11] It was practically exact and numerically proven that one could obtain the solutions of the SE with the free ICI method as accurately as one desires.

For the real helium atom, however, there are still many other physical effects that are not contained in the SE we solved previously. The first correction would be the quantum effect of nuclear motion:[19] The previous solution was in the fixed-nucleus (Born–Oppenheimer) approximation. The purpose of the present paper is to consider further the quantum effect of nuclear motion, i.e., to perform the calculations at moving-nucleus level. Then, the result may be considered to be the nonrelativistic limit. The next correction would be to include the relativistic effects and we have actually already solved the Dirac–Coulomb equation (DCE) of the helium atom by the free ICI formalism in the fixed-nucleus approximation.[17] The further corrections would then be the combined relativistic and moving-nucleus level and further to introduced the QED effect.[20–22] These studies are important for the precise physics to determine the fundamental physical constants. They are also useful in some model studies of photonic crystals, quantum dots, etc.[23,24] For accurately calculating these higher-order corrections by the perturbation method, one needs highly accurate zeroth order wave functions of the nonrelativistic limit.

In this paper, we perform highly accurate nonrelativistic free ICI calculations for the ground states of helium atom and its isoelectronic ions at moving-nucleus level. We perform fully variational calculations for the Hamiltonian including the so-called mass-polarization term. Although this term is often perturbatively treated, the higher order terms become significant for the calculations of the QED corrections.[25] The calculations for the excited states will be given in the forthcoming paper.[26]

II. DEFINITION, FORMULATION, AND COMPUTATIONAL DETAILS

We want to solve the SE of helium atom and its isoelectronic ions, dealing not only electrons but also nuclei quantum mechanically in the Hamiltonian. It corresponds to the non-Born–Oppenheimer (non-BO) calculations of atoms and molecules and its Hamiltonian is written as

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TABLE I. The specific index ranges of the free ICI wave functions given by Eqs. (7) and (8) as a function of the order n of the free ICI calculations. The free ICI formulation generates all combinations of the indices satisfying the equalities and the inequalities in the table.

Eq. (7) (Elaborate free ICI wave function)[a]
(i) $-2n \leqslant l_i < -n$, $0 \leqslant l_i+m_i+n_i \leqslant 2n+l_i$, $j_i=0,1$
(ii) $-n \leqslant l_i \leqslant -1$, $0 \leqslant l_i+m_i+n_i \leqslant n$, $j_i=0,1$
(iii) $0 \leqslant l_i \leqslant n$, $0 \leqslant l_i+m_i+n_i \leqslant n$, $j_i=0,1$
(iv) $n_k=0$, $0 \leqslant l_k+m_k-d_k \leqslant n-1$, $0 \leqslant l_k+m_k \leqslant n$

Eq. (8) (Simplified free ICI wave function)[b]
(i) $-2n \leqslant l_i < -n$, $0 \leqslant n_i \leqslant 2n+l_i$, $0 \leqslant l_i+m_i+n_i \leqslant 2n+l_i-n_i$, $j_i=0,1$
In case $n_i=n$, $m_i=0$ and $j_i=0$.
(ii) $-n \leqslant l_i \leqslant -1$, $0 \leqslant n_i \leqslant n$, $0 \leqslant l_i+m_i+n_i \leqslant \min(n, 2n+l_i-n_i)$, $j_i=0,1$
In case $n_i=n$, $m_i=0$ and $j_i=0$.
(iii) $0 \leqslant l_i \leqslant n$, $0 \leqslant l_i+m_i+n_i \leqslant n$, $j_i=0,1$

[a]At $n=1$, the functions in the index representations $[l_i,m_i,n_i,j_i]=[-1,0,1,1],[-2,2,0,1],[-2,0,2,1]$ and $[l_k,m_k,n_k,d_k]=[-1,2,0,1]$ were eliminated.
[b]At $n=1$, the function in the index representation $[l_i,m_i,n_i,j_i]=[-2,2,0,1]$ was eliminated.

$$H = -\sum_i \frac{1}{2m_e}\nabla_i^2 - \sum_A \frac{1}{2m_A}\nabla_A^2 + \sum_i \sum_A \frac{Z_e Z_A}{r_{iA}} + \sum_{i>j} \frac{Z_e Z_e}{r_{ij}} + \sum_{A>B} \frac{Z_A Z_B}{R_{AB}}, \tag{1}$$

where i and A denote electrons and nuclei, respectively, m_e and m_A are their masses, and Z_e and Z_A are their charges, respectively. We call this level of Hamiltonian as moving-nuclei level or non-BO level in contrast to the fixed-nuclei or BO approximation. Eliminating the motion of the center of mass, the Hamiltonians for helium and its isoelectronic ions are expressed in atomic unit as

$$H = -\frac{1}{2\mu}\sum_{i=1}^{2} \nabla_i^2 - \sum_{i=1}^{2} \frac{Z}{r_i} + \frac{1}{r_{12}} - \frac{1}{m_N}\nabla_1 \cdot \nabla_2, \tag{2}$$

where μ is the effective mass defined by $\mu=m_e m_N/(m_e+m_N)$ in which m_e is equal to unity in atomic unit and m_N is the nuclear mass. The last term represents the so-called mass-polarization operator: The nucleus with finite mass has finite momentum together with the electrons and the center of mass polarizes from the position of the nucleus. However, this term is miner in the total Hamiltonian because it is multiplied by a very small factor $1/m_N$ compared with $1/m_e$. In the fixed-nucleus approximation ($m_N=\infty$), this term is neglected and the effective mass μ becomes unity.

Since we are dealing with the ground state of S symmetry, our wave functions are expressed only with the interparticle coordinate $\{r_1,r_2,r_{12}\}$ (Ref. 11) or the $\{s,t,u\}$ coordinate[1,11] given by

$$s = r_1 + r_2, \quad t = r_1 - r_2, \quad u = r_{12}. \tag{3}$$

The Hamiltonians of many-electron atoms in the fixed-nucleus level were formulated extensively by Ruiz[27] and the Hamiltonians for general three-body problems in the moving-nuclei level were explicitly written down by Harris.[28] The above electron-nuclear Hamiltonian can be rewritten in the $\{s,t,u\}$ coordinate as

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

where the last term is the mass-polarization operator.

The ICI wave function is defined by a recursion formula and first we have to fix the g function and the initial function ψ_0.[13,14] Here, we used the functions that showed the best performance in the previous calculations of helium and its isoelectronic ions,[11] namely,

$$g = -\frac{1}{V_{Ne}} + \frac{1}{V_{ee}}, \tag{5}$$

$$\psi_0 = [1 + \ln(s+u)]\exp(-\alpha s), \tag{6}$$

in which V_{Ne} and V_{ee} are the nuclear attraction and electron repulsion potentials, respectively. In the free ICI calculations, the recurrence number is redefined as "order" n and the number of the independent functions at order n is called as "dimension" M_n. The free ICI wave functions generated with the use of the g and ψ_0 given by Eqs. (5) and (6) are expressed as

$$\psi_n = \sum_i c_i s^{l_i} t^{m_i} u^{n_i} [\ln(s+\beta u)]^{j_i} \exp(-\alpha s) + \sum_k c_k s^{l_k} t^{m_k} u^{n_k} 1/(s+\beta u)^{d_k} \exp(-\alpha s), \tag{7}$$

where l_i and l_k run positive and negative integers including 0, $\{m_i,n_i\}$ and $\{m_k,n_k\}$ run non-negative integers (m_i and m_k are even integers for singlet and odd integers for triplet), d_k runs positive integers, and j_i and j_k are either 0 or 1. The conditions $l_i+m_i+n_i \geqslant 0$ and $l_k+m_k+n_k-d_k \geqslant 0$ must be satisfied for the square integrability of the wave function. The ranges of these integers included in Eq. (7) are the functions of the order n of the free ICI calculations. Table I shows their specific relations which apply to any orders n except for unity

for which the relations are summarized in the footnotes. The ranges of these indices are characterized by the special choices of the g and ψ_0 functions used in the free ICI calculations. They are usually different from the ordering of the basis functions used in the ordinary variational calculations. The variables $\{c_i, c_k\}$ in the free ICI wave function given by Eq. (7) are calculated here with the variation principle.

The second term of Eq. (7) was newly generated in the present free ICI formalism by applying the mass-polarization operator $\nabla_1 \cdot \nabla_2$ to the logarithm function that is important in the three-particle collision area,[11] and so this second term represents the multiple effect of mass-polarization and three-particle collision. We expect such multiple effect to be small for the present helium and its isoelectronic atoms. However, if one can imagine the system in which the quantum effect of nuclear motion is significant, i.e., with light nuclear mass, and the three-particle coalescence region is important, i.e., with large nuclear charge, then the second term of Eq. (7) would become important. As such system, we will examine the imaginary three-body system with $m_N=m_e=1$ and $Z=10$: We call this system as "eneon" (electron weight neon) $[e^- e^{10+} e^-]^{8+}$. The exotic atom with $m_N=m_e=1$ and $Z=1$ is positronium negative ion (Ps^-).

However, since the mass-polarization term is small in the Hamiltonian of helium and its isoelectronic ions, we may neglect the mass-polarization term in the functional generation step of the free ICI formalism, and we obtain the wave function

$$\psi_n = \sum_i c_i s^{l_i} t^{m_i} u^{n_i} [\ln(s+\beta u)]^{j_i} \exp(-\alpha s), \tag{8}$$

which is of the same functional form as that extensively used in our previous study of helium and its isoelectronic ions.[11] Table I also shows the specific ranges of the integers included in Eq. (8) as the function of the order n of the free ICI calculations. (For $n=1$, see footnote.) The variables $\{c_i\}$ in the free ICI wave function given by Eq. (8) were variationally calculated using the Hamiltonian given by Eq. (4) that includes the mass-polarization term. We call this function as simplified free ICI wave function.

Before entering into calculations, we must fix the nuclear mass data from the available experimental database. Table II summarizes the results in atomic unit (a.u.). For the mass of helium nucleus, we used the alpha particle mass given by CODATA 2006 in NIST.[29] For H^-, we used the proton mass also given by CODATA 2006. For each isoelectronic ions of $Z \geqslant 3$, we first selected the isotope having the highest natural probability and searched the atomic mass from NIST, which was provided in the atomic mass unit (amu) based on the mass of the carbon nucleus ^{12}C as 12. The electron mass have to be excluded from the atomic mass, where we used 0.000 548 579 909 43 amu as the mass of one electron, also given by CODATA. Then, they were converted from amu to a.u., in which we used the proton mass as a standard.

TABLE II. The nuclear mass data of helium and its isoelectronic ions ($Z=1-10$) used in the present paper.

Z	Atom	m_N (a.u.)
1	$^1H^-$	1 836.152 672 47[a]
2	^4He	7 294.299 536 5[b]
3	$^7Li^+$	12 786.393 087 3
4	$^9Be^{2+}$	16 424.203 212 4
5	$^{11}B^{3+}$	20 063.736 514 0
6	$^{12}C^{4+}$	21 868.662 136 3
7	$^{14}N^{5+}$	25 519.042 727 8
8	$^{16}O^{6+}$	29 148.946 104 8
9	$^{19}F^{7+}$	34 622.970 927 5
10	$^{20}Ne^{8+}$	36 433.989 510 7

[a]Proton mass given by CODATA 2006 in Ref. 29.
[b]Alpha particle mass given by CODATA 2006 in Ref. 29.

III. RESULTS

A. Convergence of the free ICI calculations of helium

We first examine the convergence behavior of the moving-nucleus free ICI calculations of helium atom. We first use the simplified wave function given by Eq. (8). Table III shows a nice convergence of the calculated energy up to the order $n=27$. There, we used the same values of the optimal α that were given in our previous paper of Ref. 11. Actually, we also optimized this nonlinear parameter in the present moving-nucleus case but we got almost the same α values as those of the fixed-nucleus case.[11] The most accurate energy we obtained was **−2.903 304 557 729 580 294 733 816 943 892 697 752 659 27**3 965 a.u. at $n=27$ with the dimension $M_n=22\,709$. In spite of the presence of the mass-polarization term in the Hamiltonian, the accuracy was over 40 digits similarly to the previous fixed-nucleus case.[11] Although the results cannot be directly compared to the previous reference data because of the difference in the nuclear mass data, Cox *et al.*[19] obtained the energy of −2.903 304 555 a.u. with $m_N=7294.299\,537$ a.u. and Korobov and Yelkhovsky[21] −2.903 304 557 727 940 23 (1) a.u. with $m_N=7294.299\,508$ (16) a.u. The latter agrees with ours to 12 digits. To examine the effect due to the difference in the nuclear mass data, we performed the calculations using the same nuclear mass data as that used by Korobov and Yelkhovsky,[21] which is different from ours ($m_N=7294.299\,536\,5$) at 10^{-5} digit. At $n=7$ ($M_n=569$), we obtained the energy of **−2.903 304 557 727 940 258** 852 a.u. which accorded with the Korobov's energy up to 10^{-17}: It was lower and so variationally better than theirs even with the quite smaller dimension than theirs, 1200.[21] Compared to the energy obtained with the present nuclear mass data ($m_N=7294.299\,536\,5$), the difference appeared at 10^{-12}.

Thus, the free ICI calculations showed very good convergence to the exact solution of the SE also for the moving-nucleus case. However, regrettably, the numerical accuracy is limited by the experimental precision of the nuclear mass data of helium atom, which is "only" 11 decimal figures. In contrast, as described above, the theory has already achieved 40 digits of accuracy.

TABLE III. Energy of the electron-nuclear ground state of helium atom calculated with the free ICI wave function given by Eq. (8) with $\beta=1$.

n[a]	M_n[b]	Optimal α[c]	Energy (a.u.)[d]
0	2	1.827	**−2.8**64 969
1	10	1.475	**−2.903** 117
2	34	1.627	**−2.903 304**188
3	77	1.679	**−2.903 304 55**5 789
4	146	1.683	**−2.903 304 557 71**7 808
5	247	1.679	**−2.903 304 557 729 5**10 966
6	386	1.693	**−2.903 304 557 729 579** 708
7	569	1.704	**−2.903 304 557 729 580 28** 9 281
8	802	1.707	**−2.903 304 557 729 580 294 6**64 340
9	1091	1.713	**−2.903 304 557 729 580 294 732** 636
10	1442	1.724	**−2.903 304 557 729 580 294 733 7**94 158
11	1861	1.738	**−2.903 304 557 729 580 294 733 816** 463
12	2354	1.757	**−2.903 304 557 729 580 294 733 816 9**33 146
13	2927	1.779	**−2.903 304 557 729 580 294 733 816 943** 638
14	3586	1.806	**−2.903 304 557 729 580 294 733 816 943 88**6 051
15	4337	1.837	**−2.903 304 557 729 580 294 733 816 943 892 4**77
16	5186	1.866	**−2.903 304 557 729 580 294 733 816 943 892 68**6 467
17	6139	1.899	**−2.903 304 557 729 580 294 733 816 943 892 696** 832
18	7202	1.93	**−2.903 304 557 729 580 294 733 816 943 892 697 6**52 304
19	8381	1.96	**−2.903 304 557 729 580 294 733 816 943 892 697 7**39 769
20	9682	1.99	**−2.903 304 557 729 580 294 733 816 943 892 697 75**0 806
21	11111	2.02	**−2.903 304 557 729 580 294 733 816 943 892 697 752** 366
22	12674	2.05	**−2.903 304 557 729 580 294 733 816 943 892 697 752 6**09 223
23	14377	2.08	**−2.903 304 557 729 580 294 733 816 943 892 697 752 65**0 058
24	16226	2.11	**−2.903 304 557 729 580 294 733 816 943 892 697 752 65**7 471
25	18227	2.14	**−2.903 304 557 729 580 294 733 816 943 892 697 752 658** 911
26	20386	2.17	**−2.903 304 557 729 580 294 733 816 943 892 697 752 659 2**08 852
27	22709	2.20	**−2.903 304 557 729 580 294 733 816 943 892 697 752 659 27**3 965
Ref.21[e]			−2.903 304 557 727 940 23(1)

[a]Number of iteration, or order.
[b]Number of basis functions at order n.
[c]We used the same values of α as those in Ref. 11.
[d]The bold digits are those that are believed to be converged.
[e]The nuclear mass data is different from in our calculations.

Next, we examine the difference between the wave functions given by Eqs. (7) and (8). The better wave function of Eq. (7) gave at order $n=8$, for example, the energy of **−2.903 304 557 729 580 24 69**94 a.u. with $M_n=1782$ with the optimal value of $\alpha=1.681$, while the simplified function given by Eq. (8) gave the energy **−2.903 304 557 729 580 29 6**64 a.u. with $M_n=802$, as shown in Table III. At the same order n, these two functions gave almost the same energies, although the numbers of the independent functions are very small in the latter case. Exactly, the same trend continues up to a large order n, which numerically indicates that the simplified function of Eq. (8) is sufficient at least for helium atom.

B. Multiple effects of nuclear motion and three-particle collisions: Eneon

As stated in the previous section, the second terms of Eq. (7) arose from the free ICI formulation by the application of the mass-polarization operator to the logarithmic form of the wave function. This means that this second terms represent the multiple effects of the nuclear motion and the three-particle collision. This effect was shown above to be small for the helium atom. Here, we examine how large is this effect for the imaginary "atom," eneon $[e^- e^{10+} e^-]^{8+}$, introduced in the previous section.

For eneon, the elaborated wave function given by Eq. (7) gave the energy of **−49.227 218 040 961 842 410** 436 a.u. at order $n=8$ with $M_n=1782$ and the optimal value of $\alpha=5.139$, while the simpler function given by Eq. (8) gave the substantially higher energy of **−49.227 218 040 961** 602 822 840 a.u. at order $n=8$ with $M_n=802$ and the optimal value of $\alpha=5.314$. This result may be compared to the more accurate energy of **−49.227 218 040 961 842 410 731** a.u. that we obtained at the order $n=10$ ($M_n=3267$) with the former wave function given by Eq. (7). In contrast to the helium case, the latter simpler wave function of eneon showed the worse convergence to the exact energy: It gave the energy of **−49.227 218 040 961 842 40**9 423 a.u. at the order $n=11$ with $M_n=1861$ and optimal $\alpha=4.976$, which was still higher than the energy at $n=8$ ($M_n=1782$) with the former elaborate function in spite of the larger number of independent functions. This indicates, as expected, that the elaborate wave

TABLE IV. Ground-state energies and the expectation values of $\langle r_1 \rangle$ and $\langle r_{12} \rangle$ of helium atom and its isoelectronic ions ($Z=1-10$) at $n=20$ ($M_n=9682$) except for helium ($Z=2$) at $n=27$ ($M_n=22\,709$). For each atom, the upper and lower values correspond to the fixed-nucleus and moving-nucleus levels, respectively. The bold digits are those that are believed to be converged.

Z	Atom	Optimal α[a]	Energy (a.u.)[b]	Ref. 19[c] (a.u.)	$\langle r_1 \rangle$	$\langle r_{12} \rangle$
1	$^1H^-$	0.4	**−0.527 751 016 544 377 196 590 814 566 747 511** 383 045 02	−0.527 751 016 4	**3.992 642 036 44**	**4.412 694 497 99**
			−0.527 445 881 109 440 729 069 818 738 420 952 436 230 10	−0.527 445 880 9	**3.995 676 553 89**	**4.415 692 603 55**
2	^4He	2.2	**−2.903 724 377 034 119 598 311 159 245 194 404 446 696 9**05 37	−2.903 724 377	**1.256 585 170 95**	**1.422 070 255 53**
			−2.903 304 557 729 580 294 733 816 943 892 697 752 659 273 96	−2.903 304 558	**1.256 772 599 55**	**1.422 247 512 60**
3	$^7Li^+$	3.2	**−7.279 913 412 669 305 964 919 459 221 006 611 682** 572 35	−7.279 913 413	**0.765 035 334 02**	**0.862 315 375 45**
			−7.279 321 519 805 463 947 061 498 356 313 505 544 193 59	−7.279 321 520	**0.765 098 340 78**	**0.862 373 348 72**
4	$^9Be^{2+}$	4.5	**−13.655 566 238 423 586 702 081 730 194 612 159 391** 360 60	−13.655 566 24	**0.550 561 293 88**	**0.618 756 314 06**
			−13.654 709 268 249 465 622 206 337 643 805 570 003 859 73	−13.654 709 27	**0.550 596 092 71**	**0.618 787 842 79**
5	$^{11}B^{3+}$	5.8	**−22.030 971 580 242 781 541 655 702 043 566 870 37**9 775 99	−22.030 971 58	**0.430 121 204 12**	**0.482 435 849 68**
			−22.029 846 048 811 936 755 417 986 955 963 130 743 257 20	−22.029 846 05	**0.430 143 279 64**	**0.482 455 656 48**
6	$^{12}C^{4+}$	7.1	**−32.406 246 601 898 530 310 557 357 969 530 254 56**6 016 97	−32.406 246 60	**0.352 949 031 11**	**0.395 316 907 59**
			−32.404 733 488 948 165 850 769 986 535 624 649 761 861 04	−32.404 733 49	**0.352 965 564 42**	**0.395 331 642 57**
7	$^{14}N^{5+}$	8.4	**−44.781 445 148 772 704 645 185 760 848 954 056 77**6 028 12	−44.781 445 15	**0.299 268 269 53**	**0.334 839 661 69**
			−44.779 658 349 447 581 412 368 317 194 804 403 691 821 04	−44.779 658 35	**0.299 280 239 36**	**0.334 850 277 51**
8	$^{16}O^{6+}$	9.7	**−59.156 595 122 757 925 558 549 892 445 559 527 70**0 907 85	−59.156 595 12	**0.259 765 875 35**	**0.290 406 415 38**
			−59.154 533 122 409 840 900 830 556 999 577 998 463 093 42	−59.154 533 12	**0.259 774 946 99**	**0.290 414 430 99**
9	$^{19}F^{7+}$	11.0	**−75.531 712 363 959 491 104 878 015 579 533 576 56**0 909 77	−75.531 712 36	**0.229 478 401 79**	**0.256 381 544 52**
			−75.529 499 582 511 856 906 176 189 003 800 362 267 854 27	−75.529 499 58	**0.229 485 134 81**	**0.256 387 476 36**
10	$^{20}Ne^{8+}$	12.3	**−93.906 806 515 037 549 421 469 184 180 000 241 06**6 651 70	−93.906 806 51	**0.205 517 570 51**	**0.229 491 873 88**
			−93.904 195 745 865 722 002 761 072 767 810 774 255 305 93	−93.904 195 75	**0.205 523 291 42**	**0.229 496 902 17**

[a]We used the same values of α as those in Ref. 11.
[b]The energy at the fixed-nucleus level is from Ref. 11.
[c]The nuclear mass data are different from those used in our calculations.

function given by Eq. (7) becomes essential for the system, such as eneon, that has a light nuclear mass and a large nuclear charge.

C. Helium isoelectronic ions

We applied the same free ICI scheme to the calculations of the moving-nucleus level for helium isoelectronic ions from $Z=1$ (H^-) to $Z=10$ (Ne^{8+}) using the simplified wave function given by Eq. (8). Table IV shows the summary of the calculated energies at $n=20$ ($M_n=9682$) for all the ions except for the neutral helium atom for which the data at $n=27$ ($M_n=22\,709$) were given. The energies with the fixed-nucleus approximation were summarized from the previous paper[11] for comparison. In the table, the upper row for each atom or ion shows the energy with the fixed-nucleus approximation (E_{FN}) and the lower row the energy with the moving-nucleus level (E_{MN}). Table IV also shows the energies reported by Cox *et al.*[19]

For all the iso-electronic ions, the present energies seem to be the best ones reported so far at the moving-nucleus level. For $Z=1$ (H^-), the energy obtained at $n=20$ ($M_n=9682$) seems to be slightly worse in quality than other ions because in H^- two electrons are rather weakly bound so that the logarithm singularity does not improve the result so dramatically.

Table IV also shows the expectation values $\langle r_1 \rangle$ and $\langle r_{12} \rangle$ of the wave functions with the fixed (the upper row) and moving (the lower row) nucleus levels. These values for H^- ($Z=1$) are very large and of the order of about 4 a.u. This fact corresponds well with the small electron affinity of hydrogen atom and indicates that one electron is almost dissociative. As Z increases, these expectation values become smaller and smaller: $\langle r_1 \rangle$ of Ne^{8+} was 0.206 a.u. in contrast to that of H^-, 4.00 a.u. in the moving-nucleus level. The differences of $\langle r_1 \rangle$ and $\langle r_{12} \rangle$ between the fixed and moving-nucleus levels become small as Z increases, because the effects of moving nucleus become smaller as the mass of the nucleus becomes heavier. The difference in $\langle r_1 \rangle$ was 10^{-3} order for H^-, 10^{-4} order for He, and 10^{-5} order for the other ions and that of $\langle r_{12} \rangle$ was 10^{-3} order for H^-, 10^{-4} order for He, 10^{-5} order for $Z=3-8$, and 10^{-6} order for F^{7+} and Ne^{8+}.

To analyze the quantum effect of nuclear motion in some detail, we introduced the energy differences defined by

$$\Delta E_{RM} = \mu E_{FN} - E_{FN}, \tag{9}$$

$$\Delta E_{MN\text{-}FN} = E_{MN} - E_{FN}, \tag{10}$$

$$\Delta E_{MP} = \Delta E_{MN\text{-}FN} - \Delta E_{RM}. \tag{11}$$

ΔE_{RM} represents the effect of reduced mass because μE_{FN} means the energy for the Hamiltonian that does not include the mass-polarization term in comparison with Eq. (2) but includes the reduced mass effect in the kinetic operator, i.e.,

$$H_{RM} = -\frac{1}{2\mu}\sum_{i=1}^{2}\nabla_i^2 - \sum_{i=1}^{2}\frac{Z}{r_i} + \frac{1}{r_{12}}. \tag{12}$$

The wave function $\psi_{RM}(\mathbf{r}_1,\mathbf{r}_2)$ for the Hamiltonian of Eq. (12) is related to the wave function $\psi_{FM}(\mathbf{r}_1,\mathbf{r}_2)$ for the fixed-nucleus Hamiltonian,

TABLE V. The energy differences ΔE_{RM}, $\Delta E_{\mathrm{MN\text{-}FN}}$, and ΔE_{MP} defined by Eqs. (9)–(11), respectively, and the expectation value $\langle -1/m_N \nabla_1 \cdot \nabla_2 \rangle_1$ of the mass-polarization operator for the wave functions of the Hamiltonian given by Eq. (12). The last column shows the difference between $\langle -1/m_N \nabla_1 \cdot \nabla_2 \rangle_1$ and ΔE_{MP}. The data for helium are at $n=27$ ($M_n=22\,709$) and the data for the isoelectronic ions (except for $Z=2$) are at $n=20$ ($M_n=9682$).

Z	Atom	$\Delta E_{\mathrm{RM}}=\mu E_{\mathrm{FN}}-E_{\mathrm{FN}}$ (a.u.)	$\Delta E_{\mathrm{MN\text{-}FN}}=E_{\mathrm{MN}}-E_{\mathrm{FN}}$ (a.u.)	$\Delta E_{\mathrm{MP}}=\Delta E_{\mathrm{MN\text{-}FN}}-\Delta E_{\mathrm{RM}}$ (a.u.)	$\langle -1/m_N \nabla_1 \cdot \nabla_2 \rangle_1$	$\langle -1/m_N \nabla_1 \cdot \nabla_2 \rangle_1 - \Delta E_{\mathrm{MP}}$
1	$^1H^-$	$2.872\,657\,370\,6\times10^{-4}$	$3.051\,354\,349\,4\times10^{-4}$	$1.786\,969\,787\,9\times10^{-5}$	$1.788\,739\,999\,8\times10^{-5}$	$1.770\,211\,959\,7\times10^{-8}$
2	^4He	$3.980\,267\,516\,8\times10^{-4}$	$4.198\,193\,045\,4\times10^{-4}$	$2.179\,255\,286\,1\times10^{-5}$	$2.180\,139\,004\,7\times10^{-5}$	$8.837\,187\,079\,2\times10^{-9}$
3	$^7Li^+$	$5.693\,039\,514\,0\times10^{-4}$	$5.918\,928\,638\,4\times10^{-4}$	$2.258\,891\,244\,5\times10^{-5}$	$2.259\,672\,365\,8\times10^{-5}$	$7.811\,213\,441\,8\times10^{-9}$
4	$^9Be^{2+}$	$8.313\,788\,305\,6\times10^{-4}$	$8.569\,701\,741\,2\times10^{-4}$	$2.559\,134\,356\,2\times10^{-5}$	$2.560\,057\,832\,2\times10^{-5}$	$9.234\,760\,720\,1\times10^{-9}$
5	$^{11}B^{3+}$	$1.097\,994\,562\,0\times10^{-3}$	$1.125\,531\,430\,8\times10^{-3}$	$2.753\,686\,884\,9\times10^{-5}$	$2.754\,708\,903\,3\times10^{-5}$	$1.022\,018\,388\,7\times10^{-8}$
6	$^{12}C^{4+}$	$1.481\,789\,997\,5\times10^{-3}$	$1.513\,112\,950\,4\times10^{-3}$	$3.132\,295\,288\,2\times10^{-5}$	$3.133\,580\,576\,7\times10^{-5}$	$1.285\,288\,555\,8\times10^{-8}$
7	$^{14}N^{5+}$	$1.754\,755\,884\,5\times10^{-3}$	$1.786\,799\,325\,1\times10^{-3}$	$3.204\,344\,064\,4\times10^{-5}$	$3.205\,663\,003\,0\times10^{-5}$	$1.318\,938\,687\,3\times10^{-8}$
8	$^{16}O^{6+}$	$2.029\,389\,519\,6\times10^{-3}$	$2.062\,000\,348\,1\times10^{-3}$	$3.261\,082\,845\,8\times10^{-5}$	$3.262\,429\,457\,6\times10^{-5}$	$1.346\,611\,879\,7\times10^{-8}$
9	$^{19}F^{7+}$	$2.181\,486\,130\,6\times10^{-3}$	$2.212\,781\,447\,6\times10^{-3}$	$3.129\,531\,705\,4\times10^{-5}$	$3.130\,758\,329\,3\times10^{-5}$	$1.226\,623\,965\,0\times10^{-8}$
10	$^{20}Ne^{8+}$	$2.577\,379\,814\,7\times10^{-3}$	$2.610\,769\,171\,8\times10^{-3}$	$3.338\,935\,709\,0\times10^{-5}$	$3.340\,320\,077\,0\times10^{-5}$	$1.384\,368\,004\,6\times10^{-8}$

$$H_{\mathrm{FN}} = -\frac{1}{2}\sum_{i=1}^{2}\nabla_i^2 - \sum_{i=1}^{2}\frac{Z}{r_i} + \frac{1}{r_{12}}, \tag{13}$$

which is obtained from Eq. (12) at the limit of $m_N=\infty$, i.e., $\mu=1$, by

$$\psi_{\mathrm{RM}}(\mathbf{r}_1,\mathbf{r}_2) = \psi_{\mathrm{FM}}(\mathbf{r}_1/\mu,\mathbf{r}_2/\mu). \tag{14}$$

Next, the term $\Delta E_{\mathrm{MN\text{-}FN}}$ represents all the effects of the moving nucleus in comparison with the fixed-nucleus approximation. This is the difference of the energies given in the upper and lower rows of Table IV. Finally, the term ΔE_{MP} means the effects of the mass-polarization term itself in the total effect of the moving nucleus, $\Delta E_{\mathrm{MN\text{-}FN}}$.

Table V shows these energy differences, ΔE_{RM}, $\Delta E_{\mathrm{MN\text{-}FN}}$, and ΔE_{MP} for helium and its isoelectronic ions. Comparing ΔE_{RM} with $\Delta E_{\mathrm{MN\text{-}FN}}$, one understands that the reduced mass effect is dominant within $\Delta E_{\mathrm{MN\text{-}FN}}$. We note that $\Delta E_{\mathrm{MN\text{-}FN}}$ is always positive: The energies with moving nucleus are always higher than those with fixed nucleus. ΔE_{RM} and $\Delta E_{\mathrm{MN\text{-}FN}}$ increase as the nuclear mass increases: Of the order of 10^{-4} for $Z=1-4$ and 10^{-3} for $Z=5-10$. However, the ratio of $\Delta E_{\mathrm{MN\text{-}FN}}$ against the total energy becomes small as the nuclear mass increases. For helium, ΔE_{RM} was $3.980\,267\,516\,8\times10^{-4}$ a.u. and $\Delta E_{\mathrm{MN\text{-}FN}}$ was $4.198\,193\,045\,4\times10^{-4}$ a.u. In contrast, for Ne^{8+}, ΔE_{RM} was $2.577\,379\,814\,7\times10^{-3}$ a.u. and $\Delta E_{\mathrm{MN\text{-}FN}}$ was $2.610\,769\,171\,8\times10^{-3}$ a.u. The mass-polarization effect ΔE_{MP} also slightly increases as the nuclear mass increases and its order is 10^{-5} for all the atom and ions ($Z=1-10$).

Table V also summarizes the expectation value $\langle -1/m_N \nabla_1 \cdot \nabla_2 \rangle_1$ of the mass polarization operator for the wave functions of the reduced mass Hamiltonian given by Eq. (12). When the effect of the mass polarization is calculated by the perturbation theory, this is the first order term. Since ΔE_{MP} in Table V is the variational result, the difference between ΔE_{MP} and $\langle -1/m_N \nabla_1 \cdot \nabla_2 \rangle_1$ represents the higher-order effect, which was also shown in the last column of Table V. We see that the most part of the mass polarization effect is represented by the first order term and the higher order effect is very small. For helium, ΔE_{MP} was $2.179\,255\,286\,1\times10^{-5}$ a.u. and $\langle -1/m_N \nabla_1 \cdot \nabla_2 \rangle_1$ was $2.180\,139\,004\,7\times10^{-5}$ a.u., and the difference of them was only $8.837\,187\,079\,2\times10^{-9}$ a.u. For Ne^{8+}, ΔE_{MP} was $3.338\,935\,709\,0\times10^{-5}$ a.u. and $\langle -1/m_N \nabla_1 \cdot \nabla_2 \rangle_1$ was $3.340\,320\,077\,0\times10^{-5}$ a.u., and the difference was $1.384\,368\,004\,6\times10^{-8}$ a.u. The higher-order effect was slightly larger for Ne^{8+} than for helium. Since the present free ICI wave function is quite accurate, even this order of quite small difference is able to be distinguished and discussed.

IV. CONCLUSION

In this report, we applied the free ICI method to solve the electron-nuclear SE of helium atom and its isoelectronic ions. We have obtained very accurate and essentially exact wave functions whose energies are correct over 40 digits for helium atom, about 30 digits for H^-, and 35 digits for the other ions: These accuracies are similar to those previously obtained with the fixed-nucleus approximation.[11] The present accurate solutions may be considered to be the nonrelativistic limit.

The largest part of the moving-nucleus effect came from the introduction of the reduced mass and its order was within $10^{-3}-10^{-4}$ a.u.: It was larger for the heavier atom than for the light atom. The energy contribution from the mass polarization operator was in 10^{-5} a.u. We compared the fully variational mass-polarization effect with the perturbative first order term calculated with the wave function for the Hamiltonian of Eq. (12) in the fixed-nucleus approximation. The first order perturbation energy was dominant within the total mass-polarization effect. The higher-order effect on the energy arose in the order of $10^{-8}-10^{-9}$ a.u. However, for the expectation values of $\langle r_1 \rangle$ and $\langle r_{12} \rangle$, the corresponding differences were of the order of 10^{-3} for H^-, 10^{-4} for helium, and 10^{-5} for the other ions, which indicated that the wave function was not sufficiently correct if we do not include the higher-order effects. Since the free ICI wave functions obtained in this article are fully variational and essentially exact for the nonrelativistic Hamiltonian, our wave functions would become quite reasonable zeroth order wave functions when we study the relativistic and QED corrections perturbatively.

The free ICI formalism generated the elaborate wave function given by Eq. (7), but for the present cases of helium and its isoelectronic ions, the simplified wave function given

by Eq. (8) was mostly satisfactory. However, to examine the role of the second term of the elaborate wave function of Eq. (7), which appeared as a result of applying the mass-polarization operator to the logarithmic three-particle collision part of the wave function, we introduced the imaginary atom, eneon, $[e^-e^{10+}e^-]^{8+}$. Eneon is characterized by the fact that the quantum effect of nuclear motion should be large and the three-particle collisions are also important. As a result, the second term of the elaborate wave function of Eq. (7) became very important, indicating that the free ICI formalism certainly reflects the basic physics of the system. More details of these exotic three-body atoms including Ps^- will be discussed elsewhere.

Since the present free ICI theory can be applied to any system when its Hamiltonian is clearly defined, one can theoretically describe the nature of the system to any accuracy one wants to have without any uncertainty of numerical errors. If one solves the SE and the DCE including various physical effects, one can analyze the detailed physics involved in the real nature. Further, when we have to consider other effects, such as QED, nuclear size effects, and so on, the perturbation method based on the accurate zeroth order free ICI wave function will become useful and will be considered in the near future.

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