Lower Rydberg ^2D states of the lithium atom: Finite-nuclear-mass calculations with explicitly correlated Gaussian functions

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Very accurate variational nonrelativistic calculations are performed for the five lowest Rydberg ^2D states ($1s^2nd^1$, $n = 3, \ldots, 7$) of the lithium atom (^{7}Li). The finite-nuclear-mass approach is employed and the wave functions of the states are expanded in terms of all-electron explicitly correlated Gaussian function. Four thousand Gaussians are used for each state. The calculated relative energies of the states determined with respect to the ^2S $1s^22s^1$ ground state are systematically lower than the experimental values by about 2.5 cm^{-1}. As this value is about the same as the difference between the experimental relative energy between ^{7}Li$^+$ and ^{7}Li in their ground-state energy and the corresponding calculated nonrelativistic relative energy, we attribute it to the relativistic effects not included in the present calculations.

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I. INTRODUCTION

The NIST atomic spectra database [1] list 10 ^2D states among the 182 states of the lithium atom. These states correspond to the Rydberg electron configurations $1s^2nd$, where $n = 3, 4, \ldots, 12$. A literature search reveals that only the lowest state of this series has been calculated with high accuracy using the variational method by Yan and Drake [2]. Their energy obtained using the infinite-nuclear-mass approach was $-7.335\,523\,541\,10(43)$ a.u. (an extrapolated result). We recently recalculated this energy using an extended set of explicitly (or exponentially) correlated Gaussian (ECG) basis functions and we obtained the value $-7.335\,523\,542\,82$ a.u., which is noticeably lower than that of Yan and Drake (in the present work an even lower energy value of $-7.335\,523\,542\,97$ a.u. was obtained). We also calculated the energy of the lowest ^2D state of ^{7}Li, as well as the energy of the second-lowest state, using the finite-nuclear-mass approach. The calculation was an example included in the work [3] that featured implementation of the ECG variational method for calculating D states of small atomic systems. In that approach, high accuracy of the results is achieved by employing the analytical energy gradient determined with respect to the ECG nonlinear parameters in optimizing those parameters by the variational energy minimization [3–5].

Our ECG method for atomic D states [3] not only enables us to perform calculations with an infinite nuclear mass, but also enables finite-nuclear mass calculations. This is possible because the Hamiltonian we use in the calculations is obtained by rigorously separating out the center-of-mass motion from the all-particle laboratory-frame Hamiltonian; thus, it explicitly retains the dependency on masses of all particles of the systems (the electrons and the nucleus). Therefore, the energy of the ground and excited states determined in the calculations at the basis set limit correspond to exact solutions of the nonrelativistic Schrödinger equation.

Very accurate quantum mechanical calculations of the ground and excited states of small atoms have always provided testing grounds for new approaches for atomic calculations. Very accurate gas-phase spectra of these systems make such testing possible. Excited D states of small atoms are among the most precisely measured [1]. Therefore, calculations using state-of-the-art methods is an interesting undertaking.

As the ECG functions depend on the interelectron distances, they provide a very effective basis for calculations that deal with the electron correlation effects. Very accurate results for three-, four-, and five-electron atoms (with all electrons in s states or one electron in a p state and the rest in s states) have been obtained with those functions [6–13]. The main advantage of using Gaussians in atomic calculations is due to the simplicity of the Hamiltonian and overlap integrals with those functions, which can be evaluated analytically in a compact form for an arbitrary number of electrons. However, Gaussians do not satisfy the Kato cusps conditions and are too fast decaying at large distances. These deficiencies cause a certain slowdown of the convergence to the exact nonrelativistic wave function. Fortunately, as the calculations have shown [6–13], they can be effectively remedied by using longer expansions and by performing extensive optimization of the Gaussian nonlinear parameters using the variational energy minimization.

II. THE HAMILTONIAN

The standard atomic quantum-mechanical calculations are performed with infinite nuclear mass, that is, assuming the Born-Oppenheimer (BO) approximation. If a higher accuracy is needed, the BO energy is augmented by corrections accounting for the finite mass of nucleus. As our approach aims at calculating the atomic states with very high accuracy, the account for the finite nuclear mass is done at the zero-order level by using a Hamiltonian that explicitly depends on the nuclear mass. This Hamiltonian, called the internal Hamiltonian, is obtained from the laboratory-frame nonrelativistic Hamiltonian by rigorously separating out the center-of-mass motion. For an atom with N electrons, this is done by a transformation from the laboratory-frame coordinates to a new set of coordinates comprising three Cartesian coordinates of the center of mass and $3N - 3$ internal Cartesian coordinates

describing the positions of the electrons with respect to the nucleus. By eliminating the center-of-mass motion we obtain the following internal Hamiltonian:

$$\hat{H} = -\frac{1}{2}\left(\sum_{i=1}^{n}\frac{1}{\mu_i}\nabla_{\mathbf{r}_i}^2 + \sum_{\substack{i,j=1\\i\neq j}}^{n}\frac{1}{m_0}\nabla'_{\mathbf{r}_i}\nabla_{\mathbf{r}_j}\right)$$
$$+ \sum_{i=1}^{n}\frac{q_0 q_i}{r_i} + \sum_{i>j=1}^{n}\frac{q_i q_j}{r_{ij}}, \quad (1)$$

where $n = N - 1$, $\mathbf{r}_i$ is the distance between the ith electron and the nucleus, m_0 is the nucleus mass ($12\,786.3933 m_e$ for ^{7}Li and $10\,961.898 m_e$ for ^{6}Li, where $m_e = 1$ is the electron mass), q_0 is its charge, q_i are electron charges, and $\mu_i = m_0 m_i/(m_0 + m_i)$ are electron reduced masses. The Hamiltonian (1) describes the motion of n (pseudo)electrons, whose masses are the reduced masses, in the central field of the nuclear charge. This motion is coupled through the Coulombic interactions, $\sum_{i=1}^{n}\frac{q_0 q_i}{r_i} + \sum_{i>j=1}^{n}\frac{q_i q_j}{r_{ij}}$, where $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$, and through the mass polarization term, $-\frac{1}{2}\sum_{\substack{i,j=1\\i\neq j}}^{n}(1/m_0)\nabla'_{\mathbf{r}_i}\nabla_{\mathbf{r}_j}$ (prime indicates the matrix or vector transpose).

III. THE BASIS SET

In this work we consider a Rydberg series of the five lowest ^2D states of the lithium atom. Even though the states are described as corresponding to the $1s^2 nd^1$, $n = 3,4,\ldots,7$, configurations, they also contain small contributions from other configurations, in particular the $1s^1 2p^2$ configuration. To effectively describe all these contributions with ECGs the following functions need be included in the basis set [3]:

$$\phi_k = \left(x_{i_k}x_{j_k} + y_{j_k}y_{i_k} - 2z_{i_k}z_{j_k}\right)\exp[-\mathbf{r}'(A_k \otimes I_3)\mathbf{r}], \quad (2)$$

where electron labels i_k and j_k are either equal or not equal to each other and they can vary from 1 to n. A_k in (2) is an $n \times n$ symmetric matrix, $\otimes$ is the Kronecker product, I_3 is a 3×3 identity matrix, and $\mathbf{r}$ is a $3n$ vector that has the form

$$\mathbf{r} = \begin{pmatrix}\mathbf{r}_1\\\mathbf{r}_2\\\vdots\\\mathbf{r}_n\end{pmatrix} = \begin{pmatrix}x_1\\y_1\\z_1\\\vdots\\x_n\\y_n\\z_n\end{pmatrix}. \quad (3)$$

Using the general quadratic form $\mathbf{r}'W_k\mathbf{r}$ in place of $(x_{i_k}x_{j_k} + y_{i_k}y_{j_k} + 2z_{i_k}z_{j_k})$, we can write the basis functions (2) as

$$\phi_k = (\mathbf{r}'\mathbf{W}_k\mathbf{r})\exp(-\mathbf{r}'\mathbf{A}_k\mathbf{r}). \quad (4)$$

$\mathbf{W}_k$ is a sparse $3n \times 3n$ symmetric matrix that for $i_k = j_k$ comprises only three nonzero elements, $W_{3(i_k-1)+1,3(i_k-1)+1} = 1$, $W_{3(i_k-1)+2,3(i_k-1)+2} = 1$, and $W_{3(i_k-1)+3,3(i_k-1)+3} = -2$, and for $i_k \neq j_k$ it comprises six elements, $W_{3(i_k-1)+1,3(j_k-1)+1} = W_{3(j_k-1)+1,3(i_k-1)+1} = \frac{1}{2}$,

$W_{3(i_k-1)+2,3(j_k-1)+2} = W_{3(j_k-1)+2,3(i_k-1)+2} = \frac{1}{2}$, and $W_{3(i_k-1)+3,3(j_k-1)+3} = W_{3(j_k-1)+3,3(i_k-1)+3} = 1$.

As the basis functions (2) are used in expanding wave functions of bound states, they have to be square integrable. This happens if the A_k matrix is positive definite. Rather than restricting the A_k matrix elements, which usually leads to cumbersome constraints, we use the following Cholesky factored form of A_k: $A_k = L_k L'_k$, where L_k is a lower triangular matrix. This makes A_k automatically positive definite for any values of the L_k matrix elements ranging from ∞ to $-\infty$. Thus, the variational energy minimization with respect to the L_k parameters can be performed without any restrictions. It should be noted that the $L_k L'_k$ representation of A_k matrix does not limit the flexibility of basis functions, because any symmetric positive matrix can be represented in a Cholesky factored form.

IV. THE WAVE FUNCTION AND ITS VARIATIONAL OPTIMIZATION

Appropriate symmetry projections are used to make the wave function antisymmetric with respect to the permutation of the electron labels. In this work, we use the spin-free formalism. In this formalism, the symmetry projections acting on the spatial parts of the wave function, that is, the basis functions, can be represented using the Young projection operators, $\hat{Y}$, which are linear combinations of permutational operators, $\hat{P}_\gamma$. As the Hamiltonian is invariant with respect to all permutations of the electrons, in the calculation of the overlap and Hamiltonian matrix elements the permutational operators can be applied to the *ket* (or the *bra*) only. More specifically, the *ket* basis functions in those matrix elements are operated on with the permutation operator $\hat{Y}^\dagger\hat{Y}$ (the dagger stands for conjugate), where the $\hat{Y}$ operator is derived using the appropriate Young tableaux for the state under consideration (for details of the formalism, see, for example, [14]). For ^2D states of lithium the Young operator can be chosen as $\hat{Y} = (\hat{1} + \hat{P}_{34})(\hat{1} - \hat{P}_{23})$, where the nucleus is labeled as 1, and the electrons are labeled as 2, 3, and 4, $\hat{1}$ is the identity operator, and $\hat{P}_{ij}$ is the permutation of the ith and jth electron labels.

In the linear coefficients of the expansion of the wave function in terms of the basis functions, the elements of the L_k matrices are optimization variables. For each basis function the i_k and j_k indices are also subject to optimization. The optimization of i_k and j_k is only done once for each basis function when the function is first added to the basis set.

The standard variational approach involving minimization of the Rayleigh-Ritz variational energy functional is used in the present calculations. The functional is minimized in terms of the L_k Gaussian parameters and the i_k and j_k indices. As described before [3], in the energy minimization with respect to L_k, we employ the analytical gradient. The calculation for each state is performed independently from other states and the parameters of the basis functions are optimized specifically for that particular state. In this process, the basis set is grown from a small randomly selected set of functions or from a small set taken from the next lower state to the final set of 4000 functions. In the growing process, functions are added to the basis set one by one with the L_k parameters guessed based on the parameters of the functions already included in the set.

TABLE I. The convergence of the total variational finite-mass energies (in hartrees) of the five lowest ^2D states of ^{7}Li with the number of the Gaussian basis functions. The ^{6}Li and $^\infty$Li energies are also shown for the basis set of 4000 Gaussians. In parantheses we show estimates of the remaining error in the norelativistic energy.

Basis	$1s^23d^1$	$1s^24d^1$	$1s^25d^1$	$1s^26d^1$	$1s^27d^1$
^{7}Li
1500	−7.334 926 995 76	−7.310 595 039 75	−7.299 333 955 70	−7.293 217 366 17	−7.289 528 735 55
2000	−7.334 927 301 78	−7.310 595 225 70	−7.299 334 059 55	−7.293 217 637 00	−7.289 529 803 71
2500	−7.334 927 304 17	−7.310 595 234 33	−7.299 334 083 67	−7.293 217 697 58	−7.289 530 047 16
3000	−7.334 927 305 17	−7.310 595 238 60	−7.299 334 093 11	−7.293 217 721 01	−7.289 530 114 13
3500	−7.334 927 305 66	−7.310 595 240 54	−7.299 334 096 82	−7.293 217 729 79	−7.289 530 142 67
4000	−7.334 927 305 99(60)	−7.310 595 241 52(200)	−7.299 334 098 85(300)	−7.293 217 734 51(500)	−7.289 530 165 34(2000)
^{6}Li
4000	−7.334 828 079 52(60)	−7.310 496 331 21(200)	−7.299 235 334 92(300)	−7.293 119 050 12(500)	−7.289 431 528 90(2000)
$^\infty$Li
4000	−7.335 523 542 97(60)	−7.311 189 578 43(200)	−7.299 927 555 94(300)	−7.293 810 713 64(500)	−7.290 122 856 24(2000)

After a function is selected, its i_k and j_k indices and the L_k parameters are optimized. At this stage, the function is checked for any linear dependency with the functions already included in the basis set and, if such linear dependency appears, the function is rejected. After a certain number of new functions are added, the whole set is reoptimized by cycling over all functions one by one and reoptimizing their L_k parameters. After parameters of a function are reoptimized, it is checked for linear dependency with all other functions in the set. If such dependency is found, the parameters of the functions are reset to their values before the reoptimization.

This elaborate scheme used in the present work to avoid linear dependency between the basis functions is necessary to keep the calculation numerically stable. An instability may arise if two or more functions become nearly identical and their linear coefficients have opposite signs. In that case, some undesirable and uncontrollable numerical noise may appear in the energy eigenvalues, leading to inefficiencies or even failures in the minimization process.

V. RESULTS

The present calculations target the lowest five states of the ^2D Rydberg series of the lithium atom. The optimization of the ECG basis sets for these states have been performed for the ^{7}Li isotope and then used to also calculate the ^2D energy levels of the ^{6}Li isotope, as well as of the lithium atom with an infinite nuclear mass ($^\infty$Li). The $^\infty$Li are shown because they can be compared with the results obtained in the standard way that involves the BO approximation.

The first set of results is presented in Table I. It shows the convergence of the total energies of the ^{7}Li states with the number of basis functions. In the table, we also show the energies of ^{6}Li and $^\infty$Li calculated with 4000 ECGs, that is, the largest basis sets used in the calculations. One can see that the energies of all five states are very well converged. As expected, the convergence is somewhat better for the lowest states than for the upper states.

The next set of results is shown in Table II. It concerns the relative energies of the five ^2D states of ^{7}Li, ^{6}Li, and $^\infty$Li with

TABLE II. Energies (in cm^{-1}) of the five lowest ^2D states of ^{7}Li determined with respect to the ground ^2S ($1s^22s^1$) state and their comparison with the experimental energies. Only the results of the calculations performed with 4000 Gaussians are shown. The uncertainty of the calculated values due to finite size of the basis is less than 0.01 cm^{-1}.

	$1s^23d^1$	$1s^24d^1$	$1s^25d^1$	$1s^26d^1$	$1s^27d^1$	$1s^2\infty d^{1[b]}$
^{7}Li
Calculated[a]	31 280.54	36 620.81	39 092.35	40 434.73	41 244.06	43 484.60
Experiment [1]	31 283.08	36 623.38	39 094.93	40 437.31	41 246.5	43 487.15
Δ[c]	−2.54	−2.57	−2.58	−2.58	−2.44	−2.55
^{6}Li
Calculated[a]	31 280.19	36 620.30	39 091.80	40 434.17	41 243.49	43 484.00
$^\infty$Li
Calculated[a]	31 283.21	36 623.90	39 095.62	40 438.12	41 247.51	43 488.22

[a]Calculated relative to the ground $1s^22s^1$ state of Li. $E(^7\text{Li}) = -7.477\,451\,930\,7$ hartree, $E(^6\text{Li}) = -7.477\,350\,681\,2$ hartree, and $E(^\infty\text{Li}) = -7.478\,060\,323\,8$ hartree taken from [8].
[b]Energy difference between the ground $1s^22s^1$ state of Li and the ground $1s^2$ state of Li$^+$. $E(^7\text{Li}^+) = -7.279\,321\,519\,72$ hartree from [3], and $E(^6\text{Li}^+) = -7.279\,223\,016\,09$ hartree and $E(^\infty\text{Li}^+) = -7.279\,913\,412\,58$ hartree calculated in this work with 500 Gaussians.
[c]Determined as the calculated energy difference minus the experimental energy difference.

TABLE III. Energy differences (in cm^{-1}) between adjacent ^2D states of ^{7}Li, ^{6}Li, and $^\infty$Li. For ^{7}Li we show the convergence of the differences with the basis-set size. For ^{6}Li and $^\infty$Li we only show the results obtained with 4000 Gaussians. For ^{7}Li the results of the calculations are compared with the experimental values.

Basis	$1s^23d^1$–$1s^24d^1$	$1s^24d^1$–$1s^25d^1$	$1s^25d^1$–$1s^26d^1$	$1s^26d^1$–$1s^27d^1$
^{7}Li				
1500	5340.25	2471.52	1342.44	809.56
2000	5340.27	2471.54	1342.40	809.39
2500	5340.27	2471.54	1342.39	809.35
3000	5340.27	2471.54	1342.39	809.34
3500	5340.27	2471.54	1342.39	809.33
4000	5340.27	2471.54	1342.39	809.33
Experiment [1]	5340.30	2471.55	1342.38	809.2
^{6}Li				
4000	5340.20	2471.50	1342.37	809.32
$^\infty$Li				
4000	5340.69	2471.73	1342.49	809.39

respect to the corresponding ground ^2S ($1s^22s^1$) states of these systems. For ^{7}Li, we also include the experimental values [1] and the differences between those values and the calculated ones. Since the present calculations do not include relativistic and QED corrections, the agreement with the experimental values cannot be expected to be perfect. As one can see, the calculated values are systematically off from the experiment by almost a constant value of -2.58 to -2.54 cm^{-1}. This almost constant discrepancy can be explained by the fact that the magnitude of the relativistic and QED corrections changes very little as the valence electron gets excited to increasingly higher d state. The magnitude of the discrepancy is consistent with the estimate of 3.4 cm^{-1} one can obtain using the simple Desclaux approximation [15]. The discrepancy for the highest $1s^27d^1$ state (-2.4 cm^{-1}) is different from -2.58 cm^{-1} because the experimental energy of this state is only given with one significant figure after the decimal point.

There is an additional data point in the table which is related to the energy difference between the Li and Li$^+$ ground states. The nonrelativistic value for this energy difference is -2.55 cm^{-1} off from the experimental value. This number is very similar to the other differences shown in the table, as it should be, because, as those other differences correspond to excitations of the valence electron to states which are increasingly further removed from the atom, the Li/Li$^+$ difference corresponds to the complete removal of the electron from the atom.

In the last table, Table III, we show the energy differences between adjacent ^2D states for ^{7}Li, ^{6}Li, and $^\infty$Li isotopes. For ^{7}Li the calculated results are compared with values determined from the experimental data. As the relativistic effects are

very similar for all five states, the energy differences agree very well with the experiment. The $1s^24d^1 \rightarrow 1s^25d^1$ and $1s^25d^1 \rightarrow 1s^26d^1$ transitions only differ from the experiment by 0.01 cm^{-1}. However, for the $1s^26d^1 \rightarrow 1s^27d^1$ there is a more noticeable difference mainly caused by not-so-accurate experimental energy value for the $1s^27d^1$ state. The results of the present calculations allow for refinement of this energy. This can be done by taking the experimental energy of the $1s^26d^1$ state of 40 437.31 cm^{-1} and adding to it our very well-converged $1s^26d^1 - 1s^27d^1$ energy difference of 809.33 cm^{-1}. Due to a negligible contribution of the relativistic and QED effects, the energy value of 41 246.64 cm^{-1} obtained this way should be quite accurate. This value is slightly different from the experimental value of 41 246.5 cm^{-1} in [1]. The same procedure can be applied to determine the energies of the ^2D states of ^{6}Li, once the energy of the $1s^23d^1$ level becomes available from the experiment.

VI. SUMMARY

The following have been accomplished in this work.

(i) Very accurate variational calculations have been performed for the first five Rydberg states of the ^{7}Li atom using all-electron ECG basis functions. The results agree very well with the experimental data.

(ii) The calculated energies allow for slight refinement of the energy of the $1s^27d^1$ state of ^{7}Li, which is known with somewhat lower precision than the energies of the lower states.

(iii) The results obtained for ^{6}Li may help in performing measurements of yet unmeasured Rydberg ^2D states of this system.

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