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Variational upper bounds for low-lying states of lithium

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We present improved calculations of variational energy eigenvalues for the $1s^22s\,^2S$, $1s^23s\,^2S$, and $1s^22p\,^2P$ states of lithium using basis sets with up to 30 224 terms in Hylleraas coordinates. The nonrelativistic energies for infinite nuclear mass are $-7.478\,060\,323\,910\,143\,7(45)$ a.u. for $1s^22s\,^2S$, $-7.354\,098\,421\,444\,316\,4(32)$ a.u. for $1s^23s\,^2S$, and $-7.410\,156\,532\,651\,6(5)$ a.u. for $1s^22p\,^2P$, which represent the most accurate variational upper bounds to date. An important advantage of the basis sets with multiple distance scales is their exceptional numerical stability.

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I. INTRODUCTION

In the last two decades, significant advances (see [1–6] and earlier references therein) have been made in high-precision calculations of energy levels for lithium and lithiumlike ions, including the leading relativistic and quantum electrodynamic (QED) terms and their finite nuclear mass corrections of orders $O(\alpha^4mc^2)$, $O(\alpha^5mc^2)$, $O((m/M)\alpha^4mc^2)$, and $O((m/M)\alpha^5mc^2)$. These results have been used, in combination with high-precision laser spectroscopy measurements [7], to determine the nuclear charge radii of Li and Be$^+$ isotopes, such as the halo nuclei ^{11}Li and ^{11}Be. The method is based on a comparison between theory and experiment for the isotope shift in atomic transition frequencies for an atom with a halo nucleus relative to a reference isotope with a normal nucleus. The nucleus contributes to the isotope shift in proportion to $\bar{r}_c^2$, where $\bar{r}_c^2$ is the rms nuclear charge radius, and so $\bar{r}_c^2$ can be determined from the measured isotope shift, provided the specific isotope shift due to electronic structure can be accurately calculated and subtracted. The theoretical approach is based on perturbation theory where the eigenvalue problem for the nonrelativistic Hamiltonian is solved to sufficiently high accuracy, and then relativistic and QED corrections are taken into account by perturbation theory. The relativistic corrections are typically accurate to less than half as many significant figures as the nonrelativistic energy, and so a high degree of accuracy is needed for the wave functions.

The purpose of this Brief Report is to report improved variational upper bounds to the energy eigenvalues of the $1s^22s\,^2S$, $1s^23s\,^2S$, and $1s^22p\,^2P$ states of lithium using much larger sizes of basis sets in Hylleraas coordinates. It is well known that the computational effort for calculating the Hamiltonian matrix elements and the overlap matrix elements is proportional to the square of the size of basis set, whereas the computational effort for solving a general eigenvalue problem is proportional to the cube of the basis size. Thus, the computation becomes more and more time-consuming as the size of the basis set increases. It is therefore necessary to resort to an efficient parallel algorithm. The significance of the results is that it represents the state of the art for what can be achieved for lithium and other three-electron atomic systems. There has been recent progress for the four-electron case of beryllium [8] using explicitly correlated Gaussian functions, but the uncertainty of 0.002 cm^{-1} for the transition energies (6 parts in 10^{10} for total energies) is still much larger than the accuracies that can be achieved, at least in principle, with fully correlated Hylleraas basis sets.

II. CONSTRUCTION OF BASIS SETS

We first outline the structure of the variational basis set according to our previous work [9] and then describe some modifications that we have introduced to obtain improved accuracy for the excited states. The unmodified form is also essentially the same as that adopted by Puchalski and Pachucki [5,10] in their calculations. The wave function is a linear combination of terms of the form (in atomic units throughout)

$$\psi = \mathcal{A}\phi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3), \tag{1}$$

where

$$\phi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = r_1^{j_1}r_2^{j_2}r_3^{j_3}r_{12}^{j_{12}}r_{23}^{j_{23}}r_{31}^{j_{31}}e^{-\alpha r_1-\beta r_2-\gamma r_3} \times r_1^{\ell_1}r_2^{\ell_2}r_3^{\ell_3}\mathcal{Y}^{LM}_{(\ell_1\ell_2)\ell_{12},\ell_3}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\chi_1 \tag{2}$$

$$\mathcal{Y}^{LM}_{(\ell_1\ell_2)\ell_{12},\ell_3}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = \sum_{m_i}\langle\ell_1m_1\ell_2m_2|\ell_1\ell_2\ell_{12}m_{12}\rangle\langle\ell_{12}m_{12}\ell_3m_3|\ell_{12}\ell_3LM\rangle \times Y_{\ell_1m_1}(\mathbf{r}_1)Y_{\ell_2m_2}(\mathbf{r}_2)Y_{\ell_3m_3}(\mathbf{r}_3) \tag{3}$$

is the vector-coupled product of spherical harmonics for the three electrons to form a state of total angular moment L and z-component M,

$$\chi_1 = \alpha(1)\beta(2)\alpha(3) - \beta(1)\alpha(2)\alpha(3) \tag{4}$$

is the spin function with the total spin $1/2$, and

$$\mathcal{A} = (1) - (12) - (13) - (23) + (123) + (132) \tag{5}$$

is the three-particle antisymmetrizer. The ℓ_i's are chosen according to

$$(\ell_1,\ell_2,\ell_3) = (0,0,0)_{\rm A} \quad \text{for } S \text{ states},$$
$$(\ell_1,\ell_2,\ell_3) = (0,0,1)_{\rm A},\ (0,1,0)_{\rm B} \quad \text{for } P \text{ states}.$$

As described previously [9], all terms in Eq. (2) should be included such that

$$j_1 + j_2 + j_3 + j_{12} + j_{23} + j_{31} \leqslant \Omega, \tag{6}$$

and the convergence of the eigenvalues is studied as Ω is progressively increased. However, terms that may potentially cause near-linear dependence are omitted. For example, if $\ell_1 = \ell_2$ and $\alpha \approx \beta$, then terms with $j_1 > j_2$ are omitted, as well as terms with $j_1 = j_2$ when $j_{23} > j_{31}$. The presence of the near-linear dependency problem in a basis set may be detected by diagonalizing the positive-definite overlap matrix to see if there are any abnormally small or negative eigenvalues. Furthermore, the first block $(0,0,0)_A$ for S states or $(0,0,1)_A$ for P states is further divided into five sectors according to correlations among the three electrons:

$$\begin{aligned}
&\text{sector 1, all } j_{12}, \quad j_{23} = 0,\ j_{31} = 0,\\
&\text{sector 2, all } j_{12}, \quad j_{23} = 0,\ j_{31} \neq 0,\\
&\text{sector 3, all } j_{12}, \quad j_{23} \neq 0,\ j_{31} = 0,\\
&\text{sector 4, } j_{12} = 0, \quad j_{23} \neq 0,\ j_{31} \neq 0,\\
&\text{sector 5, } j_{12} \neq 0, \quad j_{23} \neq 0,\ j_{31} \neq 0.
\end{aligned}$$

The distinguishing feature for each sector is that the nonlinear parameters α, β, and γ are different and independently optimized for each sector to minimize the energy, as further described below. Thus, the basis sets contain a total of five sectors for S states and six sectors for P states including $(0,1,0)_B$. The size of each sector is separately determined by assigning to each an Ω_i according to

$$\{\Omega_1,\Omega_2,\Omega_3,\Omega_4,\Omega_5\} = \{\Omega,\Omega,\Omega,\Omega,\Omega\}$$
$$\{\Omega_1,\Omega_2,\Omega_3,\Omega_4,\Omega_5,\Omega_6\} = \{\Omega,\Omega,\Omega,\Omega,\Omega,\Omega-2\}$$

for S states and P states, respectively. The sixth sector, $(0,1,0)_B$, is very important in enhancing the rate of convergence for P states. However, in order to control the rapid growth of overall size of the basis set, we set the control parameter to be $\Omega_6 = \Omega - 2$.

In solving the generalized eigenvalue problem, we used the power method, where the most time-consuming part is the Cholesky decomposition for the matrix $\mathbf{H} - E_g\mathbf{O}$, where $\mathbf{H}$ is the Hamiltonian matrix, $\mathbf{O}$ is the overlap matrix, and E_g is the guessed eigenvalue. The inverse of this matrix then converges to the eigenvalue closest to E_g. There are several kinds of parallel algorithms for the Cholesky decomposition in the literature. The algorithm used in this Brief Report is based on the work by Chi [11] and has been modified by us so that it can be applied to any symmetric matrix, including non-positive-definite ones. The main idea of parallelization is to distribute data in a wrap manner to each processor, and then computations and communications are done simultaneously. In our calculations, we found near-linear speedup and stability of the performance using dozens of processors. A few days' job in serial algorithms can now be completed in a few hours using parallel algorithms. For the ground state with $\Omega = 15$, $N = 27\,720$, and using 30 CPUs in parallel, a complete cycle takes a total of about 11 h, with 2.7 h for matrix element generation, 4.5 h for eigenvector calculation via the power method, and 3.9 h to evaluate the derivatives $\partial E/\partial\alpha_i$, $\partial E/\partial\beta_i$, and $\partial E/\partial\gamma_i$ for each sector. The CPU type is an Intel Xeon E5440 running at 2.83 GHz. Each iteration adjusts the α's, β's, and γ's to reach the zeros of the derivatives by application of Newton's method, as described by Drake and Makowski [12] for the helium case.

III. RESULTS AND BASIS SET ADJUSTMENTS

Table I lists our variational energies for the ground state of Li, together with other recent calculations. The convergence ratio $R(\Omega)$ is defined by the ratio of successive differences:

$$R(\Omega) = \frac{E(\Omega-1) - E(\Omega-2)}{E(\Omega) - E(\Omega-1)}. \tag{7}$$

The energy extrapolated to $\Omega = \infty$ is estimated by assuming a constant $R(\Omega)$ for $\Omega \geqslant \Omega_{\max}$:

$$E(\infty) = E(\Omega_{\max}) + \frac{E(\Omega_{\max}) - E(\Omega_{\max}-1)}{R_{\max} - 1}. \tag{8}$$

The uncertainty is taken to be one half of the amount of extrapolation.

The results in Table I were obtained using the basis sets constructed according to the scheme described above and used in our previous work [9]. We call these basis sets the "old" ones compared to the "new" ones which are described below. We have found that, for the ground state, the energy eigenvalue converges smoothly to the 14th digit, with the estimated percentage error of 5 parts in 10^{15}. This represents the most precise result published in the literature. All the numerical calculations were performed using the standard quadruple precision arithmetic (about 32 decimal digits) in FORTRAN. We checked the numerical stability by repeating the calculations using the multiprecision QD arithmetic [13] (about 64 decimal digits) and found no noticeable loss of significant figures in quadruple precision.

For the $3\,^2S$ and $2\,^2P$ states, however, we found slow convergence for the energy eigenvalues as Ω increases. The resulting energies are one or two orders of magnitude less accurate than the ground-state energy. In order to improve the rate of convergence for these excited states, we made

TABLE I. Nonrelativistic energies for the ground state of Li, using the "old" basis sets.[a]

Ω	Number of terms	$E(\Omega)$	$R(\Omega)$
		Li: $1s^22s\ ^2S$	
8	1 589	−7.478 060 320 886 434	
9	2 625	−7.478 060 323 556 497	
10	4 172	−7.478 060 323 850 012	9.096
11	6 412	−7.478 060 323 899 259	5.960
12	9 576	−7.478 060 323 908 100	5.569
13	13 944	−7.478 060 323 909 554	6.083
14	19 860	−7.478 060 323 910 021	3.112
15	27 720	−7.478 060 323 910 113	5.068
∞		−7.478 060 323 910 136(12)	

[a] $\Omega = \infty$ denotes the extrapolated value from Eq. (8). Units are atomic units.

TABLE II. Nonrelativistic energies for the $2\,^2S$, $2\,^2P$ and $3\,^2S$ states of Li, using modified basis sets. The comparison calculations are from Sims *et al.* [14], Stanke *et al.* [15], Puchalski *et al.* [5], and Puchalski and Pachucki [16]. Units are atomic units.

Ω	Number of terms	$E(\Omega)$	$R(\Omega)$
		Li: $1s^22s\,^2S$	
10	3 910	−7.478 060 323 880 889 238	
11	6 039	−7.478 060 323 905 362 409	
12	9 056	−7.478 060 323 909 450 281	5.986
13	13 248	−7.478 060 323 909 950 385	8.174
14	18 935	−7.478 060 323 910 102 364	3.290
15	26 520	−7.478 060 323 910 134 843	4.679
∞		−7.478 060 323 910 143 7(45)	
Ref. [14]	16 764	−7.478 060 323 451 9	
Ref. [15]	10 000	−7.478 060 323 81	
Ref. [5]	13 944	−7.478 060 323 909 560	
Ref. [5]	∞	−7.478 060 323 910 10(32)	
		Li: $1s^22p\,^2P$	
10	3 024	−7.410 156 531 219 66	
11	4 824	−7.410 156 532 310 89	
12	7 440	−7.410 156 532 558 34	4.409
13	11 118	−7.410 156 532 625 75	3.670
14	16 164	−7.410 156 532 640 83	4.470
15	23 004	−7.410 156 532 648 43	1.983
16	30 224	−7.410 156 532 650 66	3.402
∞		−7.410 156 532 651 6(5)	
Ref. [16]	($\Omega = 12$)	−7.410 156 532 628 6	
Ref. [16]	∞	−7.410 156 532 665(14)	
		Li: $1s^23s\,^2S$	
10	3 910	−7.354 098 421 345 692 670	
11	6 039	−7.354 098 421 430 788 086	
12	9 056	−7.354 098 421 441 885 268	7.668
13	13 248	−7.354 098 421 443 757 418	5.298
14	18 935	−7.354 098 421 444 256 717	3.746
15	26 520	−7.354 098 421 444 310 034	9.369
∞		−7.354 098 421 444 316 4(32)	
Ref. [14]	17 180	−7.354 098 420 933	
Ref. [15]	10 000	−7.354 098 421 13	
Ref. [16]	($\Omega = 12$)	−7.354 098 421 379 9	
Ref. [16]	∞	−7.354 098 421 426(19)	

two significant changes to the variational basis sets. First, we introduced truncations for sector 5:

$$\begin{aligned}&\text{sector } 5', S \text{ states}:\\ &\quad \text{all } j_1 + j_2 + j_3 + j_{12} + j_{23} + j_{31} \leqslant \Omega - 3;\\ &\quad \text{omit terms with } j_1 > j_2 \text{ or } j_{23} > j_{31} \text{ if } j_1 = j_2,\end{aligned}$$

$$\begin{aligned}&\text{sector } 5', P \text{ states}:\\ &\quad \text{all } j_1 + j_2 + j_3 + j_{12} + j_{23} + j_{31} \leqslant \Omega - 2;\\ &\quad \text{omit terms with } j_1 > j_3 \text{ or } j_{12} > j_{23} \text{ if } j_1 = j_3.\end{aligned}$$

Second, for both the S and the P states, we divided the first sector into two subsectors:

$$\begin{aligned}&\text{subsector 1a}: \; j_{12} = 0,\; j_{23} = 0,\; j_{31} = 0,\\ &\text{subsector 1b}: \; j_{12} \neq 0,\; j_{23} = 0,\; j_{31} = 0.\end{aligned}$$

After optimization of the nonlinear parameters, the energy eigenvalue decreases significantly in comparison with the old basis sets. For example, for the $2\,^2P$ state, the new basis set gives rise to the energy eigenvalue −7.410 156 532 640 83 using 16 164 terms, whereas the old basis set gives rise to the eigenvalue −7.410 156 532 632 11 using 20 536 terms. Similarly for the $3\,^2S$ state, for the case of $\Omega = 13$ corresponding to the total number of terms 13 248, the energy eigenvalue is −7.354 098 421 443 757, which is even lower than that of $\Omega = 15$ (27 720 terms), i.e., −7.354 098 421 442 16, using the old partitioning. Table II lists the convergence studies for the $2\,^2P$ and $3\,^2S$ states and a comparison with some other calculations. The overall accuracy achieved is 7 parts in 10^{14} for the $2\,^2P$ state and about 5 parts in 10^{16} for the $2\,^2S$ and $3\,^2S$ states.

IV. DISCUSSION

In summary, we have extended our variational calculations of lithium low-lying states to very large sizes of basis sets in Hylleraas coordinates using an efficient parallel algorithm for the evaluation of matrix elements and for the Cholesky decomposition. We have also demonstrated the possibility of enhancing the rate of convergence by repartitioning the basis sets so that more important sectors can be emphasized. It would be equally significant to achieve similar accuracy for the higher-lying excited states.

A complete calculation and comparison with experiment also requires the finite nuclear mass, relativistic, and QED corrections. The present work lays the foundation for further improvements in the accuracy of these terms over previous calculations [3,16], especially for the isotope shifts that are of key importance in measurements of the nuclear charge radius.

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