

# Refinement of the experimental energy levels of higher $^2D$ Rydberg states of the lithium atom with very accurate quantum mechanical calculations

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Very accurate variational non-relativistic calculations are performed for four higher Rydberg  $^2D$  states ( $1s^2nd^1$ ,  $n = 8, \dots, 11$ ) of the lithium atom ( $^7\text{Li}$ ). The wave functions of the states are expanded in terms of all-electron explicitly correlated Gaussian functions and finite nuclear mass is used. The exponential parameters of the Gaussians are optimized using the variational method with the aid of the analytical energy gradient determined with respect to those parameters. The results of the calculations allow for refining the experimental energy levels determined with respect to the  $^2S$   $1s^22s^1$  ground state. © 2011 American Institute of Physics. [doi:10.1063/1.3591836]

## I. INTRODUCTION

The NIST atomic spectra database<sup>1</sup> lists ten  $^2D$  states among the 182 states of the lithium atom. These states correspond to the Rydberg electron configurations  $1s^2nd$ , where  $n = 3, 4, \dots, 12$ . An examination of the relative energies of these states reveals that higher Rydberg states of these systems, as well as their isotopes and ions, have been measured much less precisely than the lower lying states. For example, while for the lowest four  $^2D$  states of  $^7\text{Li}$  (the  $1s^23d^1$ ,  $1s^24d^1$ ,  $1s^25d^1$ , and  $1s^26d^1$  states) the relative energies with respect to the ground  $^2S$   $1s^22s^1$  state are reported with the precision of two significant digits after the decimal point (in wave numbers), the higher states (the  $1s^27d^1$ ,  $1s^28d^1$ , and  $1s^29d^1$  states) are reported with only one significant digit after the point, and the highest states (the  $1s^210d^1$ ,  $1s^211d^1$ , and  $1s^212d^1$  states) are reported with no digits after the point. Also, the  $^2D$   $1s^212d^1$  state is the highest for which the energy level is given. It is equal to  $42\,725\text{ cm}^{-1}$ .

Recently we presented a set of very high-level calculations performed for the lowest five  $^2D$  of the  $^7\text{Li}$  atom where the relative nonrelativistic energies of those states were converged with the accuracy better than  $0.01\text{ cm}^{-1}$ .<sup>2</sup> In the calculations we employed all-electron explicitly correlated Gaussian functions and optimized their exponential parameters with a variational approach that employs the analytical energy gradient determined with respect to those parameters. 4 000 Gaussians were used for each state.

The gradient-aided optimization has been key to obtain very accurate results in our calculations performed with various types of explicitly correlated Gaussian basis functions for a number of atomic and molecular systems.<sup>3–9</sup> The algorithms for calculating the energy and the energy gradient used in the  $^7\text{Li}$   $^2D$ -state calculations,<sup>2</sup> as well as in the present calculations, were presented in our previous works.<sup>10–12</sup> They have been derived using a non-relativistic Hamiltonian that explicitly depends on the mass of the

nucleus. This Hamiltonian, called the internal Hamiltonian,  $\hat{H}_{int}$ , is obtained by rigorously separating the kinetic energy of the center-of-mass motion from the laboratory-frame Hamiltonian.  $\hat{H}_{int}$  has the following form in atomic units:

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

where  $n$  is the number of electrons,  $\mathbf{r}_i$  is the distance between the  $i$ th electron and the nucleus,  $m_0$  is the nucleus mass ( $12\,786.3933m_e$  for  $^7\text{Li}$  and  $10\,961.898m_e$  for  $^6\text{Li}$ , 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 [Eq. (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/vector transpose).

As  $\hat{H}_{int}$  is explicitly dependent on the mass of the nucleus, it allows for direct calculation of energy levels of a particular isotope without resorting to accounting for the finite mass of the nucleus using the perturbation approach. Such perturbation calculations are performed in the commonly used approach after the initial nonrelativistic calculation is done with the mass of the nucleus set to infinity. The finite-nuclear-mass calculation in this work are performed for the  $^6\text{Li}$  and  $^7\text{Li}$  isotopes. We have also performed infinite-nuclear-mass calculations by setting the mass of the nucleus in Eq. (1) to infinity.

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## II. THE REFINING PROCEDURE

Very accurate quantum mechanical calculations of the ground and excited states of small atoms have always provided grounds for fruitful interplay between the experiment and theoretical calculations. They make possible the testing of new theoretical approaches for very accurate atomic calculations. However, the calculations we recently performed on the five lowest Rydberg  $^2D$  states of the  $^7\text{Li}$  atom<sup>2</sup> opens another possible way of the theoretical/experimental interaction. It involves refining the experimentally obtained energy levels of high Rydberg states of small atoms with the theoretical calculations. Such refining was suggested in the work concerning the lowest five  $^2D$  states of the  $^7\text{Li}$  atom.<sup>2</sup> In that work we showed that, when the excitation level increases from the lowest  $^2D 1s^2 3d^2$  state to the fourth  $1s^2 6d^2$  state, the energy difference between the experimental and the calculated energy converges to a constant value of  $-2.58 \text{ cm}^{-1}$ . As the difference is clearly due to not including in the calculations the relativistic and QED effects, its constant value indicates that these effects become virtually identical as the level of excitation in the Rydberg series increases. An unexpected deviation from the  $-2.58 \text{ cm}^{-1}$  limit appears for the fifth  $1s^2 7d^1$  state. This deviation happens not because the energy of this state is less tightly converged in the calculations, but because the experimental value is not as accurate as for the lower states. Recall that this experimental value is given with only one significant figure after the decimal point.<sup>1</sup>

Another interesting observation can be made by the analysis of the calculated and the experimental energy differences (or transition energies) between adjacent  $^2D$  states. As the excitation level increases the calculated energy differences converge almost exactly to the experimental energy differences. From the calculations, the differences are: 5340.27, 2471.54, and 1342.39  $\text{cm}^{-1}$  for the transitions between the  $1s^2 3d^1 \leftarrow 1s^2 4d^1$ ,  $1s^2 4d^1 \leftarrow 1s^2 5d^1$ , and  $1s^2 5d^1 \leftarrow 1s^2 6d^1$  states, respectively, and from the experiment they are 5340.30, 2471.55, and 1342.38  $\text{cm}^{-1}$ . Based on this trend and taking into account that the calculated transitions are converged to the level better than  $0.01 \text{ cm}^{-1}$ , one would expect that for the  $1s^2 6d^1 \leftarrow 1s^2 7d^1$  transition the experiment and the calculation should give virtually the same transition energies, but this again does not happen because the experiment is not precise enough.

The above results allowed for refinement of the experimental energy of the  $1s^2 7d^1$  state reported as 41 246.5  $\text{cm}^{-1}$  in Ref. 1. This is done by taking the experimental energy of the  $1s^2 6d^1$  state of 40 437.31  $\text{cm}^{-1}$  and adding to it our calculated, very well-converged,  $1s^2 7d^1$ - $1s^2 6d^1$  energy difference of 809.33  $\text{cm}^{-1}$ .<sup>2</sup> Due to a negligible contribution of the relativistic and QED effects, the energy value of 41 246.64  $\text{cm}^{-1}$  obtained this way should be more accurate than the experimental value of 41 246.5  $\text{cm}^{-1}$ .<sup>1</sup> In the present work the refining procedure is applied to the energy levels of the  $1s^2 8d^1$ ,  $1s^2 9d^1$ ,  $1s^2 10d^1$ , and  $1s^2 11d^1$   $^2D$  Rydberg states of  $^7\text{Li}$ . The experimental energies of these states are reported as 41 771.3, 42 131.3, 42 389 and 42 578  $\text{cm}^{-1}$ ,<sup>1</sup> respectively. As it takes significant effort to achieve tight enough convergence of the calcula-

tions for high Rydberg states to be used in the refinement, considerable computational resources have been employed in the present calculations. Besides  $^7\text{Li}$  we have also calculated the energies of the corresponding  $^2D$  states of  $^6\text{Li}$  and  $^\infty\text{Li}$ . The calculation for the latter system were done to provide a reference for the conventional calculations done with a fixed nucleus.

## III. BASIS SET AND ITS OPTIMIZATION

The basis set of explicitly correlated Gaussians used in this work to describe the  $^2D$  states of the Li atom has the following form:<sup>12</sup>

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

where electron labels  $i_k$  and  $j_k$  are either equal or not equal to each other and can vary from 1 to  $n$ .  $A_k$  in Eq. (2) is an  $n \times n$  symmetric matrix,  $\otimes$  is the Kronecker product,  $I_3$  is a  $3 \times 3$  identity matrix, and  $\mathbf{r}$  is a  $3n$  vector of the electron coordinates. To assure that the Gaussians [Eq. (2)] are square integrable – this happens when the  $A_k$  matrix is positive definite – we use the following Cholesky factored form of  $A_k$ :  $A_k = L_k L_k'$ , where  $L_k$  is a lower triangular matrix with matrix elements ranging from  $\infty$  to  $-\infty$ . With that,  $A_k$  is automatically positive definite and the Gaussian is square integrable. Also the variational minimization of the energy, if it is done with respect to the  $L_k$  parameters, can be carried out without any constraints.

We use the spin-free formalism to implement to correct permutational symmetry of the wave function. In this formalism, one constructs a symmetry projector acting on the spatial parts of the wave function to enforce the desired symmetry properties. The construction can be done using the standard procedure involving Young operators as described, for example, in Ref. 13. 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  $i$ th and  $j$ th electron labels. As the internal Hamiltonian [Eq. (1)] is fully symmetric with respect to all electron permutations, in the calculation of the overlap and Hamiltonian matrix elements,  $\hat{Y}$  may be applied to the *ket* basis functions only (as  $\hat{Y}^\dagger \hat{Y}$ ).

The basis set for each of the four states considered in this work has been optimized separately. The optimization involved minimization of the variational energy functional in terms of the  $L_k$  parameters and the  $i_k$  and  $j_k$  indices of the Gaussians. As before, the analytical gradient has been employed in the minimization. A more detailed description of the procedure can be found in our previous works.<sup>2,12</sup> The basis set optimization have been only performed for the  $^7\text{Li}$  states. In the  $^6\text{Li}$  and  $^\infty\text{Li}$  calculations we only readjusted the linear expansion coefficients of the wave function in terms of the Gaussians (through the diagonalization of the Hamiltonian/overlap matrix).

TABLE I. The convergence of the total variational nonrelativistic finite-nuclear-mass energies (in hartrees) of the  $1s^27d^1$ ,  $1s^28d^1$ ,  $1s^29d^1$ ,  $1s^210d^1$ , and  $1s^211d^1$   $^2D$  states of  $^7\text{Li}$  with the number of the Gaussian basis functions. The  $^6\text{Li}$  and  $^\infty\text{Li}$  energies are also shown for the largest basis set of Gaussians used for the particular.

	Basis	$1s^27d^1$	$1s^28d^1$	$1s^29d^1$	$1s^210d^1$	$1s^211d^1$
$^7\text{Li}$	2500	-7.289 530 047 16	-7.287 136 416 89	-7.285 494 619 23	-7.284 316 321 71	-7.283 431 377 49
	3000	-7.289 530 114 13	-7.287 136 759 19	-7.285 495 308 73	-7.284 318 710 52	-7.283 438 066 11
	3500	-7.289 530 142 67	-7.287 136 888 58	-7.285 495 777 44	-7.284 320 229 54	-7.283 444 693 31
	4000	-7.289 530 165 34	-7.287 136 955 73	-7.285 496 027 21	-7.284 321 216 56	-7.283 448 518 87
	4500	-7.289 530 175 47	-7.287 136 992 14	-7.285 496 180 65	-7.284 321 866 40	-7.283 450 758 38
	5000		-7.287 137 013 90	-7.285 496 265 89	-7.284 322 271 47	-7.283 452 070 90
	5500		-7.287 137 027 21	-7.285 496 323 31	-7.284 322 501 61	-7.283 452 874 54
	6000		-7.287 137 036 58	-7.285 496 359 46	-7.284 322 641 12	-7.283 453 426 08
	6500		-7.287 137 042 83	-7.285 496 385 62	-7.284 322 738 45	-7.283 453 824 34
	7000			-7.285 496 404 42	-7.284 322 808 00	-7.283 454 092 25
$^6\text{Li}$		-7.289 431 539 04	-7.287 038 437 52	-7.285 397 820 45	-7.284 224 239 28	-7.283 355 534 82
$^\infty\text{Li}$		-7.290 122 866 37	-7.287 729 546 68	-7.286 088 778 00	-7.284 915 091 83	-7.284 046 308 13

TABLE II. Energies (in  $\text{cm}^{-1}$ ) of the  $1s^28d^1$ ,  $1s^29d^1$ ,  $1s^210d^1$ , and  $1s^211d^1$   $^2D$  states of  $^7\text{Li}$  determined with respect to the ground  $^2S$  ( $1s^22s^1$ ) state and their comparison with the experimental energies. The comparison also includes the results for the  $1s^25d^1$ ,  $1s^26d^1$ , and  $1s^27d^1$  states taken from Ref. 2. Only the results of the calculations performed with the largest basis set used for each state are shown.

		$1s^25d^1$	$1s^26d^1$	$1s^27d^1$	$1s^28d^1$	$1s^29d^1$	$1s^210d^1$	$1s^211d^1$	$1s^2\infty d^1$ <sup>b</sup>
$^7\text{Li}$	Calculated <sup>a</sup>	39 092.35	40 434.73	41 244.04	41 769.29	42 129.41	42 386.96	42 577.64	43 484.60
	Experiment <sup>1</sup>	39 094.93	40 437.31	41 246.5	41 771.3	42 131.3	42 389.	42 578.	43 487.15
	$\Delta^c$	-2.58	-2.58	(-2.5)	(-2.0)	(-1.9)	(-2.0)	(0.0)	-2.55
$^6\text{Li}$	Calculated <sup>a</sup>	39 091.80	40 434.17	41 243.48	41 768.71	42 128.78	42 386.35	42 577.01	43 484.00
$^\infty\text{Li}$	Calculated <sup>a</sup>	39 095.62	40 438.12	41 247.50	41 772.78	42 132.88	42 390.48	42 581.15	43 488.22

<sup>a</sup>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.

<sup>b</sup>Energy difference between the ground  $1s^22s^1$  state of Li and the ground  $1s^2$  state of  $\text{Li}^+$ .  $E(^7\text{Li}^+) = -7.279 321 519 72$ ,  $E(^6\text{Li}^+) = -7.279 223 016 09$ , and  $E(^\infty\text{Li}^+) = -7.279 913 412 58$  hartree (from Ref. 12).

<sup>c</sup>Calculated energy difference minus experimental energy difference.

TABLE III. Energy differences (in  $\text{cm}^{-1}$ ) between the  $1s^27d^1$ ,  $1s^28d^1$ ,  $1s^29d^1$ ,  $1s^210d^1$ , and  $1s^211d^1$   $^2D$  states and the  $1s^26d^1$   $^2D$  state of  $^7\text{Li}$ ,  $^6\text{Li}$ , and  $^\infty\text{Li}$ . For  $^7\text{Li}$  we show the convergence of the differences with the basis set size. For  $^6\text{Li}$  and  $^\infty\text{Li}$  we only show the results obtained with the largest basis set used for each state. For  $^7\text{Li}$  the results of the calculations are compared with the experimental values.

	Basis	$1s^26d^1 - 1s^27d^1$	$1s^26d^1 - 1s^28d^1$	$1s^26d^1 - 1s^29d^1$	$1s^26d^1 - 1s^210d^1$	$1s^26d^1 - 1s^211d^1$
$^7\text{Li}$	2500	809.35	1334.69	1695.02	1953.63	2147.85
	3000	809.34	1334.62	1694.87	1953.11	2146.39
	3500	809.33	1334.59	1694.77	1952.78	2144.93
	4000	809.33	1334.58	1694.72	1952.56	2144.10
	4500	809.33	1334.57	1694.69	1952.42	2143.60
	5000		1334.56	1694.67	1952.33	2143.32
	5500		1334.56	1694.65	1952.28	2143.14
	6000		1334.56	1694.65	1952.25	2143.02
	6500		1334.56	1694.64	1952.23	2142.93
	7000			1694.64	1952.21	2142.87
	Experiment <sup>1</sup>	809.2	1334.0	1694.0	1952.0	2141.0
$^6\text{Li}$		809.32	1334.54	1694.61	1952.19	2142.84
$^\infty\text{Li}$		809.39	1334.66	1694.77	1952.36	2143.04

TABLE IV. Energies (in  $\text{cm}^{-1}$ ) of the  $1s^27d^1$ ,  $1s^28d^1$ ,  $1s^29d^1$ ,  $1s^210d^1$ , and  $1s^211d^1$   $^2D$  states of  $^7\text{Li}$  obtained by adding the best values of the calculated  $1s^2nd^1 - 1s^26d^1$  ( $n = 7, \dots, 11$ ) energy differences to the experimental energy of the  $1s^26d^1$  state of  $40\,437.31 \text{ cm}^{-1}$ . Rough estimates of the errors of the calculated energies are given in parentheses.

State	Calculation	Experiment
$1s^27d^1$	41 246.64(1)	41 246.5
$1s^28d^1$	41 771.87(1)	41 771.3
$1s^29d^1$	42 131.95(2)	42 131.3
$1s^210d^1$	42 389.52(10)	42 389.0
$1s^211d^1$	42 580.18(30)	42 578.0

#### IV. RESULTS

While it was sufficient to use 4000 Gaussians in the basis set to achieve the sub  $0.01 \text{ cm}^{-1}$  convergence of the transition energies for the five lowest  $^2D$  Rydberg states of  $^7\text{Li}$ , in the calculations of higher members of the series more basis functions are needed to achieve the satisfactory convergence of the energy. As it is shown in Table I, it takes 6000 Gaussians to have eight digits in the energy of the  $1s^28d^1$  state converge, but even with 7000 Gaussians the seventh digit of the energy of the  $1s^211d^1$  state is not quite yet converged. In Table I we also show the energies for  $^6\text{Li}$  and  $^\infty\text{Li}$  obtained with the basis sets generated for  $^7\text{Li}$  without reoptimization of the Gaussian exponential parameters.

The energies from Table I obtained with the largest basis set generated for each state are used to determine the relative energies with respect to the ground  $1s^22s^1$  state shown in Table II. The comparison of these energies with the  $^7\text{Li}$  experimental values<sup>1</sup> shows that (as mentioned above), where those latter values are available with the accuracy of two significant figures after the decimal point, the calculated/experimental difference is constant and equal to  $-2.58 \text{ cm}^{-1}$ . This difference (see Table II) is, as one can expect, very close to the difference between the calculated and experimental ionization energies of  $^7\text{Li}$  of  $-2.55 \text{ cm}^{-1}$ . In the table, the ground  $1s^2$  state of  $^7\text{Li}^+$  is called  $1s^2\infty d^1$  for consistency. The reason the value of the difference is not exactly equal to  $-2.58 \text{ cm}^{-1}$  can be related to the relativistic and QED effects in the  $1s^2nd^1$  states not being quite yet constant with the  $n$  value at  $n = 11$ .

In order for the refinement procedure to work, the energy difference between the  $1s^26d^1$  state (the highest state for which the experimental energy is determined with two significant digits after the decimal point) and the  $1s^2nd^1$ , where  $n > 6$ , has to be well converged. This convergence is shown in Table III. As one can see, while the values of the difference for the  $n = 7, 8$ , and 9 states are essentially converged, the

convergence for the next state ( $n = 10$ ) is within  $0.03\text{--}0.10 \text{ cm}^{-1}$  and for the  $n = 11$  state it is about  $0.1\text{--}0.3 \text{ cm}^{-1}$ . Clearly, more basis functions are needed to fully converge the energy for this last state. Though it is doable, at present it exceeds the practical limits of our computational capabilities.

The  $(1s^2nd^1 - 1s^26d^1)$  energy differences obtained with the largest basis sets generated for particular states, along with the experimental energy of the  $1s^26d^1$  state and the above-described refinement procedure are used to generate the estimates for the energies of the  $1s^2nd^1$ ,  $n = 7, \dots, 11$ , states. These estimates are compared with the experimental values in Table IV. Based on the convergence patterns we assigned to each energy a rough estimate of the error. The comparison allows us to claim that the refined values of the state energies are more accurate than the experimental counterparts.

#### V. SUMMARY

In conclusion, it should be noted that at present time the above refinement procedure can only be applied to higher Rydberg states where the relativistic and QED contributions to the transition energies between the considered states are negligible. Also, the procedure assumes that relatively high Rydberg state is experimentally very accurately determined (in our case it is the  $1s^26d^1$  state for the  $^2D$  Rydberg series of the  $^7\text{Li}$  atom). The same procedure can also be applied to determine the energies of states not yet experimentally measured such as the  $1s^2nd^1$   $^2D$  Rydberg states of  $^7\text{Li}$  for  $n > 12$ .

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