

# Exact Theory Applied to the Lithium Atom

Hiroshi Nakatsuji\* and Hiroyuki Nakashima



Cite This: *J. Chem. Theory Comput.* 2024, 20, 8001–8009



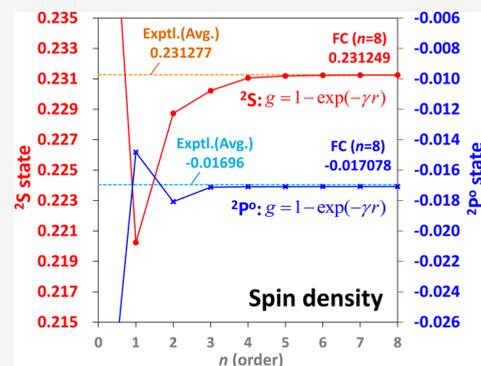
Read Online

ACCESS |

Metrics & More

Article Recommendations

**ABSTRACT:** The free complement (FC) theory for solving the scaled Schrödinger equation (SSE) was applied to the Li atom for calculating the exact wave functions, the energies, and the various properties of the ground doublet S and excited P states. The SSE is equivalent to the Schrödinger equation (SE) but does not have the divergence difficulty of the variational equation of the SE. Because the Li atom is a three-electron system, the variational exact FC calculations for solving the SSE are possible using the function  $g = 1 - \exp(-\gamma r)$  as the “correct” scaling function of the SSE. The “reasonable” scaling function  $g = r$  was also used as comparative calculations. We performed variational calculations to the order eight of the FC theory and could obtain essentially exact solutions of the SSE or SE with the “correct”  $g$  function of the FC theory. We report here the values of the exact energy, spin density, electron density, and electron–nuclear and electron–electron cusp values of the doublet S and P states. They agreed very well with the experimental values and the best theoretical values presented by Drake and collaborators. This is a simple example that the exact theory gives the exact solutions.



## 1. INTRODUCTION

For many years after the Schrödinger equation (SE)

$$(H - E)\psi = 0 \quad (1)$$

was established, the SE was thought not to be soluble. This was a big problem because the SE was believed to govern the world composed of atoms and molecules: if we can obtain the exact solutions of the SE, we can give exact predictions of the chemical phenomena. A reason for this difficulty lay in the divergence difficulty of the variational equation of the SE that occurs when we try to solve the SE exactly by using the variational principle. This divergence difficulty was solved in 2004 by one of the authors by introducing the scaled Schrödinger equation (SSE)<sup>1</sup> given by

$$g(H - E)\psi = 0 \quad (2)$$

where the positive function  $g$  was called the “scaling function”, which is the positive functions of the electron–nuclear and electron–electron distances,  $r_{iA}$  and  $r_{ij}$ , respectively, like

$$g = \sum_{i,A} g_{iA}(r_{iA}) + \sum_{i<j} g_{ij}(r_{ij}) \quad (3)$$

where  $i, j$  denote electrons and  $A, B$  denote nuclei. A solution of the SSE is written in a recursive formula as

$$\psi_n = [1 + C_n g(H - E_{n-1})]\psi_{n-1} \quad (4)$$

which is called the simplest iterative complement interaction (SICI) formula, where  $\psi_n$  and  $E_n$  represent the wave function and energy at the order  $n$  and  $C_n$  is a variational parameter at

order  $n$ . This equation shows that the exact solution of the SSE includes the scaling functions  $g$ , and therefore, the scaling function is very important for solving the SSE or SE efficiently.<sup>1</sup> In the above equations,  $H$  is the Hamiltonian of the atoms and molecules and is given by

$$H = -\sum_i \frac{1}{2} \Delta_i - \sum_A \frac{1}{2} \Delta_A - \sum_{i,A} \frac{Z_A}{r_{iA}} + \sum_{i<j} \frac{1}{r_{ij}} + \sum_{A<B} \frac{Z_A Z_B}{r_{AB}} \quad (5)$$

where  $Z_A$  is the nuclear charge of the atom  $A$ . We note that the Coulombic potential between charged electrons and nuclei diverges when the distances of the two charged particles become zero, which is the origin of the divergence of the variational equation of the SE associated with this Hamiltonian. In actual calculations, the SICI formula given in eq 4 includes many unnecessary terms. From the SICI formula, we select only the independent analytical functions  $\phi_i^{(n)}$  and their coefficients  $c_i^{(n)}$  from the  $n$ -th order formula and obtain the form

**Received:** July 9, 2024

**Revised:** August 21, 2024

**Accepted:** August 21, 2024

**Published:** September 3, 2024



$$\psi_n = \sum_I c_I^{(n)} \phi_I^{(n)} \quad (6)$$

which was referred to as the free ICI theory.<sup>1</sup> This theory was referred to later as the free complement (FC) theory because it is composed of the free complete-element functions that span the exact wave function. This theory produces wave functions that converge to the exact solutions. Actually, in many applications, we could get essentially exact solutions in the chemical kcal/mol accuracy at  $n$  being 2–4.<sup>1–15</sup>

Based on the above formalism of the FC theory, the construction of the exact quantum chemistry based on the SSE had been performed.<sup>2–15</sup> Because the theory is exact, its solutions can become exact as  $n$  increases. From such examples, we refer to the following two typical examples. One is the superaccurate solutions of the He atom: we could calculate the energy as accurate as over 40 digits from the decimal point.<sup>7,8</sup> Other clear examples for molecules were the calculations of the potential energy curves of the nine valence states of the Li<sub>2</sub> molecule.<sup>13</sup> The experimental and theoretical FC potential curves were beautifully overlapped with each other on the absolute energy diagrams to less than 1 kcal/mol over the observed regions of the potential curves. These were the prominent proofs of the correctness of the SSE and the FC theory built on the SSE. From eqs 4 and 6, we note the important role of the scaling function  $g$  in the course of building the exact solutions of the SSE or SE. There were many other examples of such agreements between our theoretical results and the experiments.<sup>3,5,6,11,12</sup>

In this article, we apply the FC theory variationally to the doublet ground <sup>2</sup>S and excited <sup>2</sup>P<sup>0</sup> states of the Li atom by solving the SSE for this atom. We calculate not only the energy but also the properties like the electron density and the spin density at the nucleus, the density at the electron–electron (e–e) coalescence, and the electron–nuclear (e–n) and e–e cusp values. The variational method is very powerful because it gives the energy correct to the second order of the errors included in the wave function. The variational application is straightforward for the exact theory, but it becomes difficult for general atoms and molecules because the integrals of the functions depending on the interelectron distance  $r_{ij}$  become difficult as the number of electrons increases. As a scaling function, we use the “correct-type”  $g$  function<sup>14,15</sup> given by

$$g = 1 - \exp(-\gamma r) \quad (7)$$

This  $g$  function shows a correct behavior in all regions of  $r$  for both  $r_{iA}$  and  $r_{ij}$  of the Hamiltonian given by eq 4. Moreover, because of the simple Slater-type dependence of this function, it is integrable for both  $r_{iA}$  and  $r_{ij}$ . For other correct-type functions,  $g = r/(r + 1/\gamma)$ ,  $g = Ei(-\gamma^{(1)}r - \gamma^{(2)}) - Ei(-\gamma^{(2)})$ ,  $g = \arctan(\gamma r)$ , and  $g = \tanh(\gamma r)$ , the integral evaluations for the two-electron parts are not well established. For comparison with other  $g$  functions, we also examined a “reasonable-type” ordinary  $g$  function given by

$$g = r \quad (8)$$

By comparing the SSE with the SE and examining the simplest ICI formula given by eq 4, one may notice how important is the scaling function in the exact theory for solving the SSE. For very small atoms or molecules, a special choice depending on the coordinate system may give the best choice.<sup>1,6,7</sup> However, for general atoms and molecules, the correct functions given above show the proper behaviors at the limiting points at  $r = 0$  and

infinity.<sup>14</sup> We have investigated the qualities of the correct scaling functions on the He atom for which all of them could be examined with the variational principle.<sup>15</sup> There, the performance of the exponential-type  $g$  function given by eq 7 was reasonably good, although not the best. However, because this function has a form similar to the 1s Slater orbital, it is integrable in the case when general Slater functions are integrable. This is a good feature of this  $g$  function.

For developing the exact theory, the variational theory is not necessarily the best choice because the analytical integration method is not yet fully developed for general atoms and molecules.<sup>16</sup> As can be clearly seen from eqs 1 and 2, the SE and the SSE are the *local equations* that do not include integrals in the formula. This suggests that local sampling would be a good way of solving these equations. Thus, we have proposed the local sampling method<sup>17</sup> for solving the SE and developed it for actual calculations for small atoms and molecules<sup>18</sup> with the use of the Metropolis sampling method.<sup>19</sup> However, the Metropolis sampling method introduced random fluctuation errors in the calculations, which are unsuitable, particularly for studying the continuous properties like the potential energy curves or surfaces of molecules. Therefore, we have developed the direct- or inverse-transformation sampling method<sup>20,21</sup> for use in the FC calculations of atoms and molecules.<sup>22</sup> We will use this direct (or inverse-transformation) local sampling method for FC calculations of the atoms and molecules for which the variational method is not directly applicable.

Li atom is the first system of the so-called many-electron system. Therefore, many studies<sup>23–57</sup> have been performed for the purposes of examining many-electron theories with this three-electron atom. First, the Hartree–Fock calculations of the Li atom were performed by Wilson<sup>23</sup> and Roothaan et al.<sup>24</sup> James and Coolidge first employed the Hylleraas functions including correlated  $r_{ij}$  terms for the Li atom<sup>25</sup> in 1936 and improved drastically the variational energy up to  $-7.476\,075$  au, which is higher by  $\Delta E = 1.246$  kcal/mol from the now-known exact energy  $-7.478\,060\,323$  au.<sup>40,41</sup> Thereafter, a variety of studies were performed with various theoretical methods to confirm their performances. They are the studies with the ordinary configuration interaction (CI) theories,<sup>26,27</sup> the multiconfiguration self-consistent-field (MCSCF) theory,<sup>28</sup> the Hylleraas<sup>29–42</sup> and the Hylleraas-CI theories,<sup>43–48</sup> the explicitly correlated Gaussian (ECG) theory,<sup>49–55</sup> the diffusion Monte Carlo (DMC) theory,<sup>56–58</sup> and our FC theory.<sup>12</sup> Also, highly accurate calculations with a huge number of basis functions and/or freedoms had been reported to pursue the lowest variational energies. For instance, highly accurate variational calculations of the <sup>2</sup>S ground states were reported by Pachucki et al.<sup>37,38</sup> and Drake et al.<sup>41</sup> with large Hylleraas basis functions.

The purpose of the present study is to give an extensive study of this atom not only for the energy but also for many other properties by using the correct scaling function given by eq 7 of the SSE that is valid for both analytical solutions and variational solutions differently from the original SE.

## 2. CONSTRUCTION OF THE FC WAVE FUNCTION FOR THE <sup>2</sup>S AND <sup>2</sup>P<sup>0</sup> STATES OF THE LI ATOM

The essentially exact wave functions for the <sup>2</sup>S and <sup>2</sup>P<sup>0</sup> states are prepared with the FC theory from the initial wave functions of both states with the standard procedure.<sup>1–22</sup> The initial wave function for the <sup>2</sup>S ground state was constructed using the two doublet spin functions as follows

**Table 1. Results of the FC Variational Calculations of the  $^2\text{S}$  Ground State of the Li Atom up to Order  $n = 8$  with a Correct-Type  $g$  Function:  $g_{iA} = 1 - \exp(-\gamma_{iA}r_{iA})$ ,  $g_{ij} = 1 - \exp(-\gamma_{ij}r_{ij})$** 

$n^a$	$M^b$	energy (a.u.)	$\Delta E$ (kcal/mol) <sup>c</sup>	electron density at the nucleus $\langle\delta(r_0)\rangle$	spin density at the nucleus $\langle\delta s(r_0)\rangle$	density at the e–e coalescence $\langle\delta(r_{ij})\rangle$	e–n cusp value	e–e cusp value
0	2	–7.434 881 080 5	27.095	13.150 479	0.258 407 0	0.774 129	–2.794 135	0.000 000
1	14	–7.476 142 895 3	1.203	13.691 021	0.220 236 8	0.564 551	–2.970 116	0.364 115
2	56	–7.477 797 775 8	0.165	13.821 545	0.228 731 4	0.555 471	–2.995 316	0.408 826
3	168	–7.478 035 484 3	0.015 6	13.836 472	0.230 221 7	0.547 449	–2.998 221	0.462 338
4	420	–7.478 055 755 4	0.002 87	13.841 503	0.231 061 8	0.545 956	–2.999 770	0.475 881
5	924	–7.478 059 327 7	0.000 625	13.842 368	0.231 193 7	0.544 977	–3.000 035	0.487 684
6	1848	–7.478 060 021 2	0.000 190	13.842 594	0.231 233 9	0.544 664	–3.000 097	0.492 333
7	3432	–7.478 060 227 2	0.000 060 7	13.842 639	0.231 245 1	0.544 484	–3.000 093	0.495 701
8	6006	–7.478 060 288 3	0.000 022 3	13.842 639	0.231 248 5	0.544 409	–3.000 073	0.497 344
exact by Drake et al. <sup>d</sup>		–7.478 060 323 9		13.842 543(53)	0.231 249 7	0.544 329 0(37)		
experiment or exact					0.231 3 <sup>e</sup> 0.231 254 0 <sup>f</sup>		–3.0	0.5

<sup>a</sup>Order of the FC theory. <sup>b</sup>Number of cfs (dimension). <sup>c</sup>Energy differences from the estimated exact energy by ref 41. <sup>d</sup>Best nonrelativistic variational calculation by ref 41. <sup>e</sup>Experimental value of  $\langle\delta s(r_0)\rangle$  from ref 66. <sup>f</sup>Experimental value of  $\langle\delta s(r_0)\rangle$  from ref 67.

$$\psi_0^{(2S)} = \psi_0^{(2S:\text{main})} + \psi_0^{(2S:\text{spin})} \quad (9)$$

with

$$\psi_0^{(2S:\text{main})} = A[(1s1s')(\alpha\beta - \beta\alpha) \cdot (2s)\alpha] \quad (10a)$$

$$\psi_0^{(2S:\text{spin})} = A[(1s1s'2s)((\alpha\beta + \beta\alpha)\alpha - 2\alpha\alpha\beta)] \quad (10b)$$

where  $A$  denotes the antisymmetrizer and  $\alpha$  and  $\beta$  are the up-spin and down-spin functions, respectively.  $\psi_0^{(2S:\text{main})}$  corresponds to the main configuration of the  $^2\text{S}$  state, i.e., 1s orbital is occupied by two electrons and 2s orbital by a single electron.  $\psi_0^{(2S:\text{spin})}$  corresponds to the other doublet spin function, which would be important for describing the spin correlations that are important for the spin densities at the nucleus. Similarly, the initial function for the  $^2\text{P}^0$  state is given by

$$\psi_0^{(2P^0)} = \psi_0^{(2P^0:\text{main})} + \psi_0^{(2P^0:\text{spin})} \quad (11)$$

with

$$\psi_0^{(2P^0:\text{main})} = A[(1s1s')(\alpha\beta - \beta\alpha) \cdot (2p_x)\alpha] \quad (12a)$$

$$\psi_0^{(2P^0:\text{spin})} = A[(1s1s'2p_x)((\alpha\beta + \beta\alpha)\alpha - 2\alpha\alpha\beta)] \quad (12b)$$

Each orbital was written by a simple Slater function as given by

$$1s = N_{1s}\exp(-\alpha_{1s}r)$$

$$1s' = N_{1s'}\exp(-\alpha_{1s'}r)$$

$$2s = N_{2s}r\exp(-\alpha_{2s}r)$$

$$\begin{aligned} 2p_x &= N_{2p_x}\exp(-\alpha_{2p_x}r), 2p_y \\ &= N_{2p_y}\exp(-\alpha_{2p_y}r), 2p_z \\ &= N_{2p_z}\exp(-\alpha_{2p_z}r) \end{aligned} \quad (13)$$

where  $N$  represents the normalization factor. The so-called in–out correlation was expressed with the double- $\zeta$  orbitals, which were necessary to write up the two independent spin eigenfunctions such as eqs 10a,b and 12a,b. For the orbital exponents, we employed the Slater rule given many years ago,<sup>59</sup>

i.e., 1s: 2.7, 2s = 2p: 0.65, and the in–out exponents were split by multiplying 1.15 and 0.85. Thus,  $(\alpha_{1s}, \alpha_{1s'}, \alpha_{2s}, \alpha_{2p}) = (3.105, 2.295, 0.65, 0.65)$ .

The reader may think that it would be better to use more sophisticated initial functions for faster convergence. In our experience, however, the simpler is better for the initial function. With simpler functions, the number of the functions produced by the FC theory at first order becomes smaller and so on. In other words, we want to use as many functions that are produced by the FC theory as possible. Therefore, we use as simple functions as possible for the initial guess functions. From our experiences, FC theory produces the exact wave function even from the minimal Slater functions; the labor of the calculations and the physical insight are easier than using more complex initial functions. The Gaussian functions are not adopted because they do not satisfy the cusp condition, which is a necessary condition of the exact wave function.

As the parameters e–n  $\gamma_{iA}$  and e–e  $\gamma_{ij}$  of the correct scaling function of eq 7, we used  $\gamma_{iA} = 0.3$  that is obtained from the exponent 2.7 of the 1s orbital and  $\gamma_{ij} = 0.5$  that corresponds to the e–e cusp value for the  $^2\text{S}$  state. For the  $^2\text{P}^0$  state, we used  $\gamma_{iA} = 0.1$ , which gave more accurate results than the case of 0.3.

### 3. VARIATIONAL CALCULATION OF THE EXACT WAVE FUNCTION OF THE LI ATOM USING THE EXPONENTIAL-TYPE SCALING FUNCTION

We apply the variational integration method for the correct-type scaling function of  $g = 1 - \exp(-\gamma r)$  of eq 7. The integral calculations with the scaling function of  $g = r$  of eq 8 were already discussed in ref 12. A key step is the evaluation of the fully exponential four-body integrands after expanding the  $1 - \exp(-\gamma r)$  terms, which are given by

$$\begin{aligned} \int_{n_1, n_2, n_3, m_1, m_2, m_3} &= \frac{1}{64\pi^3} \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 r_{23}^{n_1-1} r_{13}^{n_2-1} r_{12}^{n_3-1} r_1^{m_1-1} \\ & r_2^{m_2-1} r_3^{m_3-1} \cdot e^{-u_1 r_{23}} e^{-u_2 r_{13}} e^{-u_3 r_{12}} e^{-w_1 r_1} e^{-w_2 r_2} e^{-w_3 r_3} \end{aligned} \quad (14)$$

where  $n_1, n_2, n_3, m_1, m_2$ , and  $m_3$  are the non-negative integers and  $u_1, u_2, u_3, w_1, w_2$ , and  $w_3$  are the exponents originating from the Slater exponents in the initial functions and modified by the  $g$  function given by eq 7. Several closed-form integral methods to evaluate eq 14 had been provided in the literatures.<sup>37,39,60–63</sup> In

**Table 2. Results of the FC Variational Calculations of the  $^2S$  Ground State of the Li Atom up to Order  $n = 8$  with a Reasonable-Type  $g$  Function:  $g_{iA} = r_{iA}$ ,  $g_{ij} = r_{ij}$** 

$n^a$	$M^b$	energy (a.u.)	$\Delta E$ (kcal/mol) <sup>c</sup>	electron density at the nucleus $\langle \delta(r_0) \rangle$	spin density at the nucleus $\langle \delta s(r_0) \rangle$	density at the e–e coalescence $\langle \delta(r_{ij}) \rangle$	e–n cusp value	e–e cusp value
0	2	–7.434 881 080 5	27.095	13.150 479	0.258 407 0	0.774 129	–2.794 135	0.000 000
1	14	–7.472 488 497 8	3.496	13.650 184	0.228 824 4	0.600 355	–2.956 556	0.244 648
2	56	–7.476 301 982 2	1.103	13.791 818	0.224 950 9	0.567 050	–2.988 217	0.354 890
3	168	–7.477 386 694 9	0.423	13.823 365	0.226 939 1	0.555 398	–2.995 709	0.409 578
4	420	–7.477 804 396 1	0.161	13.834 477	0.228 801 6	0.550 358	–2.998 349	0.440 185
5	924	–7.477 965 977 4	0.059 2	13.838 993	0.230 074 4	0.547 870	–2.999 254	0.458 576
6	1848	–7.478 026 201 6	0.021 4	13.840 966	0.230 743 0	0.546 529	–2.999 617	0.470 279
7	3432	–7.478 047 884 7	0.007 81	13.841 778	0.231 022 3	0.545 755	–2.999 715	0.478 105
8	6006	–7.478 055 060 5	0.003 30	13.842 135	0.231 155 7	0.545 290	–2.999 758	0.483 418
exact by Drake et al. <sup>d</sup>		–7.478 060 323 9		13.842 543(53)	0.231 249 7	0.544 329 0(37)		
experiment or exact					0.231 3 <sup>e</sup> 0.231 254 0 <sup>f</sup>		–3.0	0.5

<sup>a</sup>Order of the FC theory. <sup>b</sup>Number of cfs (dimension). <sup>c</sup>Energy differences from the estimated exact energy by ref 41. <sup>d</sup>Best nonrelativistic variational calculation by ref 41. <sup>e</sup>Experimental value of  $\langle \delta s(r_0) \rangle$  from ref 66. <sup>f</sup>Experimental value of  $\langle \delta s(r_0) \rangle$  from ref 67.

**Table 3. Results of the FC Variational Calculations of the  $^2P^0$  State of the Li Atom up to Order  $n = 8$  with a Correct-Type  $g$  Function:  $g_{iA} = 1 - \exp(-\gamma_{iA}r_{iA})$ ,  $g_{ij} = 1 - \exp(-\gamma_{ij}r_{ij})$** 

$n^a$	$M^b$	energy (a.u.)	$\Delta E$ (kcal/mol) <sup>c</sup>	electron density at the nucleus $\langle \delta(r_0) \rangle$	spin density at the nucleus $\langle \delta s(r_0) \rangle$	density at the e–e coalescence $\langle \delta(r_{ij}) \rangle$	e–n cusp value	e–e cusp value
0	2	–7.361 508 600 9	30.527	12.967 984	–0.039 996 6	0.758 165	–2.791 751	0.000 000
1	14	–7.405 191 053 2	3.116	13.462 464	–0.014 825 1	0.553 169	–2.954 334	0.358 584
2	56	–7.409 606 649 8	0.345	13.645 459	–0.018 078 6	0.544 396	–2.991 340	0.405 976
3	168	–7.410 054 768 1	0.063 9	13.666 427	–0.017 125 1	0.535 873	–2.997 192	0.457 828
4	420	–7.410 145 171 1	0.007 13	13.674 385	–0.017 095 5	0.533 983	–2.999 667	0.475 115
5	924	–7.410 154 236 4	0.001 44	13.675 915	–0.017 085 7	0.532 972	–3.000 179	0.487 056
6	1848	–7.410 155 968 9	0.000 354	13.676 265	–0.017 082 1	0.532 622	–3.000 257	0.492 270
7	3432	–7.410 156 349 5	0.000 115	13.676 312	–0.017 078 6	0.532 434	–3.000 229	0.495 744
8	6006	–7.410 156 465 1	0.000 042 4	13.676 289	–0.017 078 2	0.532 356	–3.000 175	0.497 457
exact by Drake et al. <sup>d</sup>		–7.410 156 532 6		13.676 064(17)	–0.017 078 7	0.532 286 4(57)		
experiment or exact					–0.016 93 <sup>e</sup> –0.016 99 <sup>f</sup>		–3.0	0.5

<sup>a</sup>Order of the FC theory. <sup>b</sup>Number of cfs (dimension). <sup>c</sup>Energy differences from the estimated exact energy by ref 41. <sup>d</sup>Best nonrelativistic variational calculation by ref 41. <sup>e</sup>Experimental value of  $\langle \delta s(r_0) \rangle$  from refs 68–70. <sup>f</sup>Experimental value of  $\langle \delta s(r_0) \rangle$  from ref 71.

1987, Fromm and Hill<sup>60</sup> proposed a sophisticated formula for this integral, but it was mathematically difficult and not very appropriate for numerical computations. On the other hand, Harris formulated the recursive relations for eq 14 about non-negative integers  $n$  and  $m$  with their initiated integrals.<sup>61–63</sup> Especially, analytical closed-form evaluations of the basic integral of the recursion were very useful.<sup>61</sup> Pachucki et al. also proposed similar recurrence schemes with their clever ideas using the integration-by-parts method<sup>37,39</sup> and their method can also calculate the special cases that, for instance, some of the exponents in eq 14 become zero. Their closed-form integration formulas by both Harris et al. and Pachucki et al. enable performing highly precise evaluations even beyond the ordinary double precision. For the present FC variational calculations, we implemented our own integration codes based on the above integration formulas by Harris and/or Pachucki et al. We programmed a Python code using the multiple-precision arithmetic package, mpmath library,<sup>64</sup> constructed with the GNU multiprecision library,<sup>65</sup> and the present FC variational

calculations were performed with setting the precision more than 64 significant digits.

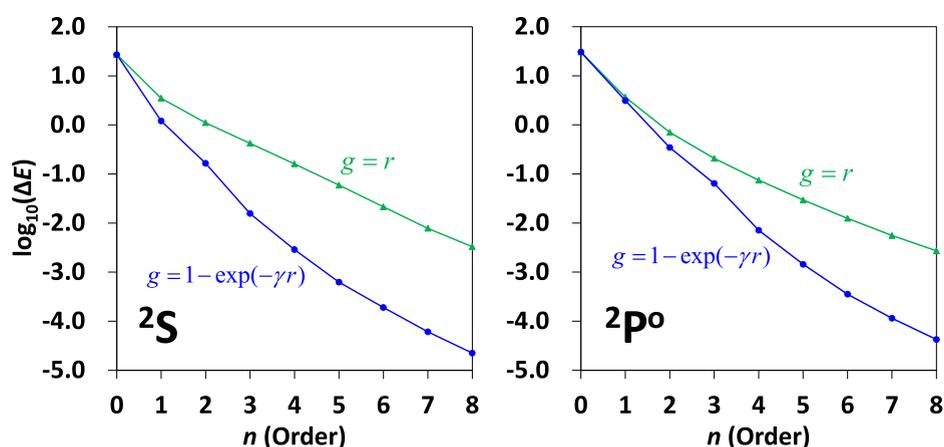
#### 4. VARIATIONAL FC RESULTS FOR THE $^2S$ AND $^2P^0$ STATES OF THE LI ATOM

We give here the results of the variational calculations from the initial stage to the order  $n = 8$  of FC theory. Tables 1 and 2 show the results for the  $^2S$  state obtained by using, respectively, the “correct-type” scaling function given by eq 7 and the “reasonable-type” scaling function given by eq 8 for both electron–nuclear and electron–electron functions. Tables 3 and 4 show the results for the  $^2P^0$  state obtained by using, respectively, the “correct-type” scaling function and the “reasonable-type” scaling function for both electron–nuclear and electron–electron functions. We calculated the energy, the energy difference from the known exact energy, electron density at the nucleus, spin density at the nucleus, the density at the e–e coalescence, the electron–nucleus cusp value whose exact value is minus the nuclear charge,  $-3$ , and the electron–electron cusp value whose exact value is  $0.5$ . We compare the present

**Table 4.** Results of the FC Variational Calculations of the  $^2P^0$  State of the Li Atom up to Order  $n = 8$  with a Reasonable-Type  $g$  Function:  $g_{iA} = r_{iA}$ ,  $g_{ij} = r_{ij}$

$n^a$	$M^b$	energy (a.u.)	$\Delta E$ (kcal/- mol) <sup>c</sup>	electron density at the nucleus $\langle \delta(r_0) \rangle$	spin density at the nucleus $\langle \delta s(r_0) \rangle$	density at the e–e coalescence $\langle \delta(r_{ij}) \rangle$	e–n cusp value	e–e cusp value
0	2	–7.361 508 600 9	30.527	12.967 984	–0.039 996 7	0.758 165	–2.791 751	0.000 000
1	14	–7.404 320 475 0	3.662	13.463 628	–0.016 379 7	0.588 819	–2.951 945	0.241 478
2	56	–7.409 031 772 0	0.706	13.622 261	–0.018 366 9	0.556 204	–2.985 633	0.350 916
3	168	–7.409 825 499 4	0.208	13.660 701	–0.017 402 5	0.543 840	–2.995 511	0.407 399
4	420	–7.410 037 604 1	0.074 6	13.670 766	–0.017 053 1	0.538 537	–2.998 290	0.438 964
5	924	–7.410 109 500 6	0.029 5	13.674 078	–0.017 172 7	0.535 915	–2.999 306	0.457 919
6	1848	–7.410 136 729 1	0.012 4	13.675 194	–0.017 110 1	0.534 522	–2.999 615	0.469 918
7	3432	–7.410 147 669 6	0.005 56	13.675 632	–0.017 043 4	0.533 729	–2.999 721	0.477 863
8	6006	–7.410 152 213 5	0.002 71	13.675 827	–0.017 058 1	0.533 251	–2.999 757	0.483 308
exact by Drake et al. <sup>d</sup>		–7.410 156 532 6		13.676 064(17)	–0.017 078 7	0.532 286 4(57)		
experiment or exact					–0.016 93 <sup>e</sup> –0.016 99 <sup>f</sup>		–3.0	0.5

<sup>a</sup>Order of the FC theory. <sup>b</sup>Number of cfs (dimension). <sup>c</sup>Energy differences from the estimated exact energy by ref 41. <sup>d</sup>Best nonrelativistic variational calculation by ref 41. <sup>e</sup>Experimental value of  $\langle \delta s(r_0) \rangle$  from refs 68–70. <sup>f</sup>Experimental value of  $\langle \delta s(r_0) \rangle$  from ref 71.



**Figure 1.** Convergence speeds of  $\Delta E$  (kcal/mol) as  $\log_{10}(\Delta E)$  in the FC variational calculations with  $g_{iA} = r_{iA}$ ,  $g_{ij} = r_{ij}$  and  $g_{iA} = 1 - \exp(-\gamma r_{iA})$ ,  $g_{ij} = 1 - \exp(-\gamma r_{ij})$  for the (left)  $^2S$  and (right)  $^2P^0$  states of the Li atom.

calculated values with the experimental values or the known exact values. The experimental values of the spin density at the nucleus are due to Kusch and Taub<sup>66</sup> in 1949 and Beckmann, Böklen, and Elke<sup>67</sup> in 1974 for the  $^2S$  state, and by Brog, Eck, and Wieder<sup>68,69</sup> in 1967, by Lyons and Das<sup>70</sup> in 1970, and by Orth, Ackermann, and Otten<sup>71</sup> in 1975 for the  $^2P^0$  state. In 2012, Drake and others<sup>41</sup> performed highly accurate calculations of this atom for both  $^2S$  ground and  $^2P^0$  excited states and, therefore, we also compare the present results to their highly accurate results.

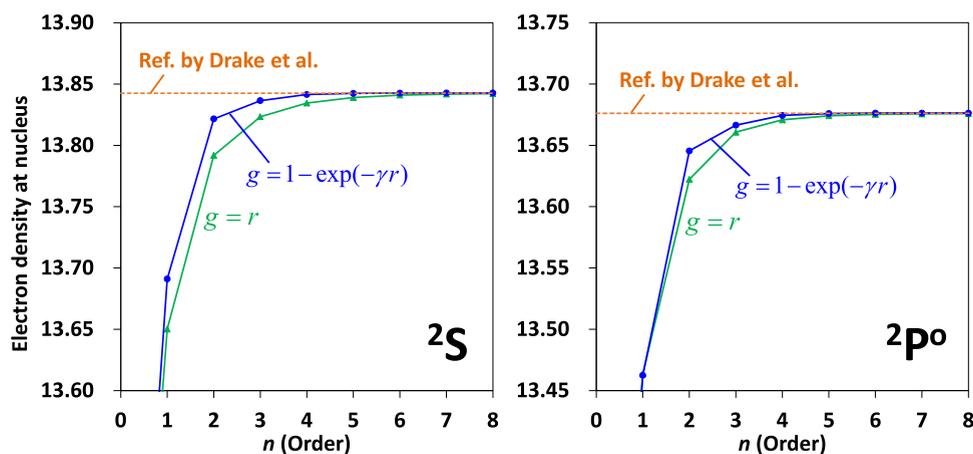
First, the energy was quickly improved as the order of the FC theory increases when we use the correct  $g$  function of  $g = 1 - \exp(-\gamma r)$  for both  $^2S$  and  $^2P^0$  states (Tables 1 and 3, respectively). However, when we used the  $g = r$  function, this improvement became much worse (Tables 2 and 4). In Table 1 ( $^2S$ , correct  $g$ ), the  $\Delta E$  value at  $n = 8$  has four zeros after the period, but in Table 2 ( $^2S$ ,  $g = r$ ), it has only two zeros after the period. The same behaviors appeared for the  $^2P^0$  state in Tables 3 and 4. For the properties, Drake et al. gave essentially exact results. When we compare the present results with those of Drake's, the results of Tables 1 and 3, which are both with the correct  $g$  functions, agree well with each other. However, the agreement becomes much worse when we refer to the results of

Tables 2 and 4, which are the results with the  $g = r$  function. The same trends were also seen for the e–n and e–e cusp values. Although the correct  $g$  function gives almost the exact cusp values at  $n = 8$  for both the  $^2S$  and  $^2P^0$  states, the  $g = r$  function gives poorer results. Thus, the correct  $g$  function gives much better results than the reasonable  $g = r$  function not only for the energy but also for all of the properties calculated here.

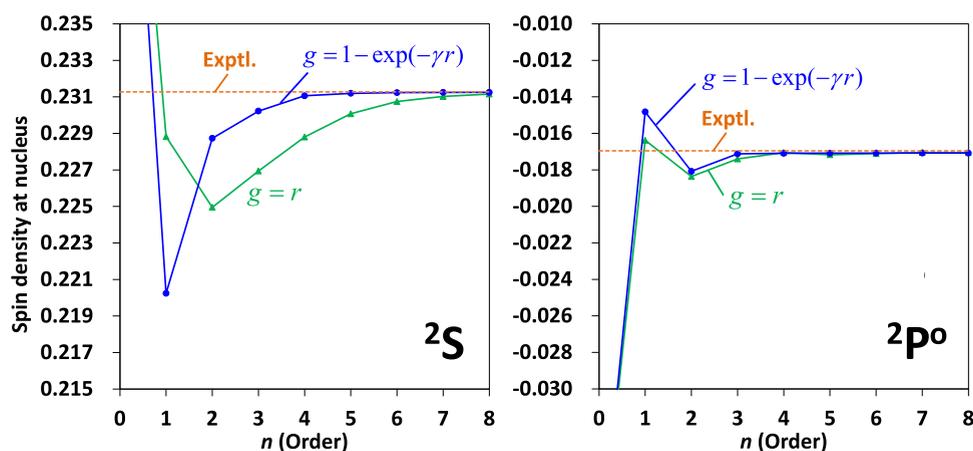
An interesting observation is seen for the  $^2P^0$  state with respect to the spin density at the nucleus. The present value is  $-0.017078$ , but the experimental values were  $-0.01693$ <sup>68–70</sup> and  $-0.01699$ .<sup>71</sup> Which are correct? Drake et al. gave the result  $-0.017078$ , which completely agrees with our theoretical result. For the  $^2S$  state, the present result for the spin density with the correct  $g$  function is 0.231248, Drake's result is 0.231250, and the experimental values were 0.2313<sup>66</sup> and 0.2312540.<sup>67</sup> These results seem to support the theoretical results.

## 5. CONVERGENCE BEHAVIORS OF THE ENERGIES AND PROPERTIES OF THE $^2S$ AND $^2P^0$ STATES OF THE LI ATOM TOWARD THE EXACT LEVEL

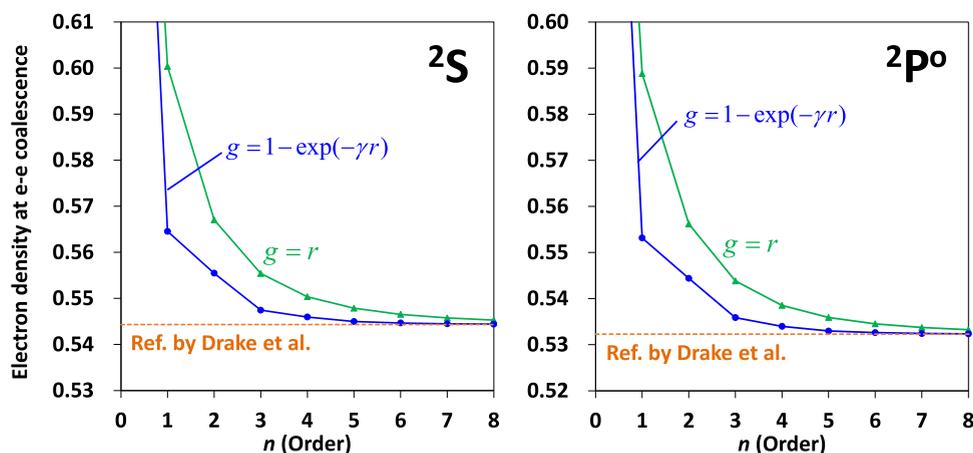
Although the above discussions on the calculated results were based only on the results of the highest order 8 of the FC



**Figure 2.** Convergence behaviors of the electron densities at nucleus:  $\langle\delta(r_0)\rangle$  in the FC variational calculations with  $g_{iA} = r_{iA}$ ,  $g_{ij} = r_{ij}$  and  $g_{iA} = 1 - \exp(-\gamma_{iA}r_{iA})$ ,  $g_{ij} = 1 - \exp(-\gamma_{ij}r_{ij})$  for the (left)  $^2S$  and (right)  $^2P^0$  states of the Li atom, compared to the reference values.<sup>41</sup>



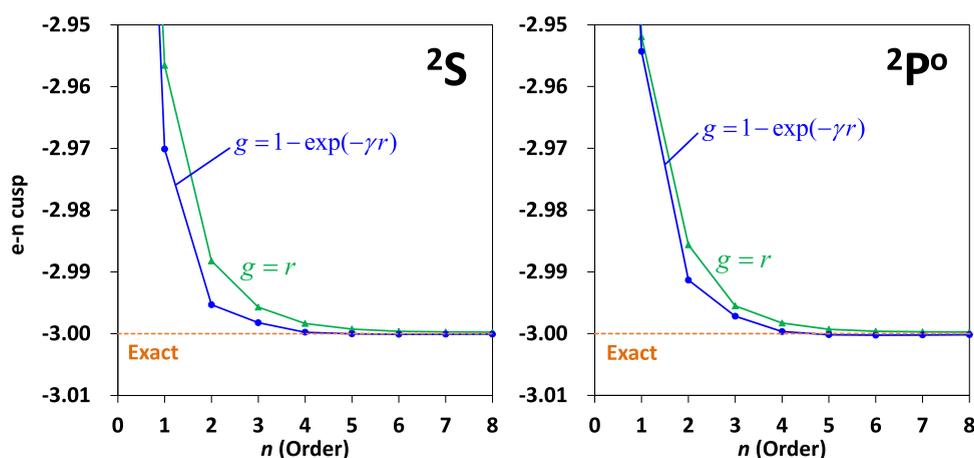
**Figure 3.** Convergence behaviors of the spin densities at nucleus:  $\langle\delta s(r_0)\rangle$  in the FC variational calculations with  $g_{iA} = r_{iA}$ ,  $g_{ij} = r_{ij}$  and  $g_{iA} = 1 - \exp(-\gamma_{iA}r_{iA})$ ,  $g_{ij} = 1 - \exp(-\gamma_{ij}r_{ij})$  for the (left)  $^2S$  and (right)  $^2P^0$  states of the Li atom, compared to the experimental values averaged from refs 66 and 67 for  $^2S$  and averaged from refs 68–71 for  $^2P^0$ .



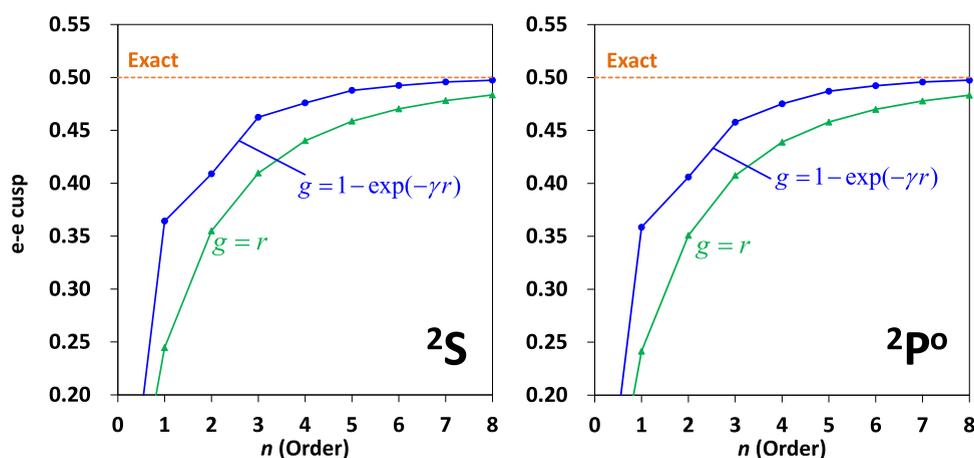
**Figure 4.** Convergence behaviors of the electron densities at the e–e coalescences:  $\langle\delta(r_{ij})\rangle$  in the FC variational calculations with  $g_{iA} = r_{iA}$ ,  $g_{ij} = r_{ij}$  and  $g_{iA} = 1 - \exp(-\gamma_{iA}r_{iA})$ ,  $g_{ij} = 1 - \exp(-\gamma_{ij}r_{ij})$  for the (left)  $^2S$  and (right)  $^2P^0$  states of the Li atom, compared to the reference values.<sup>41</sup>

calculations, the converging behaviors with increasing the order  $n$  of the FC theory toward the exact ones were different for different properties. Such a difference is seen most easily by plotting the value against the order  $n$ . Figures 1–6 show such behaviors for  $\Delta E$ , electron density at the nucleus, spin density at the nucleus, and density at the e–e coalescence, e– $n$  cusp value,

and e–e cusp value, respectively. The left and right curves of each figure correspond to the  $^2S$  and  $^2P^0$  states, respectively, and the blue and green curves show the results of the “correct”  $g$  function,  $g = 1 - \exp(-\gamma r)$ , and the “reasonable” one  $r$ . Between them, we are interested only in the blue curve due to the “correct”  $g$  function,  $g = 1 - \exp(-\gamma r)$ .



**Figure 5.** Convergence behaviors of the e–n cusp values in the FC variational calculations with  $g_{iA} = r_{iA}$ ,  $g_{ij} = r_{ij}$  and  $g_{iA} = 1 - \exp(-\gamma_i r_{iA})$ ,  $g_{ij} = 1 - \exp(-\gamma_{ij} r_{ij})$  for the (left)  $^2S$  and (right)  $^2P^0$  states of the Li atom, compared to the exact value, i.e.,  $-3.0$ .



**Figure 6.** Convergence behaviors of the e–e cusp values in the FC variational calculations with  $g_{iA} = r_{iA}$ ,  $g_{ij} = r_{ij}$  and  $g_{iA} = 1 - \exp(-\gamma_i r_{iA})$ ,  $g_{ij} = 1 - \exp(-\gamma_{ij} r_{ij})$  for the (left)  $^2S$  and (right)  $^2P^0$  states of the Li atom, compared to the exact value, i.e.,  $0.5$ .

Figure 1 shows the plot of the  $\log_{10}(\Delta E)$  against order  $n$ . Even though this is a log plot, the energy converges much more rapidly with the function  $g = 1 - \exp(-\gamma r)$  than with  $g = r$  for both the  $^2S$  and  $^2P^0$  states. At order 8, the former  $g$  function gives 2 orders of magnitude quicker convergence than the latter. Figure 2 shows the convergence behavior of the electron density at the nucleus. With the blue correct function, the electron density converges well at order 4 for the  $^2S$  and  $^2P^0$  states. Figure 3 shows the convergence behavior of the spin density at the nucleus, which is an interesting property, reflecting the spin correlations in atoms and molecules. From order 2, both  $g$  functions start the convergence from below. With the more reliable blue curves, the spin density almost converges at order 5 for the  $^2S$  state and at order 3 for the  $^2P^0$  state, the latter converging slightly below the experimental value, suggesting the examination of the other effect like the relativistic effect on the theoretical side or the experimental value itself. Figure 4 shows the behavior for the electron density at the e–e coalescence. Again, the blue curves show much quicker convergence in comparison to the green curves. With the blue curve, the electron densities almost converge at order 6 for both the  $^2S$  and  $^2P^0$  states. Figure 5 shows the convergence behaviors of the e–n cusp values whose exact value is  $-3$  (minus the nuclear charge) for both the  $^2S$  and  $^2P^0$  states. The blue curves converge essentially at order 4 for both states. Figure 6 shows the convergence behaviors of the

e–e cusp value. Because this is a two-electron property, the convergence is slow for both states. Even with the correct  $g$  function (blue curve), the FC theory gave an almost converged value of  $0.5$  at order 8 for both states.

From Figures 1–6, we see that to perform reliable prediction, we need the “correct”  $g$  function, and even with it, we need calculations higher than the order 3 or 4 for the one-electron properties, but for the two-electron property, which is only the e–e-cusp value here, we need more than the order 8 of the present theory. The convergence speed with the scaling function  $g = r$  was very slow, and therefore, we recommend using the “correct”  $g$  function,  $g = 1 - \exp(-\gamma r)$ , or other correct  $g$  functions given under eq 7.

## 6. CONCLUDING REMARKS

In the previous paper,<sup>15</sup> we examined the performances of the various correct  $g$  functions for the two-electron He atom on the basis of the variational principle. For the three-electron Li atom, the evaluation of the analytical integrals for the functions including two-electron scaling functions becomes feasible only for the exponential-type  $g$  function given by eq 7. So, we could examine the role of the “correct” scaling function only for this  $g$  function. However, even so, we could show the powerful role of the correct scaling function in contrast to the ordinary “reasonable” function  $r$ . For the  $^2S$  and  $^2P^0$  states of the Li

atom, the convergence of the energy to the exact one with the correct  $g$  function was already 2 orders of magnitude quicker at order 8 of the FC theory than that of the reasonable function  $r$ , as seen from Tables 1 and 2 for the  $^2S$  state and from Tables 3 and 4 for the  $^2P^0$  state. This is also seen in Figure 1. This clearly shows that the theoretical “correct” nature of the  $g$  function is very important in actual computational situations.

Such an efficiency of the correct  $g$  function over the function  $r$  was also seen for the other properties of the Li atom in both  $^2S$  and  $^2P^0$  states. A remarkable situation was seen for the spin density at the nucleus of the  $^2P^0$  state of the Li atom. At order 8 of the FC theory with the correct  $g$  function, the present calculated value of the spin density at the nucleus,  $-0.0170782$ , became almost identical to the value  $-0.0170787$  obtained by Drake et al. with their highly accurate calculations.<sup>41</sup> On the other hand, the experimental values<sup>68–71</sup> reported in 1967 and 1970 and 1975 as shown in Table 3 were  $-0.01693$  and  $-0.1699$ . Some detailed examination seems to be necessary for both the experimental and theoretical sides. We will check the relativistic effects, though it might be small for this light atom.

## AUTHOR INFORMATION

### Corresponding Author

Hiroshi Nakatsuji – Quantum Chemistry Research Institute, Kyoto 606-8305, Japan; [orcid.org/0000-0002-8162-3220](https://orcid.org/0000-0002-8162-3220); Email: [h.nakatsuji@qcri.or.jp](mailto:h.nakatsuji@qcri.or.jp)

### Author

Hiroyuki Nakashima – Quantum Chemistry Research Institute, Kyoto 606-8305, Japan; [orcid.org/0000-0002-3758-5159](https://orcid.org/0000-0002-3758-5159)

Complete contact information is available at: <https://pubs.acs.org/10.1021/acs.jctc.4c00884>

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors acknowledge the computer centers of the Research Center for Computational Science in the Institute for Molecular Science (IMS), Okazaki, Japan, for huge supports and encouragements given to our research project (Project: 23-IMS-C011). In particular, we would like to appreciate Prof. Masahiro Ehara and Dr. Motoshi Kamiya for their generous and technical supports in using their superparallel machines efficiently. This work was also supported by JSPS KAKENHI grant numbers 22H02045 and 23H01930.

## REFERENCES

- (1) Nakatsuji, H. Scaled Schrödinger equation and the exact wave function. *Phys. Rev. Lett.* **2004**, *93*, No. 030403.
- (2) Nakatsuji, H. General Method of Solving the Schrödinger Equation of Atoms and Molecules. *Phys. Rev. A* **2005**, *72*, No. 062110.
- (3) Nakatsuji, H. Discovery of a general method of solving the Schrödinger and Dirac equations that opens a way to accurately predictive quantum chemistry. *Acc. Chem. Res.* **2012**, *45*, 1480–1490.
- (4) Nakatsuji, H.; Nakashima, H. Analytically Solving Relativistic Dirac-Coulomb Equation for Atoms and Molecules. *Phys. Rev. Lett.* **2005**, *95*, No. 050407.
- (5) Nakatsuji, H.; Ehara, M. Iterative CI General Singles and Doubles (ICIGSD) Method for Calculating the Exact Wave Functions of the Ground and Excited States of Molecules. *J. Chem. Phys.* **2005**, *122*, No. 194108.

(6) Kurokawa, Y.; Nakashima, H.; Nakatsuji, H. Free ICI (Iterative Complement Interaction) Calculations of Hydrogen Molecule. *Phys. Rev. A* **2005**, *72*, No. 062502.

(7) Nakashima, H.; Nakatsuji, H. Solving the Schrödinger equation for helium atom and its isoelectronic ions with the free iterative complement interaction (ICI) method. *J. Chem. Phys.* **2007**, *127*, No. 224104.

(8) Kurokawa, Y. I.; Nakashima, H.; Nakatsuji, H. Solving the Schrödinger equation of helium and its isoelectronic ions with the exponential integral (Ei) function in the free iterative complement interaction method. *Phys. Chem. Phys.* **2008**, *10*, 4486–4494.

(9) Nakatsuji, H.; Nakashima, H. Solving the Schrödinger equation of molecules by relaxing the antisymmetry rule: Inter-exchange theory. *J. Chem. Phys.* **2015**, *142*, No. 194101.

(10) Nakatsuji, H.; Nakashima, H.; Kurokawa, Y. I. Solving the Schrödinger equation of atoms and molecules: Chemical-formula theory, free-complement chemical-formula theory, and intermediate variational theory. *J. Chem. Phys.* **2018**, *149*, No. 114105.

(11) Nakatsuji, H.; Nakashima, H.; Kurokawa, Y. I. Solving the Schrödinger equation of atoms and molecules with the free-complement chemical-formula theory: First-row atoms and small molecules. *J. Chem. Phys.* **2018**, *149*, No. 114106.

(12) Nakatsuji, H.; Nakashima, H. Solving the Schrödinger equation with the free-complement chemical-formula theory. Variational study of the ground and excited states of Be and Li atoms. *J. Chem. Phys.* **2019**, *150*, No. 044105.

(13) Nakatsuji, H.; Nakashima, H. Potential curves of the lower nine states of  $Li_2$  molecule: Accurate calculations with the free complement theory and the comparisons with the SAC/SAC-CI results. *J. Chem. Phys.* **2022**, *157*, No. 094109.

(14) Nakatsuji, H.; Nakashima, H.; Kurokawa, Y. I. Accurate scaling functions of the scaled Schrödinger equation. *J. Chem. Phys.* **2022**, *156*, No. 014113.

(15) Nakatsuji, H.; Nakashima, H. Accurate scaling functions of the scaled Schrödinger equation. II. Variational Examination of the correct scaling functions with the Free Complement theory applied to the helium atom. *J. Chem. Theory Comput.* **2024**, *20*, 3749–3765.

(16) Hammond, B. L.; Lester, W. A., Jr.; Reynolds, P. J. *Monte Carlo Methods in Ab Initio Quantum Chemistry*; World Scientific: Singapore, 1994.

(17) Nakatsuji, H.; Nakashima, H.; Kurokawa, Y.; Ishikawa, A. Solving the Schrödinger Equation of Atoms and Molecules without Analytical Integration Based on the Free Iterative-Complement-Interaction Wave Function. *Phys. Rev. Lett.* **2007**, *99*, No. 240402.

(18) Nakatsuji, H.; Nakashima, H. Free-complement local-Schrödinger-equation method for solving the Schrödinger equation of atoms and molecules: Basic theories and features. *J. Chem. Phys.* **2015**, *142*, No. 084117.

(19) Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. Equation of state calculations by fast computing machines. *J. Chem. Phys.* **1953**, *21*, 1087–1092.

(20) Tsusuda, T. *Monte Carlo Method and Simulation*; BaiFuKan: Tokyo, 1995.

(21) *Non-Uniform Random Variate Generation*; Devroye, L., Ed.; Springer: New York, NY, 1986.

(22) Nakatsuji, H.; Nakashima, H. Direct local sampling method for solving the Schrödinger equation with the free complement - local Schrödinger equation theory. *Chem. Phys. Lett.* **2022**, *806*, No. 140002.

(23) Wilson, E. B., Jr. Wave functions for the ground state of lithium and three-electron ions. *J. Chem. Phys.* **1933**, *1*, 210–218.

(24) Roothaan, C. C. J.; Sachs, L. M.; Weiss, A. W. Analytical self-consistent field functions for the atomic configurations  $1s^2$ ,  $1s^2 2s$ , and  $1s^2 2s^2$ . *Rev. Mod. Phys.* **1960**, *32*, No. 186.

(25) James, H. M.; Coolidge, A. S. On the ground state of lithium. *Phys. Rev.* **1936**, *49*, No. 688.

(26) Chung, K. T. Ionization potential of the lithiumlike  $1s^2 2s$  states from lithium to neon. *Phys. Rev. A* **1991**, *44*, No. 5421.

- (27) Jitrik, O.; Bunge, C. F. Atomic configuration interaction and studies of He, Li, Be, and Ne ground states. *Phys. Rev. A* **1997**, *56*, No. 2614.
- (28) Tong, M.; Jönsson, P.; Fischer, C. F. Convergence studies of atomic properties from variational methods: total energy, ionization energy, specific mass shift, and hyperfine parameters for Li. *Phys. Scr.* **1993**, *48*, No. 446.
- (29) Larsson, S. Calculations on the  $^2S$  ground state of the lithium atom using wave functions of Hylleraas type. *Phys. Rev.* **1968**, *169*, No. 49.
- (30) Kleindienst, H.; Beutner, S. The influence of linked correlation terms for the Li ground state. *Chem. Phys. Lett.* **1989**, *164*, 291–293.
- (31) King, F. W. Lower bound for the nonrelativistic ground state energy of the lithium atom. *J. Chem. Phys.* **1995**, *102*, 8053–8058.
- (32) Yan, Z.-C.; Drake, G. W. F. Eigenvalues and expectation values for the  $1s^2 2s^2 S$ ,  $1s^2 2p^2 P$ , and  $1s^2 3d^2 D$  states of lithium. *Phys. Rev. A* **1995**, *52*, No. 3711.
- (33) Yan, Z.-C.; Tambasco, M.; Drake, G. W. F. Energies and oscillator strengths for lithiumlike ions. *Phys. Rev. A* **1998**, *57*, No. 1652.
- (34) Puchalski, M.; Pachucki, K. Ground-state wave function and energy of the lithium atom. *Phys. Rev. A* **2006**, *73*, No. 022503.
- (35) Yan, Z.-C.; Nörtershäuser, W.; Drake, G. W. F. High precision atomic theory for Li and  $Be^+$ : QED shifts and isotope shifts. *Phys. Rev. Lett.* **2008**, *100*, No. 243002.
- (36) Puchalski, M.; Pachucki, K. Relativistic, QED, and finite nuclear mass corrections for low-lying states of Li and  $Be^+$ . *Phys. Rev. A* **2008**, *78*, No. 052511.
- (37) Puchalski, M.; Kędziera, D.; Pachucki, K. Ground state of Li and  $Be^+$  using explicitly correlated functions. *Phys. Rev. A* **2009**, *80*, No. 032521.
- (38) Puchalski, M.; Kędziera, D.; Pachucki, K. Ionization potential for excited S states of the lithium atom. *Phys. Rev. A* **2010**, *82*, No. 062509.
- (39) Puchalski, M.; Pachucki, K. Applications of four-body exponentially correlated functions. *Phys. Rev. A* **2010**, *81*, No. 052505.
- (40) Wang, L. M.; Yan, Z.-C.; Qiao, H. X.; Drake, G. W. F. Variational upper bounds for low-lying states of lithium. *Phys. Rev. A* **2011**, *83*, No. 034503.
- (41) Wang, L. M.; Yan, Z.-C.; Qiao, H. X.; Drake, G. W. F. Variational energies and the Fermi contact term for the low-lying states of lithium: Basis-set completeness. *Phys. Rev. A* **2012**, *85*, No. 052513.
- (42) Wang, L. M.; Li, C.; Yan, Z.-C.; Drake, G. W. F. Isotope shifts and transition frequencies for the S and P states of lithium: Bethe logarithms and second-order relativistic recoil. *Phys. Rev. A* **2017**, *95*, No. 032504.
- (43) Sims, J. S.; Hagstrom, S. A. Combined configuration-interaction-Hylleraas studies of atomic states. III. The four lowest  $^2S$  and four lowest  $^2P$  states of lithium. *Phys. Rev. A* **1975**, *11*, No. 418.
- (44) Pipin, J.; Bishop, D. M. Accurate variational calculations of energies of the  $2^2S$ ,  $2^2P$ , and  $3^2D$  states and the dipole, quadrupole, and dipole-quadrupole polarizabilities and hyperpolarizability of the lithium atom. *Phys. Rev. A* **1992**, *45*, No. 2736.
- (45) Lüchow, A.; Kleindienst, H. An efficient basis selection procedure for the reduction of the dimension in large Hylleraas-CI calculations. *Chem. Phys. Lett.* **1992**, *197*, 105–107.
- (46) Pestka, G.; Woźnicki, W. Hylleraas-type calculations for lithium. *Chem. Phys. Lett.* **1996**, *255*, 281–286.
- (47) Sims, J. S.; Hagstrom, S. A. Hylleraas-configuration-interaction study of the  $2^2S$  ground state of neutral lithium and the first five excited  $^2S$  states. *Phys. Rev. A* **2009**, *80*, No. 052507.
- (48) Ruiz, M. B.; Margraf, J. T.; Frolov, A. M. Hylleraas-configuration-interaction analysis of the low-lying states in the three-electron Li atom and  $Be^+$  ion. *Phys. Rev. A* **2013**, *88*, No. 012505.
- (49) Komasa, J. Dipole and quadrupole polarizabilities and shielding factors of beryllium from exponentially correlated Gaussian functions. *Phys. Rev. A* **2001**, *65*, No. 012506.
- (50) Bubin, S.; Komasa, J.; Stanke, M.; Adamowicz, L. Isotope shift in the electron affinity of lithium. *J. Chem. Phys.* **2009**, *131*, No. 234112.
- (51) Bubin, S.; Adamowicz, L. Prediction of  $^2S$  Rydberg energy levels of  $^6Li$  and  $^7Li$  based on quantum-mechanical calculations performed with explicitly correlated Gaussian functions. *Phys. Rev. A* **2013**, *87*, No. 042510.
- (52) Strasburger, K. High angular momentum states of lithium atom, studied with symmetry-projected explicitly correlated Gaussian lobe functions. *J. Chem. Phys.* **2014**, *141*, No. 044104.
- (53) Bralin, A.; Bubin, S.; Stanke, M.; Adamowicz, L. The  $^2S$  Rydberg series of the lithium atom. Calculations with all-electron explicitly correlated Gaussian functions. *Chem. Phys. Lett.* **2019**, *730*, 497–505.
- (54) Nasiri, S.; Liu, J.; Bubin, S.; Stanke, M.; Kędziorski, A.; Adamowicz, L. Oscillator strengths and interstate transition energies involving  $^2S$  and  $^2P$  states of the Li atom. *At. Data Nucl. Data Tables* **2023**, *149*, No. 101559.
- (55) Ronto, M.; Jeszenszki, P.; Mátyus, E.; Pollak, E. Lower bounds on par with upper bounds for few-electron atomic energies. *Phys. Rev. A* **2023**, *107*, No. 012204.
- (56) Brown, M. D.; Trail, J. R.; Lopez Rios, P.; Needs, R. J. Energies of the first row atoms from quantum Monte Carlo. *J. Chem. Phys.* **2007**, *126*, No. 224110.
- (57) Seth, P.; Rios, P. L.; Needs, R. J. Quantum Monte Carlo study of the first-row atoms and ions. *J. Chem. Phys.* **2011**, *134*, No. 084105.
- (58) Nasiri, S.; Zahedi, M. Quantum Monte Carlo simulations using Slater-Jastrow-backflow wave function. *Comput. Theor. Chem.* **2020**, *1189*, No. 112978.
- (59) Slater, J. C. Atomic Shielding Constants. *Phys. Rev.* **1930**, *36*, No. 57.
- (60) Fromm, D. M.; Hill, R. N. Analytic evaluation of three-electron integrals. *Phys. Rev. A* **1987**, *36*, No. 1013.
- (61) Harris, F. E. Analytic evaluation of three-electron atomic integrals with Slater wave functions. *Phys. Rev. A* **1997**, *55*, No. 1820.
- (62) Harris, F. E.; Frolov, A. M.; Smith, V. H. Exponential variational expansion in relative coordinates for highly accurate bound state calculations in four-body systems. *J. Chem. Phys.* **2003**, *119*, 8833–8841.
- (63) Harris, F. E. Recurrence formulas for fully exponentially correlated four-body wave functions. *Phys. Rev. A* **2009**, *79*, No. 032517.
- (64) <https://mpmath.org/> (accessed June 1, 2024).
- (65) <https://gmpmath.org/> (accessed June 1, 2024).
- (66) Kusch, P.; Taub, H. On the  $g_j$  values of the alkali atoms. *Phys. Rev.* **1949**, *75*, No. 1477.
- (67) Beckmann, A.; Böklen, K. D.; Elke, D. Precision measurements of the nuclear magnetic dipole moments of  $^6Li$ ,  $^7Li$ ,  $^{23}Na$ ,  $^{39}K$  and  $^{41}K$ . *Z. Phys.* **1974**, *270*, 173–186.
- (68) Brog, K. C.; Eck, T. G.; Wieder, H. Fine and hyperfine structure of the  $2^2P$  term of  $Li^6$  and  $Li^7$ . *Phys. Rev.* **1967**, *153*, No. 91.
- (69) Wieder, H.; Eck, T. G. "Anticrossing" signals in resonance Fluorescence. *Phys. Rev.* **1967**, *153*, No. 103.
- (70) Lyons, J. D.; Das, T. P. Theoretical analysis of level crossing in a  $^2P$  atomic state. *Phys. Rev. A* **1970**, *2*, No. 2250.
- (71) Orth, H.; Ackermann, H.; Otten, E. W. Fine and hyperfine structure of the  $2^2P$  term of  $^7Li$ ; Determination of the nuclear quadrupole moment. *Z. Phys. A* **1975**, *273*, 221–232.