

Prediction of 2D Rydberg energy levels of ${}^6\text{Li}$ and ${}^7\text{Li}$ based on very accurate quantum mechanical calculations performed with explicitly correlated Gaussian functions

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Very accurate variational nonrelativistic finite-nuclear-mass calculations employing all-electron explicitly correlated Gaussian basis functions are carried out for six Rydberg 2D states ($1s^2nd$, $n = 6, \dots, 11$) of the ${}^7\text{Li}$ and ${}^6\text{Li}$ isotopes. The exponential parameters of the Gaussian functions are optimized using the variational method with the aid of the analytical energy gradient determined with respect to these parameters. The experimental results for the lower states ($n = 3, \dots, 6$) and the calculated results for the higher states ($n = 7, \dots, 11$) fitted with quantum-defect-like formulas are used to predict the energies of 2D $1s^2nd$ states for ${}^7\text{Li}$ and ${}^6\text{Li}$ with n up to 30. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4801855>]

I. INTRODUCTION

Atoms in highly excited Rydberg states are formed in the interstellar medium due to the interaction with ultraviolet and X-rays radiations from various space objects.^{1,2} They are also formed due to interaction with high energy particles in shock waves resulting from supernova explosions and interstellar clouds collisions.³ Thus, astronomers have observed infrared radiation originating from transitions between excited states of Rydberg atoms (RA) (hydrogen, helium, lithium) with the principal quantum numbers varying in a large range of values. Based on the infrared radiation, one can estimate the population of states of the Rydberg atoms in stellar atmospheres, atmospheres of cooling stars (dwarfs), planetary nebulas, and clouds of interstellar gas. In the laboratory methods for investigating RA became widely established in the 1980s.⁴ These methods not only allowed increasing the effectiveness of classical single-photon light excitation but also made it possible to use two-photon excitations in RA studies. There has also been considerable interest in the processes of collisional ionization of highly excited atoms due to its practical use in laser atom cooling, Bose-Einstein condensation, controlling excitation processes of single atoms, creating quantum computer logical units, quantum teleportation, etc. Naturally occurring lithium is composed of two stable isotopes, ${}^6\text{Li}$ and ${}^7\text{Li}$, with the latter being by far the more abundant one: about 92.5% of the atoms. ${}^6\text{Li}$ and ${}^7\text{Li}$ are two of the primordial nuclides that were produced in the Big Bang. A small percentage of ${}^6\text{Li}$ is also known to be produced by nuclear reactions in certain stars.⁵

The NIST atomic spectra database⁶ lists four series of Rydberg states of the ${}^7\text{Li}$ isotope corresponding to the following electronic configurations: $1s^2ns$, $1s^2np$, $1s^2nd$, and $1s^2nf$. Among them there are ten 2D $1s^2nd$ states, with $n = 3, 4, \dots,$

12. In Table I, the experimental energies of these states determined with respect to the 2S $1s^2s$ state taken from Refs. 6 and 7 are listed and it is important to notice that the precision of the measurements decreases as n increases. For the lowest four 2D states of ${}^7\text{Li}$ and ${}^6\text{Li}$, namely, the $1s^23d$, $1s^24d$, $1s^25d$, and $1s^26d$ states, the relative energies with respect to the ground 2S $1s^2s$ state are known from Ref. 7 with the precision of 3–4 significant digits after the decimal point (in wavenumbers). The energies of four higher states of ${}^7\text{Li}$, $1s^27d$, $1s^28d$, and $1s^29d$, are known from Ref. 6 with only one significant digit after the point. The highest states measured, the $1s^210d^1$, $1s^211d^1$, and $1s^212d^1$ states, are reported with no digits after the point.

Recently, we presented a set of high accuracy calculations performed for the lowest nine 2D of the ${}^7\text{Li}$ atom where the relative nonrelativistic energies of the lower states were converged with the accuracy better than 0.01 cm^{-1} .^{8,9} 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. In this work, we have significantly increased the accuracy of the calculations of the upper six of the previously calculated nine 2D states of ${}^7\text{Li}$ by adding more basis functions to the basis set for each state. For example, the basis set for the ninth state ($1s^211d$) now consists of 11 000 Gaussians, up by 4000 from the previously used 7000.⁹ The accuracy achieved in the calculation is now sufficient to extrapolate the energies of the Rydberg 2D $1s^2nd$ states of both ${}^6\text{Li}$ and ${}^7\text{Li}$ up to $n = 30$. In generating the predictions, we use the quantum-defect and other simple related formulas.

Technical details of the algorithms for calculating the energy and the energy gradient used in Refs. 8, 9, and 12, as well as in the present calculations, were presented in our previous works.^{10,11} These algorithms were derived using the nonrelativistic Hamiltonian obtained by explicitly and rigorously

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TABLE I. Experimental energies (in cm^{-1}) of the $1s^2nd$, $n = 3, \dots, 12$, 2D states of ^7Li determined with respect to the ground 2S ($1s^22s$) state.

n	J	$^7\text{Li}^6$	$^7\text{Li}^7$	$^6\text{Li}^7$
3	3/2	31 283.08	31 283.0505(10)	31 282.6062
	5/2	31 283.12	31 283.0866(10)	31 282.6423
4	3/2	36 623.38	36 623.3360(10)	36 622.8217
	5/2	36 623.40	36 623.3511(10)	36 622.8368
5	3/2	39 094.93	39 094.861	39 094.310
	5/2	39 094.94	39 094.869	39 094.318
6	3/2	40 437.31	40 437.220	40 436.633
	5/2	40 437.32	40 437.220	40 436.633
7	3/2, 5/2	41 246.5		
8	3/2, 5/2	41 771.3		
9	3/2, 5/2	42 131.3		
10	3/2, 5/2	42 389.0		
11	3/2, 5/2	42 578.0		

separating out the kinetic energy of the center-of-mass motion from the laboratory all-particle (nucleus+electrons) Hamiltonian. This Hamiltonian, called the internal Hamiltonian, \hat{H}_{int} , has the following form in atomic units:

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

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 (12 786.3933 m_e for ^7Li and 10 961.898 m_e for ^6Li , where $m_e = 1$ is the electron mass), q_0 is its charge, q_i are electron charges, $\mu_i = m_0 m_i / (m_0 + m_i)$ are electron reduced masses, and 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 effect due to the finite-mass of the nucleus using the perturbation approach. Such perturbation approach is used in conventional calculations after the initial nonrelativistic calculations are done with the mass of the nucleus set to infinity. The finite-nuclear-mass (FNM) calculation in this work are performed for the ^6Li and ^7Li isotopes. Infinite-nuclear-mass (INM) calculations are also done by setting the mass of the nucleus in (1) to infinity.

II. BASIS SET AND ITS OPTIMIZATION

The following explicitly correlated Gaussians (ECG) are used in this work to describe the 2D $1s^2nd$ Rydberg states of the Li atom,^{8,9,12}

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

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 (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 of the electron coordinates.

The square-integrability of the Gaussians (2) is enforced by representing the A_k matrix in the following Cholesky-factored form: $A_k = L_k L_k'$, where L_k is a lower triangular matrix with matrix elements ranging from ∞ to $-\infty$. In such a form A_k is automatically positive definite and the Gaussian is square integrable. The elements of the L_k matrices are the parameters which are optimized in the variational energy minimization. It is important that this minimization can be carried out without any constraints.

The Pauli principle requires that the total wave function of the system be antisymmetric with respect to permutations of fermions. In our calculations, we have employed the spin-free formalism that allows to simplify the treatment of the permutational symmetry and deal with just the spatial part of the wave function. In this formalism, one constructs an appropriate symmetry projector acting on the spatial part of the wave function. The construction of the projector can be done using the standard procedure involving Young operators as described, for example, in Ref. 13. For doublet states of lithium, the Young operator can be chosen as: $\hat{Y} = (\hat{1} + \hat{P}_{34})(\hat{1} - \hat{P}_{23})$, where the electrons are labeled as 2, 3, and 4 (the nucleus is labeled as 1), $\hat{1}$ is the identity operator, and \hat{P}_{ij} is the permutation of the i th and j th electron labels. As the internal Hamiltonian (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 states considered in this work has been generated and optimized separately. The optimization involves minimization of the variational energy functional in terms of the L_k parameters and the i_k and j_k indices of the Gaussians. The basis-set growing process starts with a small number of ECGs and involves incremental additions of more functions, optimizing their L_k parameters and the i_k and j_k indices, and then reoptimizing the parameters of all ECGs in the basis set. As mentioned, the analytical gradient is employed in the minimization. A more detailed description of the procedure can be found in our previous works.^{8,9,12} The basis set optimization has been only carried out for the states of the main ^7Li isotope. In the ^6Li and $^\infty\text{Li}$ calculations, we only readjusted the linear coefficients of the ECG wave-function expansion (through the diagonalization of the Hamiltonian/overlap matrix).

Significant computational effort has been invested in increasing and reoptimizing the basis sets for states with $n = 7, \dots, 11$ in comparison with our previous works^{8,9} where the maximal number of ECGs used was 7000. For example, for the $n = 11$ state the basis set was increased to as many as 11 000 functions. The new improved energies for the $n = 7, \dots, 11$ states are shown in Table II. We only show the results obtained with larger basis sets than those used in our previous calculations.^{8,9} As one can see, for all six states the energies are noticeably lower than those calculated before. Particularly improved is the energy of the highest $n = 11$ state. The energies for ^6Li and $^\infty\text{Li}$ computed with the largest basis set generated for a particular state are also shown in Table II.

The results from Table II are used to generate the relative energies of the $n = 7, \dots, 11$ states of ^7Li determined with respect to the ground 2S $1s^22s$ state. They are presented

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

	Basis	$1s^26d$	$1s^27d$	$1s^28d$	$1s^29d$	$1s^210d$	$1s^211d$
^7Li	4500	-7.293 217 739 34					
	5000	-7.293 217 741 43	-7.289 530 182 64				
	5500	-7.293 217 742 68	-7.289 530 186 73				
	6000	-7.293 217 743 45	-7.289 530 189 60				
	6500	-7.293 217 744 03	-7.289 530 191 78				
	7000		-7.289 530 193 38	-7.287 137 047 53			
	7500		-7.289 530 194 37	-7.287 137 050 77	-7.285 496 418 23	-7.284 322 856 22	-7.283 454 285 38
	8000		-7.289 530 195 09	-7.287 137 053 11	-7.285 496 427 09	-7.284 322 897 99	-7.283 454 422 52
	8500		-7.289 530 195 64	-7.287 137 053 47	-7.285 496 434 24	-7.284 322 924 09	-7.283 454 512 88
	9000				-7.285 496 439 63	-7.284 322 944 12	-7.283 454 578 27
	9500					-7.284 322 958 88	-7.283 454 630 82
10 000						-7.283 454 670 69	
10 500						-7.283 454 704 15	
11 000						-7.283 454 730 88	
^6Li	11 000	-7.293 119 059 64	-7.289 431 558 66	-7.287 038 447 80	-7.285 397 855 65	-7.284 224 390 23	-7.283 356 173 46
$^\infty\text{Li}$	11 000	-7.293 810 723 15	-7.290 122 886 01	-7.287 729 556 97	-7.286 088 815 23	-7.284 915 242 80	-7.284 046 946 85

in Table III. The convergence of these relative energies with the number of the basis functions are shown. As one can see, for all considered states, except for the last $n = 11$ one, the energies are converged to better than 0.01 cm^{-1} . The results for ^6Li and $^\infty\text{Li}$ are also shown in Table III.

In our previous work,⁹ it was shown that the difference between the calculated nonrelativistic energies of the 2D $1s^2nd$ $n = 3, \dots, 7$ states of ^7Li and the experimental values⁶ converges to a constant equal to -2.58 cm^{-1} . This happens because the dominant (by far the largest) contribution to the calculated/experimental energy difference comes from relativistic and quantum-electrodynamic (QED) effects

of the lithium core electrons, which become virtually constant as the Rydberg d -electron gets increasingly more excited and diffuse. The difference of -2.58 cm^{-1} , as one can expect, is very close to the difference between the calculated ionization energy (IE) and the experimental IE of ^7Li of -2.55 cm^{-1} . These two values can be viewed as corresponding to the 2D $1s^2nd$ state with $n = \infty$. Based on the constant calculated/experimental energy difference we proposed a refinement procedure for the energies of the states which are measured less precisely in experiment.⁹ The procedure, which simply involves adding -2.58 cm^{-1} to the best nonrelativistic energy value, was applied to refine the energies of the 2D

TABLE III. Calculated nonrelativistic energies (in cm^{-1}) of the $1s^2nd$, for $n = 6, \dots, 11$ and $n = \infty$, 2D states of ^7Li determined with respect to the ground $^2S(1s^22s)^a$ state. Energies of ^6Li and $^\infty\text{Li}$, as well as the $^6\text{Li}/^7\text{Li}$ isotope shifts, are also shown.

	Basis	$1s^26d$	$1s^27d$	$1s^28d$	$1s^29d$	$1s^210d$	$1s^211d$	$1s^2\infty d$
^7Li	4500	40 434.73						
	5000	40 434.73	41 244.06					
	5500	40 434.73	41 244.06					
	6000	40 434.73	41 244.05					
	6500		41 244.05					
	7000		41 244.05	41 769.29				
	7500		41 244.05	41 769.29	42 129.37	42 386.93	42 577.56	
	8000		41 244.05	41 769.29	42 129.36	42 386.92	42 577.53	
	8500		41 244.05	41 769.29	42 129.36	42 386.92	42 577.51	
	9000				42 129.36	42 386.91	42 577.50	
	9500					42 386.91	42 577.49	
10 000						42 577.48		
10 500						42 577.47		
11 000						42 577.46		
								43 484.60
^6Li		40 434.17	41 243.48	41 768.71	42 128.78	42 386.32	42 576.87	43 484.00
Isotopic shift from ^7Li		-0.56	-0.57	-0.58	-0.59	-0.59	-0.59	-0.60
$^\infty\text{Li}$		40 438.11	41 247.50	41 772.77	42 132.88	42 390.45	42 581.01	

^aEnergies of the ground ($1s^22s$) state of Li (in hartrees):¹⁵ $E(^7\text{Li}) = -7.477\,451\,930\,7$, $E(^6\text{Li}) = -7.477\,350\,681\,2$, and $E(^{\infty}\text{Li}) = -7.478\,060\,323\,8$.

$1s^2nd^7\text{Li}$ states with $n = 7, \dots, 11$. The more accurately calculated energies of these states in the present work allow for even more precise refinement. The new, more refined energies for the $n = 7, \dots, 11$ states and the experimental energies for the $n = 3, \dots, 6$ states are now used to predict the energies of states with $n = 12, \dots, 30$. In the extrapolation procedure we use the quantum-defect expression for the energy, as well as two other simple functional forms of the extrapolant. The procedure is described in Sec. III.

III. THE QUANTUM-DEFECT EXTRAPOLATION PROCEDURE

The quantum-defect effect on the energies of Rydberg states of an atom refers to a correction applied to the equation expressing the energies in terms of the principle quantum number to take into account the fact that the inner (core) electrons do not entirely screen the charge of the nucleus in the interaction of the nucleus with the Rydberg electron.¹⁴ The quantum-defect effect is a particularly useful concept in conjunction with highly excited states of the alkalis that contain a single electron in their outer shell. For multi-electron atoms in Rydberg states with a low value of the orbital angular momentum, there is a high probability of finding the excited electron near the nucleus where it can polarize or even penetrate the ion core, modifying the potential. The resulting shift of the energy levels expressed in the atomic units is represented mathematically as an angular-momentum dependent quantum defect, δ_l ,

$$E_n^{(l)} = -\frac{1}{(n - \delta_l)^2}. \quad (3)$$

The largest shift occurs when the orbital angular momentum is equal to zero and decreases when l increases.

In the present work, we employ three quantum-defect-like extrapolation formulas (called Models 1–3). They express relative energies of ${}^2D\ 1s^2nd$ states of ${}^7\text{Li}$ with respect of the ground $1s^22s$ state as a function of n . The use of three different functional forms allows to assess (at least roughly) the accuracy of the extrapolation. The energy is determined as a difference of the excitation limit, which is equal to the ground state energy of ${}^7\text{Li}^+$, minus the quantum-defect-like term. The three models differ in the form of this last term with Model 1 being equivalent to (3), and Models 2 and 3 including some additional n -dependent higher order correction terms. The general formulas for the three models are:

$$\text{Model 1 : } E(n) = a_1 - \frac{b_1}{(n - c_1)^2}, \quad (4)$$

$$\text{Model 2 : } E(n) = a_2 - \frac{b_2}{(n - c_2)^2} + \frac{d_2}{(n + e_2)^3}, \quad (5)$$

and

$$\text{Model 3 : } E(n) = a_3 - \frac{b_3}{(n - c_3 + d_3n^2)^2}, \quad (6)$$

where a_1, b_1, c_1, a_2, b_2 , etc., are adjustable parameters. The parameters are determined by fitting the energies of $n = 3, \dots, 11$ states of ${}^7\text{Li}$. The first four ($n = 3, \dots, 6$) energies

were the experimental values taken from Ref. 6 (as each line is a doublet, an average of the two line frequencies is used), while the next five ($n = 7, \dots, 11$) are obtained from the refinement procedure described above. The $n = \infty$ limit is the experimental energy of ${}^7\text{Li}^+$ ($n = \infty$; IE = 43487.15 cm^{-1}). The fitting resulted in the following $E(n)$ expressions for the three models (in cm^{-1}),

$$\text{Model 1 : } E(n) = 43\,487.15 - \frac{109\,752}{(n - 0.001\,155\,3)^2}, \quad (7)$$

$$\text{Model 2 : } E(n) = 43\,487.15 - \frac{109\,800}{(n - 0.000\,652\,355)^2} + \frac{9133.91}{(n + 16.5388)^3}, \quad (8)$$

and

$$\text{Model 3 : } E(n) = 43\,487.15 - \frac{109\,801}{(n - 0.000\,695\,785 + 2.405\,66 \times 10^{-5}n^2)^2}. \quad (9)$$

Next, expressions (7)–(9) have been used to determine the energies of the ${}^2D\ 1s^2nd$ Rydberg series for $n = 1, \dots, 30$. The results are shown in Table IV.

Next, the approach used for ${}^7\text{Li}$ is applied to predict Rydberg energies for the ${}^2D\ 1s^2nd$ states of ${}^6\text{Li}$. Even though the experimental energy levels of ${}^6\text{Li}$ were measured for the lowest four 2D states (see Table I), we do not use them in the extrapolation. As the calculations performed in this work render nonrelativistic energies of the ${}^6\text{Li}$ isotope (shown in Table III), these energies can be used to determine the isotope shifts of these energies with respect to the energies of ${}^7\text{Li}$. These shifts are also shown in Table III. The shift values should provide very good estimates for the experimental shifts because the missing contributions from the differences in the relativistic corrections (the so-called recoil corrections) and QED corrections between ${}^6\text{Li}$ and ${}^7\text{Li}$ can be expected to be very small. Thus, by adding the nonrelativistic isotope shifts to the best energy values of the ${}^7\text{Li}$ (i.e., the first four experimental, and the next five plus the ${}^6\text{Li}^+$ energy of 43 486.55 cm^{-1} obtained from the refinement procedure) one can obtain very good estimates of the energy levels for ${}^6\text{Li}$. These estimates are used in conjunction with Eqs. (4)–(6) to obtain parameters for Models 1–3, which, in turn, are used to predict the energy levels of the ${}^6\text{Li}\ {}^2D1s^2nd$ Rydberg series for $n = 12, \dots, 30$. This has been done and the following extrapolants have been generated:

$$\text{Model 1 : } E(n) = 43\,486.55 - \frac{109\,751}{(n - 0.001\,153\,02)^2}, \quad (10)$$

$$\text{Model 2 : } E(n) = 43\,486.55 - \frac{109\,677}{(n - 0.001\,033\,06)^2} - \frac{1080.17}{(n + 1.908\,09)^3}, \quad (11)$$

TABLE IV. The energies (in cm^{-1}) of the Rydberg $1s^2nd$, $n = 3, \dots, 30$, states for ${}^6\text{Li}$ and ${}^7\text{Li}$ obtained from the three quantum-defect-like formulas (Models 1–3) discussed in the text. The energies are relative to the ${}^2S\ 1s^2s$ ground states of the respective isotopes. The “fitted data” are the points used to obtain the quantum-defect extrapolation formulas (see text). For ${}^7\text{Li}$ the first four ($n = 3, \dots, 6$) energies of the fitted data are the experimental energies and the next five ($n = 7, \dots, 11$) are energies obtained by adding $2.58\ \text{cm}^{-1}$ to the nonrelativistic energies from in Table III. For ${}^6\text{Li}$ the fitted data are obtained by adding the calculated isotope shifts to the ${}^7\text{Li}$ data.

n	${}^7\text{Li}$				${}^6\text{Li}$			
	Model 1	Model 2	Model 3	Data	Model 1	Model 2	Model 3	Data
3	31 283.09	31 283.07	31 283.14	31 283.10	31 282.62	31 282.68	31 282.70	31 282.66
4	36 623.69	36 623.47	36 623.52	36 623.38	36 623.16	36 622.96	36 623.00	36 622.88
5	39 095.04	39 094.92	39 094.94	39 094.94	39 094.48	39 094.38	39 094.39	39 094.38
6	40 437.31	40 437.28	40 437.30	40 437.32	40 436.74	40 436.73	40 436.73	40 436.75
7	41 246.57	41 246.62	41 246.62	41 246.63	41 246.00	41 246.06	41 246.05	41 246.06
8	41 771.78	41 771.86	41 771.87	41 771.87	41 771.20	41 771.29	41 771.29	41 771.29
9	42 131.84	42 131.95	42 131.96	42 131.94	42 131.25	42 131.37	42 131.38	42 131.35
10	42 389.38	42 389.50	42 389.52	42 389.49	42 388.79	42 388.91	42 388.93	42 388.90
11	42 579.92	42 580.04	42 580.07	42 580.04	42 579.33	42 579.46	42 579.48	42 579.45
12	42 724.84	42 724.96	42 724.99		42 724.24	42 724.37	42 724.41	
13	42 837.61	42 837.74	42 837.78		42 837.02	42 837.14	42 837.19	
14	42 927.10	42 927.21	42 927.26		42 926.50	42 926.62	42 926.67	
15	42 999.29	42 999.40	42 999.45		42 998.69	42 998.81	42 998.86	
16	43 058.37	43 058.47	43 058.53		43 057.77	43 057.88	43 057.94	
17	43 107.33	43 107.43	43 107.50		43 106.74	43 106.84	43 106.90	
18	43 148.37	43 148.46	43 148.53		43 147.77	43 147.86	43 147.93	
19	43 183.09	43 183.18	43 183.25		43 182.49	43 182.58	43 182.65	
20	43 212.74	43 212.82	43 212.89		43 212.14	43 212.23	43 212.30	
21	43 238.25	43 238.33	43 238.40		43 237.65	43 237.73	43 237.81	
22	43 260.37	43 260.44	43 260.51		43 259.77	43 259.84	43 259.92	
23	43 279.66	43 279.72	43 279.80		43 279.06	43 279.13	43 279.21	
24	43 296.59	43 296.65	43 296.73		43 295.99	43 296.06	43 296.14	
25	43 311.53	43 311.59	43 311.67		43 310.93	43 311.00	43 311.07	
26	43 324.78	43 324.83	43 324.92		43 324.18	43 324.24	43 324.32	
27	43 336.59	43 336.64	43 336.72		43 335.99	43 336.05	43 336.12	
28	43 347.15	43 347.20	43 347.28		43 346.55	43 346.61	43 346.68	
29	43 356.64	43 356.68	43 356.77		43 356.04	43 356.09	43 356.17	
30	43 365.19	43 365.24	43 365.32		43 364.60	43 364.65	43 364.72	
∞	43 487.15	43 487.15	43 487.15	43 487.15	43 486.55	43 486.55	43 486.55	43 486.55
Max. error	0.2959	0.0753	0.1307		0.2763	0.0776	0.1214	
RMS error	0.1288	0.0296	0.0483		0.1247	0.0289	0.0469	
Mean abs. error	0.1006	0.0200	0.0313		0.1032	0.0185	0.0332	

and

Model 3 :

$$E(n) = 43\,486.55 - \frac{109\,801}{(n - 0.000\,681\,077 + 2.460\,71 \times 10^{-5}n^2)^2}. \quad (12)$$

The energies of the ${}^6\text{Li}$ energy levels obtained using (10)–(12) are given in Table IV.

Naturally, the model with the largest number of free parameters (Model 2) provides the best fit to the original data (energies of the $n = 3, \dots, 11$ states) in Table IV. The discrepancy between the energies of $n = 12, \dots, 30$ states predicted with the different models does not exceed $0.1\text{--}0.2\ \text{cm}^{-1}$. The accuracy of the present predictions can also be evaluated by comparing the experimental values of the lowest four ${}^2D\ 1s^2nd$ states of ${}^6\text{Li}$ with the measured quantities from Ref. 7. For example, for the lowest state, the values pre-

dicted by Models 1, 2, and 3 are $31\,282.62$, $31\,282.68$, and $31\,282.70\ \text{cm}^{-1}$, respectively, while the measured value is $31\,282.6243\ \text{cm}^{-1}$ (this value is an average of two doublet lines). For the fourth state the corresponding predicted values are $40\,436.74$, $40\,436.73$, and $40\,436.73\ \text{cm}^{-1}$ from Models 1, 2, and 3, respectively, while the experimental value is $40\,436.633\ \text{cm}^{-1}$. This seems to indicate that the accuracy of the present prediction is of the order of $0.1\text{--}0.2\ \text{cm}^{-1}$. We believe that such accuracy is sufficient for the present predictions to be useful in guiding the experimental measurements of yet unmeasured 2D energy levels of ${}^6\text{Li}$ and ${}^7\text{Li}$.

IV. SUMMARY

An approach which combines high-accuracy quantum mechanical calculations, the experimental data, and the quantum-defect extrapolation formulas has been employed to predict the energies of ${}^2D\ 1s^2nd$ Rydberg states of the ${}^6\text{Li}$ and ${}^7\text{Li}$ isotopes. The calculations have been performed with

all-electron explicitly correlated Gaussian functions, whose nonlinear parameters have been extensively optimized using a method involving analytically calculated energy gradient. The predictions concern the states with $n = 12, \dots, 30$. The predicted energy values can guide experimental measurements of these quantities.

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