

Solving the electron and electron-nuclear Schrödinger equations for the excited states of helium atom with the free iterative-complement-interaction method

Hiroyuki Nakashima, Yuh Hijikata, and Hiroshi Nakatsuji^{a)}

Quantum Chemistry Research Institute, JST CREST, Kyodai Katsura Venture Plaza 106, Goryo Oohara 1-36, Nishikyo-ku, Kyoto 615-8245, Japan and Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

(Received 13 February 2008; accepted 11 March 2008; published online 17 April 2008)

Very accurate variational calculations with the free iterative-complement-interaction (ICI) method for solving the Schrödinger equation were performed for the $1sNs$ singlet and triplet excited states of helium atom up to $N=24$. This is the first extensive applications of the free ICI method to the calculations of excited states to very high levels. We performed the calculations with the fixed-nucleus Hamiltonian and moving-nucleus Hamiltonian. The latter case is the Schrödinger equation for the electron-nuclear Hamiltonian and includes the quantum effect of nuclear motion. This solution corresponds to the nonrelativistic limit and reproduced the experimental values up to five decimal figures. The small differences from the experimental values are not at all the theoretical errors but represent the physical effects that are not included in the present calculations, such as relativistic effect, quantum electrodynamic effect, and even the experimental errors. The present calculations constitute a small step toward the accurately predictive quantum chemistry.

© 2008 American Institute of Physics. [DOI: [10.1063/1.2904871](https://doi.org/10.1063/1.2904871)]

I. INTRODUCTION

Variational calculations of helium atom have often been regarded as a benchmark test of a new theory since it is the simplest two-electron real system and yet its Schrödinger equation (SE) was not solved exactly.¹ Recently, the authors have developed the free iterative-complement-interaction (ICI) theory for accurately solving the SE (Ref. 2–4) and the relativistic Dirac–Coulomb equation.⁵ The theory has been applied to several atoms and molecules and successfully given highly accurate results.^{6–9} For example, for helium atom, the free ICI method gave the energy correct to 40 decimal figures as the solution of the SE.⁸ Similar accuracy has also been recently reported for the electron-nuclear Hamiltonians of helium atom and its isoelectronic ions considering the effects of the nuclear motion.¹⁰ These calculations may be regarded as numerically proving that one can obtain the solutions of the SE as accurately as one desires with the free ICI method.

The applications of the free ICI method have ever been restricted to the ground state and a few lower lying excited states. However, the ICI methodology is general to produce both ground and excited states. In this paper, we use the free ICI method to calculate the excited states of helium atom up to very high excitation levels. They are the $1sNs$ type S symmetry ones with singlet and triplet spin multiplicities.

Accurate calculations of helium atom were performed by Drake and Yan¹¹ for the 1S and 3S states up to $N=10$. They used double exponent basis functions for each excited states.

However, since they calculated each excited state by using different basis functions, their individual states might not be completely orthogonal to each other. More recently, Kamta *et al.*¹² performed the configuration-interaction (CI) calculations with the Sturmian functions for the helium excited states with various angular momentums.

For the excited states of general molecular systems up to those of biological importance, we have developed the symmetry adapted cluster–CI methodology based on the cluster expansion formalism.^{13,14} It was incorporated in the GAUSSIAN03 program package.¹⁵ This method has long been used for studying the photorelated phenomena of small molecules to biological systems¹⁴ and, recently, it has been extended even to giant molecular crystals.¹⁶ It has been established as a useful efficient tool for studying chemistry and physics involving excited and ionized states. However, about the accuracy, this theory cannot be compared to the free ICI theory.

In this paper, we calculate the ground and excited states of helium atom at both the fixed-nucleus and moving-nucleus levels. For molecules, the first case corresponds to the Born–Oppenheimer approximation and the latter to the non-Born–Oppenheimer level. In the latter case,^{10,17} the SE for both electrons and nuclei is quantum mechanically solved and, therefore, the results may be considered as the nonrelativistic limit. So, the comparison of the present results with accurate experimental data is very interesting. It will give us a measure of the remaining physical effects such as the relativistic and quantum electrodynamic (QED) effects. The present results would also be valuable as the accurate zeroth order wave functions for perturbatively dealing with these

^{a)}Author to whom correspondence should be addressed. Electronic: h.nakatsuji@qcri.or.jp.

remaining effects.^{18,19} Since the accuracy of the present theoretical result is more than that of the experimental value, we can even discuss the order of the errors existing in the experimental values.

II. THEORY

Here, we summarize the ICI method²⁻⁴ to be pertinent for the calculations of the ground and many excited states. In our formulation of the free ICI method, we start from the simplest ICI (SICI) wave function based on the scaled SE,

$$\psi_{n+1} = [1 + C_{n+1}g(H - E_{n+1})]\psi_n, \quad (1)$$

where n is the iteration number, g is the scaling function introduced to overcome the singularity problem caused by the Coulomb potentials,^{3,4} and C_n is a variable to be determined by the variational principle. This SICI wave function has been proven to become the exact wave function at convergence.³ The choice of the initial function ψ_0 is important to accelerate the convergence speed.

In actual calculations, we introduce the free ICI method that is more flexible than the SICI. After some iteration, the right hand side of Eq. (1) is a sum of the analytical functions with some coefficients. We collect from there all the independent analytical functions as $\{\phi_i^{(n)}\}$, ($i=1, \dots, M_n$), and by a linear combination of them, we construct the wave function as

$$\psi_{n+1} = \sum_{i=1}^{M_n} c_i^{(n)} \phi_i^{(n)}, \quad (2)$$

where $\{c_i^{(n)}\}$ are the variational parameters. We call this method the free ICI method. For an increased freedom, the free ICI method converges faster than the original SICI method. In the free ICI method, we call n as “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 Eq. (1) and (2) give an expression of this equation in an analytical expansion form.

For the calculations of many excited states, the SICI method is restrictive. In our calculations, the ground and excited states belonging to the same symmetry are calculated as the lower and higher solutions of the same eigenvalue problem obtained by applying ordinary variation principle to Eq. (2): The ground and excited states, thus, automatically satisfy the correct relationships among them. The SICI method only deals with two eigenvalues at each iteration, but the free ICI method deals with M_n eigenvalues, and M_n increases as the iteration proceeds. Thus, the free ICI method is superior to the SICI method for the calculations of the excited states.

III. FORMULATION

We want to solve the SE of helium atom in both fixed-nucleus and moving-nucleus levels to calculate the ground

and $1sNs$ type excited states up to $N=24$. The Hamiltonian quantum mechanically dealing with both electrons and nucleus is written for the helium atom as¹⁰

$$H = -\frac{1}{2\mu} \sum_{i=1}^2 \nabla_i^2 - \frac{1}{m_N} \nabla_1 \cdot \nabla_2 - \sum_{i=1}^2 \frac{Z}{r_i} + \frac{1}{r_{12}} \quad (3)$$

after exactly separating the motion of the center of mass. Here, m_N represents the mass of the nucleus, μ is the reduced mass defined by $\mu = m_e m_N / (m_e + m_N)$, in which m_e is the electron mass that is equal to unity in a.u., and Z is the nuclear charge. At the fixed-nucleus case, i.e., when m_N is equal to infinity, μ is unity and the mass polarization term (the second term) disappears. For the excited states of S symmetry, the Hamiltonian and the wave functions are expressed with the interparticle coordinates $\{r_1, r_2, r_{12}\}$ or the coordinates $\{s, t, u\}$ alone, which are connected by

$$s = r_1 + r_2, \quad t = r_1 - r_2, \quad u = r_{12}. \quad (4)$$

In this paper, we use the $\{s, t, u\}$ coordinates and the explicit form of the Hamiltonian in this coordinate was given in Ref. 10.

In the free ICI method, the choices of the initial function ψ_0 and the scaling function g are important. Previously, we have examined several choices for the ground state of helium atom.⁸ In the present calculation, the g function was chosen to be the same as in Ref. 8, i.e.,

$$g = -\frac{1}{V_{Ne}} + \frac{1}{V_{ee}}, \quad (5)$$

where V_{Ne} and V_{ee} are the nuclear attraction and electron repulsion potentials, respectively. For the ψ_0 , the logarithm function previously gave excellent performance for the ground state because the logarithm singularity is very important for the three-particle coalescence region. For the higher $1sNs$ excited states, however, the probability of the three-particle collision would decrease because one electron occupies the N shell Rydberg orbital, which is quite diffuse compared to the $1s$ orbital. As a result, a different ψ_0 function might be appropriate for these excited states. In the present calculations, we used the half-integer type wave function of the form^{8,20}

$$\begin{aligned} \psi_0(L) &= (1 \pm P_{12}) \left[\{1 + s^{1/2} + u^{1/2}\} \right. \\ &\quad \left. \times \sum_{j=1}^L \exp(-\alpha_j s) \exp(-\beta_j t) \right] \\ &= (1 \pm P_{12}) \left[\{1 + s^{1/2} + u^{1/2}\} \right. \\ &\quad \left. \times \sum_{j=1}^L \exp(-\gamma_j^{(1)} r_1) \exp(-\gamma_j^{(2)} r_2) \right], \quad (6) \end{aligned}$$

where P_{12} is the permutation operator that exchanges the spatial orbitals of two electrons and the signs in front of P_{12} are plus for singlet and minus for triplet. The index L represents the number of the exponential functions included in the

TABLE I. The specific index ranges of a_i, m_i , and b_i of the free ICI wave function of Eq. (9) at order n . (At $n=1$, the functions $[a_i, m_i, b_i]=[-2, 2, 0], [-2, 2, 1/2]$ are eliminated). The free ICI method generates all of the combinations satisfying the equalities and inequalities in the table.

(I) a_i, b_i : Integer
(i) $-2n \leq a_i < -n, 0 \leq b_i \leq 2n + a_i, 0 \leq a_i + m_i + b_i \leq 2n + a_i - b_i$
(ii) $-n \leq a_i \leq -1, 0 \leq b_i < n, 0 \leq a_i + m_i + b_i \leq \min(n, 2n + a_i - b_i)$ In case $a_i + m_i + b_i = n, m_i$: Even integer.
(iii) $0 \leq a_i \leq n, 0 \leq a_i + m_i + b_i \leq n$ In case $a_i + m_i + b_i = n, m_i$: Even integer
(II) a_i : Integer, b_i : Half-integer
Change the index: b_i in the functions of (I) to $b_i + 1/2$
(III) a_i : Half-integer, b_i : Integer
(i) Change the index: a_i in the functions of (I) to $a_i + 1/2$
(ii) $-n + 1/2 \leq a_i \leq -1/2, m_i = n, b_i = n$

initial function ψ_0 : When we want to calculate the ground and excited states of helium atom from $1s1s$ to $1sNs$ states, we have to include at least about N different exponential functions that mimic the $1s$ and higher Ns orbitals, so that roughly $L \approx N$. Their orbital exponents were chosen as

$$\alpha_j = \frac{\gamma_j^{(1)} + \gamma_j^{(2)}}{2}, \quad \beta_j = \frac{\gamma_j^{(1)} - \gamma_j^{(2)}}{2}, \quad (7)$$

with

$$\gamma_j^{(1)} = 2.0, \quad \gamma_j^{(2)} = \frac{1}{j} + \frac{1 - \sigma}{j^2}, \quad (8)$$

where σ is the screening constant of the helium $1s$ orbital and taken to be $\sigma = 0.3125$.²¹ $\gamma_j^{(1)}$ represents the orbital exponent of the $1s$ orbital and $\gamma_j^{(2)}$ represents the one for the js orbital. Though $\gamma_1^{(2)}$ was 1.6875 for singlet, we used $\gamma_1^{(2)} = 1.2$ for triplet.

When we perform the free ICI formulations with the use of the g and ψ_0 functions given by Eqs. (5) and (6), the resultant free ICI wave function is written as

$$\psi_n = (1 \pm P_{12}) \sum_{j=1}^L \sum_{i=1}^K c_i^{(j)} s^{a_i} t^{m_i} u^{b_i} \exp(-\alpha_j s) \exp(-\beta_j t), \quad (9)$$

where $K = M_n/L$ and the index j represents the j th exponential set, a_i runs all integers and half integers, m_i is 0 and positive integers, and b_i runs 0 and positive integers and half integers. The condition $a_i + m_i + b_i \geq 0$ must be satisfied for the square integrability of the wave function. For the calculations with moving nucleus, we used the free ICI wave function of the same form as that obtained in the fixed-nucleus case, i.e., Eq. (9). In other words, we ignored the functions that are generated by the mass polarization operator in the electron-nuclear Hamiltonian.¹⁰ Actually, we have already seen in the previous paper¹⁰ that the contributions of such terms are quite small and negligible for helium and isoelectronic ions. Table I shows the specific index ranges of the free ICI wave function of Eq. (9) at order n . At $n=1$, the rule is exceptional and is explained in the table caption. The variables $\{c_i^{(j)}\}$ were calculated with the variation principle with the Hamiltonian given by Eq. (3) that includes the mass

polarization term when the effects of the moving nucleus is considered.

We performed all the calculations by using the M_n complement functions with $M_n = 5000 - 6000$. These complement functions were generated by the free ICI algorithm and their Hamiltonian and overlap integrals were analytically calculated: These steps were mostly done with the use of MAPLE.²² The diagonalization of the secular equation was done with the GMP library²³ for the calculations of arbitrary precision. In the calculations of moving-nucleus level, we used the alpha particle mass for the mass of helium nucleus (${}^4\text{He}$), $m_N = 7294.299\,536\,5$ (a.u.) as given by CODATA 2006 in NIST.²⁴

IV. RESULTS

A. Free ICI calculations for the fixed-nucleus Hamiltonian

We started the calculations with the g and ψ_0 given by Eqs. (5) and (6) and the fixed-nucleus Hamiltonian. The number of the exponential functions L in the ψ_0 should be about the number of the excited states we want to calculate. The calculations were performed with three different choices of $L = 16, 10$, and 6 for the orders $n = 4, 5$, and 6 , respectively, for which the dimensions of the free ICI became $M_n = 5392, 5930$, and 5724 , respectively, for both singlet and triplet states. With these calculations, we would be able to obtain the excited states at least up to $N = L$. After the diagonalization of the secular equation, the lowest solution corresponds to the ground state, the second lowest to the first excited state, and so on. These ground and excited states are automatically orthogonal and Hamiltonian orthogonal to each other.

Table II shows the calculated energies of the singlet $1sNs$ states (1S). The first column shows the results up to $N = 24$ obtained with $L = 16$ and $n = 4$ ($M_n = 5392$). The energies of the excited states of $N = 2 - 20$ were correct over 16–17 digits. The solutions for $N = 21 - 24$ were slightly worse because the number of the exponents included in the initial function was only 16, which was short as the initial guess for these higher excited states. Even so, the solution of $N = 24$ retained the accuracy correct to about 14 digits. One

TABLE II. Free ICI energies (a.u.) of the singlet $1sNs$ states (1S) calculated with the g and $\psi_0^{\text{singlet}}(L)$ given in Eqs. (5) and (6) for the fixed-nucleus Hamiltonian (the correct figures are shown in boldface) and a comparison with the reference.

N	Free ICI			Ref. 11
	$n=4$ ($M_n=5392$) with $L=16$	$n=5$ ($M_n=5930$) with $L=10$	$n=6$ ($M_n=5724$) with $L=6$	
1	-2.903 724 377 034 113 392	-2.903 724 377 034 119 550 866	-2.903 724 377 034 119 598 271 547	-2.903 724 377 034 119 479
2	-2.145 974 046 054 416 803	-2.145 974 046 054 417 411 022	-2.145 974 046 054 417 415 800 752	-2.145 974 046 054 412 8
3	-2.061 271 989 740 908 483	-2.061 271 989 740 908 649 447	-2.061 271 989 740 908 650 739 283	-2.061 271 989 740 893 0
4	-2.033 586 717 030 725 379	-2.033 586 717 030 725 446 912	-2.033 586 717 030 725 447 438 869	-2.033 586 717 030 684
5	-2.021 176 851 574 373 868	-2.021 176 851 574 373 902 539	-2.021 176 851 574 373 902 803 675	-2.021 176 851 574 32
6	-2.014 563 098 446 617 143	-2.014 563 098 446 617 163 292	-2.014 563 098 446 617 163 443 798	-2.014 563 098 446 564
7	-2.010 625 776 210 865 949	-2.010 625 776 210 865 961 562	-2.010 625 776 210 865 961 657 234	-2.010 625 776 210 802
8	-2.008 093 622 105 612 517	-2.008 093 622 105 612 526 012	-2.008 093 622 105 612 526 074 710	-2.008 093 622 105 534
9	-2.006 369 553 107 877 466	-2.006 369 553 107 877 471 748		-2.006 369 553 107 775
10	-2.005 142 991 747 992 557	-2.005 142 991 747 992 561 593		-2.005 142 991 747 844
11	-2.004 239 415 361 821 463	-2.004 239 415 361 821 466 770		
12	-2.003 554 625 012 232 644	-2.003 554 625 012 232 646 904		
13	-2.003 023 289 603 502 536	-2.003 023 289 603 502 537 990		
14	-2.002 602 761 355 122 988	-2.002 602 761 355 122 990 187		
15	-2.002 264 241 270 263 476	-2.002 264 241 270 263 309 558		
16	-2.001 987 713 181 956 782			
17	-2.001 758 915 080 010 317			
18	-2.001 567 462 439 135 929			
19	-2.001 405 648 670 772 637			
20	-2.001 267 657 216 551 210			
21	-2.001 149 031 412 258 616			
22	-2.001 046 310 060 125 636			
23	-2.000 956 772 051 261 501			
24	-2.000 878 254 201 540 989			

could obtain larger number of accurate solutions than the number of the different exponents included in the ψ_0 . For the higher excited states, the energy levels were almost degenerate. The energy difference between the states of $N=23$ and 24 was only $7.851\,784 \times 10^{-5}$ a.u. Thus, the density of states was very high there which made the calculations of these highly excited states difficult in general. For the ground state ($N=1$), the accuracy was about 15 digits, which was slightly worse than those of $N=2-20$. Since the ground state is considerably low apart from the other excited states and has different closed-shell electronic structure, it may be differently treated from the other excited states.¹⁰ The wave function with logarithm weak singularity was essential for the ground state, since the three-particle collision may occur more frequently than in the excited states.^{8,25-27}

The results with $L=10$ and $n=5$ ($M_n=5930$) are shown in the second column of Table II up to $N=15$. Because of the increased order n , the accuracies of all of the states to $N=14$ have been improved. The accuracy of the ground state was over 17 digits and those for $N=2-13$ were 18-20 digits, which were variationally better than those reported by Drake and Yan.¹¹ For $N=14$, however, the accuracy slightly got worse to be about 17 digits, and for $N=15$, the accuracy was less than 17 digits which was slightly worse than the solution with $n=4$. This is clearly due to the small L values, i.e., the lack of the adequate exponents for these excited states in the initial function ψ_0 .

The results with $L=6$ and $n=6$ ($M_n=5724$) are also shown in Table II up to $N=8$. The calculated energies of

these states were further improved. The accuracy of the ground state achieved 20 digits, and those of the other excited states achieved 20-23 digits. These results were variationally best as the energies of the excited states. This is a numerical evidence that the free ICI method is useful to calculate very accurate solutions of the SE even for the excited states.

Similar calculations for the triplet states (3S) are shown in Table III for the orders $n=4, 5$, and 6. The behaviors of the calculated results were quite similar to those for the singlet states. At the same excitation level N , the energy of the triplet state was lower than that of the singlet state, which follows Hund's rule. The accuracies of the triplet states were better than those of the singlet states by two to three digits at the same condition of the calculations. This is due to the smaller correlations between the two electrons of parallel spins for the Fermi hole. Drake and Yan¹¹ showed the results up to $N=10$: Our results for $n=5$ and 6 were variationally better than theirs. More recently, Kamta *et al.*¹² calculated the energies of the triplet states up to very high levels, but their results were less accurate than ours for all the states.

B. Free ICI calculations for the moving-nucleus Hamiltonian

Next, we performed the calculations for the moving-nucleus Hamiltonian. There are only few references of the theoretical calculations for the highly excited states of helium atom with this Hamiltonian. So, this is the first very accurate variational calculations for such states. We used the

TABLE III. Free ICI energies (a.u.) of the triplet $1sNs$ states (3S) calculated with the g and $\psi_0^{\text{triplet}}(L)$ given in Eqs. (5) and (6) for the fixed-nucleus Hamiltonian (the correct figures are shown in boldface) and comparison with the references.

N	Free ICI			Ref. 11	Ref. 12
	$n=4$ ($M_n=5392$) with $L=16$	$n=5$ ($M_n=5930$) with $L=10$	$n=6$ ($M_n=5724$) with $L=6$		
2	-2.175 229 378 236 791 299 127	-2.175 229 378 236 791 305 721 165	-2.175 229 378 236 791 305 738 966 843	-2.175 229 378 236 791 300 8	-2.175 228 3
3	-2.068 689 067 472 457 190 842	-2.068 689 067 472 457 191 993 111	-2.068 689 067 472 457 191 996 530 498	-2.068 689 067 472 457 182 2	-2.068 688 8
4	-2.036 512 083 098 236 299 162	-2.036 512 083 098 236 299 579 123	-2.036 512 083 098 236 299 580 377 172	-2.036 512 083 098 236 270	-2.036 511 98
5	-2.022 618 872 302 312 266 123	-2.022 618 872 302 312 266 321 860	-2.022 618 872 302 312 266 322 458 549	-2.022 618 872 302 312 248	-2.022 618 816
6	-2.015 377 452 992 862 437 582	-2.015 377 452 992 862 437 692 306	-2.015 377 452 992 862 437 692 638 542	-2.015 377 452 992 862 120	-2.015 377 421
7	-2.011 129 919 527 626 331 675	-2.011 129 919 527 626 331 742 916	-2.011 129 919 527 626 331 743 119 501	-2.011 129 919 527 626 070	-2.011 129 900
8	-2.008 427 122 064 721 395 284	-2.008 427 122 064 721 395 328 484	-2.008 427 122 064 721 395 328 617 608	-2.008 427 122 064 721 111	-2.008 427 109
9	-2.006 601 516 715 010 778 123	-2.006 601 516 715 010 778 153 727		-2.006 601 516 715 010 458	-2.006 601 507 7
10	-2.005 310 794 915 611 245 045	-2.005 310 794 915 611 245 067 369		-2.005 310 794 915 610 14	-2.005 310 788 4
11	-2.004 364 700 897 266 597 358	-2.004 364 700 897 266 597 374 467			-2.004 364 696 02
12	-2.003 650 626 784 731 774 752	-2.003 650 626 784 731 774 764 860			-2.003 650 623 05
13	-2.003 098 467 826 765 664 239	-2.003 098 467 826 765 664 249 638			-2.003 098 464 91
14	-2.002 662 728 645 385 867 828	-2.002 662 728 645 385 867 836 033			-2.002 662 726 32
15	-2.002 312 839 656 877 712 887	-2.002 312 839 656 877 691 135 649			-2.002 312 837 77
16	-2.002 027 644 283 129 301 417				-2.002 027 642 74
17	-2.001 792 123 370 925 548 604				-2.001 792 122 09
18	-2.001 595 376 271 437 103 412				-2.001 595 375 19
19	-2.001 429 336 322 174 226 578				-2.001 429 335 41
20	-2.001 287 930 553 410 778 107				-2.001 287 929 77
21	-2.001 166 516 338 700 203 335				-2.001 166 515 66
22	-2.001 061 495 380 029 361 233				-2.001 061 494 79
23	-2.000 970 043 984 125 442 687				-2.000 970 043 47
24	-2.000 889 921 221 492 270 140				-2.000 889 920 80

TABLE IV. Free ICI energies (a.u.) of the singlet $1sNs$ states (1S) calculated with the g and $\psi_0^{\text{singlet}}(L)$ given in Eqs. (5) and (6) for the moving-nucleus Hamiltonian (the correct figures are shown in boldface). The mass of helium nucleus, $m_N=7294.299\ 536\ 5$ a.u. was used.

N	$n=4$ ($M_n=5392$) with $L=16$	$n=5$ ($M_n=5930$) with $L=10$	$n=6$ ($M_n=5724$) with $L=6$
1	-2.903 304 557 729 574 094	-2.903 304 557 729 580 247 325	-2.903 304 557 729 580 294 694 232
2	-2.145 678 587 580 576 765	-2.145 678 587 580 577 372 955	-2.145 678 587 580 577 377 730 398
3	-2.060 989 082 349 024 914	-2.060 989 082 349 025 080 356	-2.060 989 082 349 025 081 647 625
4	-2.033 307 817 481 290 775	-2.033 307 817 481 290 843 198	-2.033 307 817 481 290 843 724 323
5	-2.020 899 726 173 541 168	-2.020 899 726 173 541 202 200	-2.020 899 726 173 541 202 464 811
6	-2.014 286 911 184 421 373	-2.014 286 911 184 421 392 790	-2.014 286 911 184 421 392 941 839
7	-2.010 350 144 451 778 455	-2.010 350 144 451 778 467 802	-2.010 350 144 451 778 467 896 681
8	-2.007 818 346 203 258 377	-2.007 818 346 203 258 385 654	-2.007 818 346 203 258 385 716 910
9	-2.006 094 518 776 602 767	-2.006 094 518 776 602 773 302	
10	-2.004 868 128 875 832 522	-2.004 868 128 875 832 526 877	
11	-2.003 964 678 560 077 649	-2.003 964 678 560 077 652 569	
12	-2.003 279 983 605 862 318	-2.003 279 983 605 862 320 464	
13	-2.002 748 722 118 365 148	-2.002 748 722 118 365 150 552	
14	-2.002 328 252 310 128 797	-2.002 328 252 310 128 798 533	
15	-2.001 989 779 223 704 279	-2.001 989 779 223 704 110 186	
16	-2.001 713 289 495 095 619		
17	-2.001 484 523 108 501 314		
18	-2.001 293 096 989 016 414		
19	-2.001 131 305 623 273 079		
20	-2.000 993 333 263 620 653		
21	-2.000 874 723 866 482 391		
22	-2.000 772 016 715 719 527		
23	-2.000 682 491 080 815 747		
24	-2.000 603 984 077 289 704		

same g and ψ_0 given by Eqs. (5) and (6) with three different sets of the exponential functions for ψ_0 , $L=16$, 10, and 6. We performed the free ICI calculations to the orders $n=4$ ($M_n=5392$), 5 ($M_n=5930$), and 6 ($M_n=5724$), respectively.

Tables IV and V show the energies for the singlet (1S) and triplet (3S) states, respectively, to $N=24$, 15, and 8 for $n=4$, 5, and 6, respectively. The convergence behaviors were almost the same as those for the fixed-nucleus case for both the

TABLE V. Free ICI energies (a.u.) of the triplet $1sNs$ states (3S) calculated with the g and $\psi_0^{\text{triplet}}(L)$ given in Eqs. (5) and (6) for the moving-nucleus Hamiltonian (The correct figures are shown in boldface). The mass of helium nucleus $m_N=7294.299\ 536\ 5$ a.u. was used.

N	$n=4$ ($M_n=5392$) with $L=16$	$n=5$ ($M_n=5930$) with $L=10$	$n=6$ ($M_n=5724$) with $L=6$
2	-2.174 930 190 712 309 581 298	-2.174 930 190 712 309 587 889 429	-2.174 930 190 712 309 587 907 223 962
3	-2.068 405 243 694 680 773 926	-2.068 405 243 694 680 775 076 129	-2.068 405 243 694 680 775 079 547 636
4	-2.036 232 827 788 694 949 940	-2.036 232 827 788 694 950 356 809	-2.036 232 827 788 694 950 358 062 268
5	-2.022 341 573 181 791 866 923	-2.022 341 573 181 791 867 121 826	-2.022 341 573 181 791 867 122 424 527
6	-2.015 101 168 236 722 510 326	-2.015 101 168 236 722 510 435 979	-2.015 101 168 236 722 510 436 311 354
7	-2.010 854 227 679 922 862 404	-2.010 854 227 679 922 862 471 992	-2.010 854 227 679 922 862 472 195 700
8	-2.008 151 806 543 955 639 167	-2.008 151 806 543 955 639 211 251	-2.008 151 806 543 955 639 211 384 429
9	-2.006 326 454 897 939 965 199	-2.006 326 454 897 939 965 230 398	
10	-2.005 035 912 200 715 982 315	-2.005 035 912 200 715 982 337 738	
11	-2.004 089 949 305 164 969 517	-2.004 089 949 305 164 969 533 649	
12	-2.003 375 974 060 731 424 668	-2.003 375 974 060 731 424 680 647	
13	-2.002 823 891 489 240 403 444	-2.002 823 891 489 240 403 454 418	
14	-2.002 388 212 546 182 926 638	-2.002 388 212 546 182 926 645 925	
15	-2.002 038 371 898 429 106 746	-2.002 038 371 898 429 084 645 998	
16	-2.001 753 215 906 614 691 760		
17	-2.001 517 727 501 912 895 779		
18	-2.001 321 007 547 138 202 209		
19	-2.001 154 990 497 678 391 712		
20	-2.001 013 604 224 887 508 127		
21	-2.000 892 206 744 952 801 036		
22	-2.000 787 200 257 694 457 623		
23	-2.000 695 761 460 329 847 604		
24	-2.000 615 649 732 689 162 022		

TABLE VI. Energy differences (a.u.) ΔE of Eq. (10) between the fixed-nucleus and moving-nucleus calculations and the mass polarization effect to the total energy ΔE_{MP} of Eq. (11) calculated with the moving-nucleus Hamiltonian for singlet and triplet states with $\psi_0(L)$ of $L=16$ and $n=4$ ($M_n=5392$). (The correct figures are shown in boldface.)

State	$\Delta E = E_{\text{MN}} - E_{\text{FN}}$		$\Delta E_{\text{MP}} = E_{\text{MN}} - \mu E_{\text{FN}}$	
	Singlet (1S)	Triplet (3S)	Singlet (1S)	Triplet (3S)
1	4.198 193 045 $392\,986 \times 10^{-4}$		2.179 255 286 088×10^{-5}	
2	2.954 584 738 400 375×10^{-4}	2.991 875 244 817 178×10^{-4}	1.300 018 067 572×10^{-6}	1.018 906 818 572×10^{-6}
3	2.829 073 918 835 689×10^{-4}	2.838 237 777 764 169×10^{-4}	3.594 335 128 525×10^{-7}	2.591 267 127 631×10^{-7}
4	2.788 995 494 346 036×10^{-4}	2.792 553 095 413 492×10^{-4}	1.465 377 376 554×10^{-7}	1.013 045 674 458×10^{-7}
5	2.771 254 008 327 003×10^{-4}	2.772 991 205 203 991×10^{-4}	7.346 602 701 094×10^{-8}	4.952 135 278 423×10^{-8}
6	2.761 872 621 957 704×10^{-4}	2.762 847 561 399 272×10^{-4}	4.190 471 355 723×10^{-8}	2.777 136 370 491×10^{-8}
7	2.756 317 590 874 937×10^{-4}	2.756 918 477 034 692×10^{-4}	2.610 833 233 836×10^{-8}	1.709 172 319 762×10^{-8}
8	2.752 759 023 541 403×10^{-4}	2.753 155 207 657 561×10^{-4}	1.734 551 782 743×10^{-8}	1.124 956 810 131×10^{-8}
9	2.750 343 312 746 984×10^{-4}	2.750 618 170 708 129×10^{-4}	1.210 044 379 615×10^{-8}	7.789 929 701 199×10^{-9}
10	2.748 628 721 600 34×10^{-4}	2.748 827 148 952 627×10^{-4}	8.771 692 217 333×10^{-9}	5.612 881 480 153×10^{-9}
11	2.747 368 017 438 14×10^{-4}	2.747 515 921 016 278×10^{-4}	6.558 614 773 699×10^{-9}	4.175 512 495 908×10^{-9}
12	2.746 414 063 703 264×10^{-4}	2.746 527 240 003 500×10^{-4}	5.030 579 585 437×10^{-9}	3.188 808 542 847×10^{-9}
13	2.745 674 851 373 874×10^{-4}	2.745 763 375 252 607×10^{-4}	3.941 915 901 710×10^{-9}	2.489 281 632 113×10^{-9}
14	2.745 090 449 941 916×10^{-4}	2.745 160 992 029 411×10^{-4}	3.145 498 816 903×10^{-9}	1.979 717 425 824×10^{-9}
15	2.744 620 465 591 969×10^{-4}	2.744 677 584 486 061×10^{-4}	2.549 556 710 339×10^{-9}	1.599 843 484 730×10^{-9}
16	2.744 236 868 611 626×10^{-4}	2.744 283 765 146 096×10^{-4}	2.094 825 692 583×10^{-9}	1.310 940 873 937×10^{-9}
17	2.743 919 715 090 025×10^{-4}	2.743 958 690 126 528×10^{-4}	1.741 873 499 994×10^{-9}	1.087 365 166 520×10^{-9}
18	2.743 654 501 195 142×10^{-4}	2.743 687 242 989 012×10^{-4}	1.463 771 201 849×10^{-9}	9.116 742 088 320×10^{-10}
19	2.743 430 474 995 577×10^{-4}	2.743 458 244 958 348×10^{-4}	1.241 702 921 637×10^{-9}	7.717 247 211 097×10^{-10}
20	2.743 239 529 305 573×10^{-4}	2.743 263 285 232 699×10^{-4}	1.062 252 283 568×10^{-9}	6.588 861 942 391×10^{-10}
21	2.743 075 457 762 253×10^{-4}	2.743 095 937 474 022×10^{-4}	9.156 783 $017\,696 \times 10^{-10}$	5.669 108 179 030×10^{-10}
22	2.742 933 444 061 087×10^{-4}	2.742 951 223 349 036×10^{-4}	7.947 926 $970\,447 \times 10^{-10}$	4.912 003 935 974×10^{-10}
23	2.742 809 704 457 540×10^{-4}	2.742 825 237 955 950×10^{-4}	6.942 158 $293\,925 \times 10^{-10}$	4.283 212 $654\,878 \times 10^{-10}$
24	2.742 701 242 512 844×10^{-4}	2.742 714 888 $031\,081 \times 10^{-4}$	6.108 213 $417\,938 \times 10^{-10}$	3.761 214 $976\,290 \times 10^{-10}$
∞	2.741 491 271 185 722×10^{-4}	2.741 491 271 185 722×10^{-4}	0	0

singlet and triplet states. The accuracies of the calculations for $n=4$ were observed to be in about 14–17 digits for all the states up to $N=24$. For the states up to $N=8$, the best performance was obtained in the calculations of the order $n=6$: The results were correct over 20–23 digits in accuracy. Thus, the convergence of the free ICI to the exact solutions was very good also for the moving-nucleus Hamiltonian.

We calculate the energy difference between the energies of the fixed-nucleus (E_{FN}) and moving-nucleus (E_{MN}) calculations, given by

$$\Delta E = E_{\text{MN}} - E_{\text{FN}}. \quad (10)$$

As previously shown,¹⁰ ΔE includes the two effects arising from the reduced mass and from the mass polarization operator, although these two effects cannot be separated as physical quantities. The fixed-nucleus energy is easily transformed to the energy for the reduced mass by μE_{FN} with the reduced mass μ . This energy is obtained from the Hamiltonian that does not include the second mass polarization term of Eq. (3) but whose μ retains the value of the finite nuclear mass. Then, the energy difference,

$$\Delta E_{\text{MP}} = E_{\text{MN}} - \mu E_{\text{FN}}, \quad (11)$$

represents the mass polarization effect in the total energy. This energy includes the effect of the mass polarization to any order because E_{MN} was variationally calculated for the Hamiltonian given by Eq. (3).

In Table VI, ΔE and ΔE_{MP} are shown for both singlet

and triplet states for the calculations of $n=4$. ΔE was always positive for all the states because the nuclear kinetic energy contained in E_{MN} was always positive. For both singlet and triplet states, when N grows up, the $1sN_s$ state converges to the one-electron ionized state, $1s\infty s$ state, which is the state of $\text{He}^+ + e^-$ and its exact energy is -2 a.u. in the fixed-nucleus approximation and $-2\mu = -1.999\,725\,850\,872\dots$ a.u. in the moving-nucleus level. So, ΔE should converge to $-2\mu - (-2) = 2.741\,491 \times 10^{-4}$ a.u. at $N=\infty$. The ground state had the largest value $\Delta E = 4.198\,193 \times 10^{-4}$ a.u., the second was the $N=2$ triplet state of $2.991\,875 \times 10^{-4}$ a.u., and the next was its singlet state of $2.954\,584 \times 10^{-4}$ a.u. When N grew up, ΔE monotonically converged to the limit of $N=\infty$, i.e., $2.741\,491 \times 10^{-4}$ a.u. and, therefore, ΔE became small as N increased. At the same quantum number N , ΔE for the triplet state was larger than that for the singlet state.

ΔE_{MP} was quite small in the moving-nucleus effect compared to the reduced-mass effect ΔE . It was $2.179\,255 \times 10^{-5}$ a.u. for the ground state, which was largest among all the states. In the ground state, two electrons occupy the $1s$ orbital and their positions are very near the nucleus, so that the polarization effect of the center of mass is thought to be large.¹⁰ The second largest state on ΔE_{MP} was the singlet $N=2$ state, $1.300\,018 \times 10^{-6}$ a.u., and then the corresponding triplet state, $1.018\,907 \times 10^{-6}$ a.u. At the same quantum number N , ΔE_{MP} for the singlet state was larger than that for the triplet state, although for ΔE , the relation was converse. In

TABLE VII. Singlet (1S) excitation energies (a.u.) from the ground to the $1sNs$ states calculated in the fixed-nucleus approximation, $E_{\text{ex}}^{\text{FN}}$ and those calculated in the moving-nucleus level $E_{\text{ex}}^{\text{MN}}$ for $N=2-24$ with $\psi_0^{\text{singlet}}(L)$ of $L=16$ and $n=4$ ($M_n=5392$). The differences from the experimental excitation energies are given as $\Delta E_{\text{ex}}^{\text{FN}}$ and $\Delta E_{\text{ex}}^{\text{MN}}$ for the fixed-nucleus and moving-nucleus levels, respectively. (the correct figures are shown in boldface).

State	Excitation energy ($E_{\text{ex}}^{\text{FN}}$)	Excitation energy ($E_{\text{ex}}^{\text{MN}}$)	Expt. ^a	Ref.	$\Delta E_{\text{ex}}^{\text{FN}}=[\text{Theor}(E_{\text{ex}}^{\text{FN}})]-[\text{Expt.}]$	$\Delta E_{\text{ex}}^{\text{MN}}=[\text{Theor}(E_{\text{ex}}^{\text{MN}})]-[\text{Expt.}]$
2	0.757 750 330 979 697	0.757 625 970 148 997	0.757 615 762 6	28	0.000 134 568 4	0.000 010 207 5
3	0.842 452 387 293 205	0.842 315 475 380 549	0.842 306 138 8	28	0.000 146 248 5	0.000 009 336 6
4	0.870 137 660 003 388	0.869 996 740 248 283	0.869 988 158 2	29	0.000 149 501 8	0.000 008 582 1
5	0.882 547 525 459 740	0.882 404 831 556 033	0.882 396 351 2	29	0.000 151 174 2	0.000 008 480 3
6	0.889 161 278 587 496	0.889 017 646 545 153	0.889 009 221 2	29	0.000 152 057 4	0.000 008 425 3
7	0.893 098 600 823 247	0.892 954 413 277 796	0.892 946 017 0	29	0.000 152 583 9	0.000 008 396 3
8	0.895 630 754 928 501	0.895 486 211 526 316	0.895 477 830 3	29	0.000 152 924 6	0.000 008 381 2
9	0.897 354 823 926 236	0.897 210 038 952 971	0.897 201 55	30	0.000 153 271 8	0.000 008 486 9
10	0.898 581 385 286 121	0.898 436 428 853 742	0.898 428 07	30	0.000 153 313 3	0.000 008 356 9
11	0.899 484 961 672 292	0.899 339 879 169 496	0.899 331 46	30	0.000 153 505 1	0.000 008 422 6
12	0.900 169 752 021 881	0.900 024 574 123 712	0.900 016 00	30	0.000 153 751 7	0.000 008 573 8
13	0.900 701 087 430 611	0.900 555 835 611 209	0.900 547 72	30	0.000 153 362 7	0.000 008 110 9
14	0.901 121 615 678 990	0.900 976 305 419 445	0.900 968 23	30	0.000 153 386 8	0.000 008 076 6
15	0.901 460 135 763 850	0.901 314 778 505 870	0.901 306 67	30	0.000 153 462 3	0.000 008 105 1
16	0.901 736 663 852 157	0.901 591 268 234 472				
17	0.901 965 461 954 103	0.901 820 034 621 073				
18	0.902 156 914 594 977	0.902 011 460 740 558				
19	0.902 318 728 363 341	0.902 173 252 106 301				
20	0.902 456 719 817 562	0.902 311 224 465 953				
21	0.902 575 345 621 855	0.902 429 833 863 092				
22	0.902 678 066 973 988	0.902 532 541 013 855				
23	0.902 767 604 982 852	0.902 622 066 648 758				
24	0.902 846 122 832 572	0.902 700 573 652 284				
∞	0.903 724 377 034 113	0.903 578 706 856 692	0.903 569 891		0.000 154 486 0	0.000 008 815 8

^aThe unit converted from cm^{-1} (original paper) to a.u.

the triplet state, two electrons cannot occupy the same spatial coordinates by the Pauli exclusion principle, so that the two electrons tend to be apart from each other. As the excitation level becomes higher, ΔE_{MP} becomes very small. For $N=24$, the order of ΔE_{MP} was 10^{-10} . For highly excited states, the state is similar to the ionized state: One electron is very far from the nucleus and is extremely delocalized, so that the mass polarization effect becomes almost negligible and the simple reduced-mass effect becomes dominant in ΔE .

C. Excitation energies

We examine here the excitation energies from the ground state to the $1sNs$ excited states and compare the present theoretical results with the available experimental data.²⁸⁻³⁰ The accuracies of the experimental values were less than ten decimal figures in a.u. and they were limited to $N=15$ for singlet and 17 for triplet, so that our theoretical results with $n=4$ were sufficient in accuracy to compare with the experimental values. We show in Tables VII and VIII the excitation energies from the ground state for the singlet and triplet states, respectively. In each table, the excitation energies for both of the fixed-nucleus ($E_{\text{ex}}^{\text{FN}}$) and moving-nucleus ($E_{\text{ex}}^{\text{MN}}$) levels are presented, and $\Delta E_{\text{ex}}^{\text{FN}}$ and $\Delta E_{\text{ex}}^{\text{MN}}$ show the differences between the theoretical and experimental values for both the fixed-nucleus and moving-nucleus levels. At the bottom of the tables, we gave the value for $N=\infty$, which is the ionization energy.

In Tables VII and VIII, we see the natural trends that the spacing of the neighboring excitation energies becomes

smaller and smaller as N increases and that the triplet excitation energy to the Ns state is smaller than the corresponding singlet one. The theoretical excitation energies agreed quite well with the experimental values and the agreement was improved when the quantum effect of the nuclear motion was considered. The differences from the experimental values at the fixed-nucleus approximation $\Delta E_{\text{ex}}^{\text{FN}}$ were almost constant at around 0.000 15 a.u. except for a few low-level states, and those for the moving-nucleus level $\Delta E_{\text{ex}}^{\text{MN}}$ were much smaller and also almost constant around at 0.000 008 again except for a few low-level states. The inclusion of the effect of nuclear motion increased the accuracy of the theoretical results by the two orders of magnitude up to 10^{-6} a.u.

The present theoretical results for the moving-nucleus Hamiltonian are considered to be a nonrelativistic limit, so that we mainly discuss the difference $\Delta E_{\text{ex}}^{\text{MN}}$ from the experimental value at this level of accuracy. Since the accuracy of the present theoretical result is high enough as a solution of the electron-nuclear SE, the source of the difference $\Delta E_{\text{ex}}^{\text{MN}}$ lies in the relativistic effect, the QED effect, and even the errors in the experimental value: The theoretical and numerical errors do not exist at this level of digits of the present results. Since the values of $\Delta E_{\text{ex}}^{\text{MN}}$ were fairly constant for N larger than 5, around 0.000 008 1–0.000 008 5, these values and the large deviations for $N=2$ and 3 for singlet and for $N=2-4$ for triplet would be physically meaningful and would have some clear origins. We expect that the relativistic and QED effects are the main sources of the value

TABLE VIII. Triplet (3S) excitation energies (a.u.) from the ground to the $1sN_s$ states calculated in the fixed-nucleus approximation, $E_{\text{ex}}^{\text{FN}}$ and those calculated in the moving-nucleus level $E_{\text{ex}}^{\text{MN}}$ for $N=2-24$ calculated with $\psi_0^{\text{triplet}}(L)$ of $L=16$ and $n=4$ ($M_n=5392$). The differences from the experimental excitation energies are given as $\Delta E_{\text{ex}}^{\text{FN}}$ and $\Delta E_{\text{ex}}^{\text{MN}}$ for the fixed-nucleus and moving-nucleus levels, respectively (the correct figures are shown in boldface).

State	Excitation energy ($E_{\text{ex}}^{\text{FN}}$)	Excitation energy ($E_{\text{ex}}^{\text{MN}}$)	Expt. ^a	Ref.	$\Delta E_{\text{ex}}^{\text{FN}}=[\text{Theor}(E_{\text{ex}}^{\text{FN}})]-[\text{Expt.}]$	$\Delta E_{\text{ex}}^{\text{MN}}=[\text{Theor}(E_{\text{ex}}^{\text{MN}})]-[\text{Expt.}]$
2	0.728 494 998 797 322	0.728 374 367 017 265	0.728 357 411 6	28	0.000 137 587 2	0.000 016 955 4
3	0.835 035 309 561 656	0.834 899 314 034 893	0.834 888 253 7	28	0.000 147 055 9	0.000 011 060 3
4	0.867 212 293 935 877	0.867 071 729 940 879	0.867 062 4720 1	29	0.000 149 821 9	0.000 009 257 9
5	0.881 105 504 731 801	0.880 962 984 547 782	0.880 954 1830 0	29	0.000 151 321 7	0.000 008 801 5
6	0.888 346 924 041 251	0.888 203 389 492 852	0.888 194 786 3	29	0.000 152 137 7	0.000 008 603 2
7	0.892 594 457 506 487	0.892 450 330 049 651	0.892 441 823 8	29	0.000 152 633 7	0.000 008 506 2
8	0.895 297 254 969 392	0.895 152 751 185 618	0.895 144 298 8	29	0.000 152 956 1	0.000 008 452 4
9	0.897 122 860 319 103	0.896 978 102 831 634	0.896 969 45	30	0.000 153 408 0	0.000 008 650 5
10	0.898 413 582 118 502	0.898 268 645 528 858	0.898 259 99	30	0.000 153 593 4	0.000 008 656 8
11	0.899 359 676 136 847	0.899 214 608 424 409	0.899 205 93	30	0.000 153 746 6	0.000 008 678 9
12	0.900 073 750 249 382	0.899 928 583 668 843	0.899 919 59	30	0.000 154 161 9	0.000 008 995 4
13	0.900 625 909 207 348	0.900 480 666 240 334	0.900 471 95	30	0.000 153 956 4	0.000 008 713 4
14	0.901 061 648 388 728	0.900 916 345 183 391	0.900 907 63	30	0.000 154 018 8	0.000 008 715 6
15	0.901 411 537 377 236	0.901 266 185 831 145	0.901 257 33	30	0.000 154 209 0	0.000 008 857 5
16	0.901 696 732 750 984	0.901 551 341 822 959	0.901 543 24	30	0.000 153 494 4	0.000 008 103 4
17	0.901 932 253 663 188	0.901 786 830 227 661	0.901 778 62	30	0.000 153 635 0	0.000 008 211 6
18	0.902 129 000 762 676	0.901 983 550 182 436				
19	0.902 295 040 711 939	0.902 149 567 231 896				
20	0.902 436 446 480 703	0.902 290 953 504 687				
21	0.902 557 860 695 413	0.902 412 350 984 621				
22	0.902 662 881 654 084	0.902 517 357 471 880				
23	0.902 754 333 049 988	0.902 608 796 269 244				
24	0.902 834 455 812 621	0.902 688 907 996 885				
∞	0.903 724 377 034 113	0.903 578 706 856 692	0.903 569 891		0.000 154 486 0	0.000 008 815 8

^aThe unit converted from cm^{-1} (original paper) to a.u.

of $\Delta E_{\text{ex}}^{\text{MN}}$. They are certainly expected to be large for the lower states of $N=2-4$. Since the speed of the electrons moving around the nucleus becomes larger as N becomes smaller, the relativistic effect is expected to become larger as N becomes smaller. Further, from the irregular changes of the values of $\Delta E_{\text{ex}}^{\text{MN}}$ in the order of 10^{-7} a.u., we also estimate the existence of some experimental errors in this order. For the ionization potential, the value of $\Delta E_{\text{ex}}^{\text{MN}}$ lay in the same order as above,²⁸ although it was a bit large in the order of 10^{-7} a.u. as a limiting value of the excitation energy at $N=\infty$.

In the experimental side, the accurate data of the excitation energy were available only up to $N=15$ for singlet and $N=17$ for triplet and the data for the higher $1sN_s$ states are now not available. So, the present theoretical values give highly accurate predictions for these states.

V. CONCLUSION

In this report, we used the free ICI methodology to solve the SE of the helium atom not only for the ground state but also for many excited states. We solved the SE for both the fixed-nucleus and moving-nucleus Hamiltonians and calculated the ground and excited states of S symmetry ($1sN_s$) up to $N=24$ for both singlet and triplet states. This is the first extensive applications of the free ICI method to the systematic calculations of many excited states. We were successful in obtaining very accurate excited states that are variationally better than the existing theoretical results for all the states up to $N=24$. In the free ICI formalism, we can easily calculate

the excited states by introducing appropriate initial functions that mimic the target excited states into the initial function ψ_0 . In the present calculations, this has been done by introducing many different exponents in the ψ_0 . From such ψ_0 , the free ICI method generated the complement functions not only for the ground state but also for the excited states. The solutions for all the states of the same symmetry were obtained by a single diagonalization, so that all of them satisfy the Ritz-type variational principle and the orthogonality to each other.

We compared the calculated theoretical excitation energies with the experimental data. The results for the fixed-nucleus Hamiltonian reproduced the experimental excitation energies up to 10^{-3} a.u. Those for the moving-nucleus Hamiltonian, which correspond to the nonrelativistic limit, further agreed with the experimental values to 10^{-5} a.u. The remaining differences from the experimental excitation energies originate from the physical effects such as relativistic effect, QED effect, and also from the experimental errors. The present theoretical results are correct at the nonrelativistic Schrödinger level to higher digits than the experimentally reported values. Further theoretical improvements would be obtained by introducing the relativistic effects and the QED effects. We have already reported that the free ICI method is also useful for solving the relativistic Dirac-Coulomb equation of helium atom and its isoelectronic ions.⁵ When we study the QED effect by the perturbation method, the present results and the results for the Dirac-Coulomb equation would be the excellent zeroth order functions.

Thus, we have been able to show that with the free ICI methodology for solving the SE, we can obtain highly accurate theoretical results that are, in some sense, more accurate than the existing experimental values and, therefore, that have truly accurate predictive power. This is a step for accurately formulating predictive quantum chemistry and science based on the calculations of the Schrödinger accuracy, which we want to systematically build up in future.

ACKNOWLEDGMENTS

This study has partially been financially supported by the Grant for Creative Scientific Research from the Ministry of Education, Science, Culture, and Sports of Japan.

¹E. A. Hylleraas, *Z. Phys.* **54**, 347 (1929).

²H. Nakatsuji, *J. Chem. Phys.* **113**, 2949 (2000); H. Nakatsuji and E. R. Davidson, *ibid.* **115**, 2000 (2001).

³H. Nakatsuji, *Phys. Rev. Lett.* **93**, 030403 (2004).

⁴H. Nakatsuji, *Phys. Rev. A* **65**, 062110 (2005).

⁵H. Nakatsuji and H. Nakashima, *Phys. Rev. Lett.* **95**, 050407 (2005).

⁶Y. Kurokawa, H. Nakashima, and H. Nakatsuji, *Phys. Rev. A* **72**, 062502 (2005).

⁷H. Nakatsuji, *Bull. Chem. Soc. Jpn.* **78**, 1705 (2005).

⁸H. Nakashima and H. Nakatsuji, *J. Chem. Phys.* **127**, 224104 (2007).

⁹H. Nakatsuji, H. Nakashima, Y. Kurokawa, and A. Ishikawa, *Phys. Rev. Lett.* **99**, 240402 (2007).

¹⁰H. Nakashima and H. Nakatsuji, *J. Chem. Phys.* **128**, 154107 (2008).

¹¹G. W. F. Drake and Z. Yan, *Chem. Phys. Lett.* **229**, 486 (1994).

¹²G. L. Kamta, B. Piraux, and A. Scrinzi, *Phys. Rev. A* **63**, 040502 (2001).

¹³H. Nakatsuji, *Chem. Phys. Lett.* **59**, 362 (1978); See: <http://qcri.or.jp/sacci/>

¹⁴M. Ehara, J. Hasegawa, and H. Nakatsuji, in *Theory and Applications of Computational Chemistry*, edited by C. Dykstra, G. Frenking, K. Kim, and G. Scuseria (Elsevier Science, New York, 2006).

¹⁵M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 03, Gaussian, Inc., Pittsburgh, PA, 2003.

¹⁶H. Nakatsuji, T. Miyahara, and R. Fukuda, *J. Chem. Phys.* **126**, 084104 (2007).

¹⁷H. Cox, S. J. Smith, and B. T. Sutcliffe, *Phys. Rev. A* **49**, 4533 (1994).

¹⁸G. W. F. Drake, *Phys. Rev. Lett.* **59**, 1549 (1987).

¹⁹V. Korobov and A. Yelkhovsky, *Phys. Rev. Lett.* **87**, 193003 (2001).

²⁰A. J. Thakkar and T. Koga, *Phys. Rev. A* **50**, 854 (1994).

²¹P. W. Atkins, *Physical Chemistry*, 6th ed. (Oxford University Press, Oxford, 1998).

²²Computer code MAPLE, Waterloo Maple Inc., Waterloo, Ontario, Canada, see <http://www.maplesoft.com/>.

²³About the GMP library, see <http://swox.com/gmp/> and <http://www.cs.nyu.edu/exact/core/gmp/>.

²⁴See: <http://physics.nist.gov/cuu/Constants/>

²⁵J. H. Bartlett, Jr., *Phys. Rev.* **51**, 661 (1937).

²⁶T. H. Gronwall, *Phys. Rev.* **51**, 655 (1937).

²⁷V. A. Fock, *Izv. Akad. Nauk SSSR, Ser. Fiz.* **18**, 161 (1954).

²⁸J. E. Sansonetti and W. C. Martin, *J. Phys. Chem. Ref. Data* **34**, 1559 (2005).

²⁹W. C. Martin, *Phys. Rev. A* **36**, 3575 (1987).

³⁰W. C. Martin, *J. Phys. Chem. Ref. Data* **2**, 257 (1973).