

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

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(Received 8 March 2013; published 18 April 2013)

Accurate variational quantum-mechanical calculations are performed for the nine lowest 2S ($1s^2ns$), $n = 2, \dots, 10$ states of the lithium atom. The effect of the finite nuclear mass is explicitly included in the calculations allowing for the determination of the isotopic shifts of the energy levels. The wave functions of the states are expanded in terms of all-electron explicitly correlated Gaussian functions and their exponential parameters are variationally optimized with the aid of the analytical energy gradient determined with respect to those parameters. The experimental results for the lower states ($n = 3, \dots, 6$) and the calculated results for the higher states ($n = 7, \dots, 10$) fitted with quantum-defect-like formulas are used to predict the energies of 2S $1s^2ns$ states for ${}^7\text{Li}$ and ${}^6\text{Li}$ with n up to 30.

DOI: [10.1103/PhysRevA.87.042510](https://doi.org/10.1103/PhysRevA.87.042510)

PACS number(s): 31.15.ac, 31.15.V–

I. INTRODUCTION

High-precision calculations of energy levels for lithium and lithiumlike ions have been a subject of several recent works [1–10]. We have also contributed to this effort [11–13]. The most accurate calculations have included leading relativistic and quantum electrodynamics (QED) corrections of orders $O(\alpha^4 mc^2)$, $O(\alpha^5 mc^2)$, $O((m/M)\alpha^4 mc^2)$, and $O((m/M)\alpha^5 mc^2)$. Particularly accurate have been the calculations involving Hylleraas basis functions, because these functions describe very well the medium- and long-range electron correlation, as well as the behavior of the wave function at short and contact ranges of the electron-electron and electron-nucleus distances. High-accuracy atomic calculations can also be performed with all-electron explicitly correlated Gaussian functions (ECG). These functions are currently the only viable alternative to perform such calculations for atoms with more than three electrons. Moreover, even for atoms with just three electrons, ECG calculations for some higher excited states, especially involving electrons with nonzero angular momenta, are more accurate than Hylleraas calculations. An example of such a case are our recent ECG calculations of nine 2D Rydberg excited states of lithium [12,13] where the most accurate transition energies available in the literature were obtained.

It should also be mentioned that, as the transition energies associated with higher excited states are accurately measured in experiment mainly due to weak intensities of the corresponding spectral lines, calculations performed with Gaussians are sufficiently accurate to provide valuable assistance to experimental attempts to remeasure these lines with higher accuracy. For example, the calculations of the lithium 2D states [12,13] allowed refining some higher transition energies whose measurements were significantly less accurate than the transitions involving the lowest states.

In this work we continue to use the highly accurate predictive ability of the ECG calculations to determine the

energies of the still unmeasured 2S states of ${}^7\text{Li}$ and ${}^6\text{Li}$. The NIST atomic spectra database [14] 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 2S $1s^2ns$ states, with $n = 2, 3, \dots, 11$. In Table I the experimental energies of these states determined with respect to the 2S $1s^2s$ state taken from Refs. [14,15] are listed and it is important to notice that the precision of the measurements decreases as n increases. The measured energies of ${}^6\text{Li}$ [15] are also shown. For the lowest four 2S states of ${}^7\text{Li}$ and ${}^6\text{Li}$, namely the $1s^23s$, $1s^24s$, $1s^25s$, and $1s^26s$ states, the relative energies with respect to the ground 2S $1s^2s$ state are reported in Ref. [15] with the precision of three to four significant digits after the decimal point (in wave numbers). The energies of three higher states, $1s^27s$, $1s^28s$, and $1s^29s$, are reported [14] with only one significant digit after the point. Two highest states measured, the $1s^210s^1$ and $1s^211s^1$ states, are reported [14] with no digits after the point.

Even though the calculations with ECGs show very high accuracy for the ground and lower-lying states, as the excitation level increases it becomes progressively more difficult to converge the energy and the wave function as tight as for those lower states. Undoubtedly the increasing number of the radial nodes in the wave function is the reason. As the present calculations will show, while less than 5000 ECGs are enough to converge two significant figures after the decimal point in the transition energy of the first 2S excited state, 12 500 ECGs is hardly enough to reach a similar convergence level for the eight excited state.

High accuracy in the ECG calculations can only be achieved if the ECG nonlinear parameters are extensively optimized in the calculations. In this work the ECG basis is variationally optimized independently for each considered state. The optimization employs a procedure that involves the analytical energy gradient determined with respect to the parameters. The use of the gradient significantly accelerates the convergence of the optimization process.

The nonrelativistic Hamiltonian for the lithium atom representing the internal state of the system (we call it

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TABLE I. Experimental energies (in cm^{-1}) of the $1s^2ns$, $n = 2, \dots, 11$ and $n = \infty$, 2S states of ${}^7\text{Li}$ and ${}^6\text{Li}$ (from Refs. [14] and [15]), determined with respect to the ground 2S ($1s^22s$) state.

n	${}^7\text{Li}$ [14]	${}^7\text{Li}$ [15]	${}^6\text{Li}$ [15]
2	0.	0.	0.
3	27 206.12	27 206.095 2	27 205.712 9
4	35 012.06	35 012.032 6	35 011.543 2
5	38 299.50	38 299.462 7	38 298.928 3
6	39 987.64	39 987.586(3)	39 987.027
7	40 967.9		
8	41 587.1		
9	42 003.3		
10	42 298.		
11	42 510.		
∞	43 487.150		

“internal Hamiltonian,” \hat{H}_{int}) used in the present work is obtained by separating out the center-of-mass motion from the laboratory-coordinate-system Hamiltonian (for more details see, for example, Ref. [16]). The separation is rigorous and leads to the following \hat{H}_{int} expressed in atomic units:

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

where \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), $q_0 = +3$ is its charge, $q_i = -1$ are electron charges, and $\mu_i = m_0 m_i / (m_0 + m_i)$ are electron reduced masses. For a four-particle (three-electron) atom $n = 3$. The prime indicates the matrix or vector transpose.

The internal Hamiltonian (1) explicitly depends on the mass of the nucleus. Thus, the calculated energy levels for different isotopes are slightly shifted with respect to each other. The shifts can be directly determined from the variational calculations without resorting to additional perturbation-theory calculations, which are typically done following infinite-mass calculations to determine the mass effects. The mass-dependent internal Hamiltonian can also be used to calculate the energy spectrum for an atom with an infinite nuclear mass (in this case ${}^\infty\text{Li}$). As such calculations can be directly compared with previous literature results, they are also performed in this work.

II. CALCULATIONS

The all-electron explicitly correlated Gaussians (ECGs) used in this work to describe the 2S states of the Li atom have the following form:

$$\phi_k = \exp[-\mathbf{r}' (A_k \otimes I_3) \mathbf{r}], \quad (2)$$

where A_k 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. Gaussians (2) are square integrable if the A_k matrix is positive definite. To assure this requirement is always met we use the following Cholesky-factored form of A_k : $A_k = L_k L_k'$, where L_k is a lower triangular matrix. Even if the values of the L_k matrix elements vary from ∞ to $-\infty$, A_k in the form of $L_k L_k'$ is automatically positive definite and the Gaussian is square integrable. Thus it is convenient to replace the elements of the A_k matrices by the elements of the L_k matrices as the variational parameters because then the optimization can be carried out without any constraints. This helps to expedite the calculations.

The proper permutational symmetry of the wave function is implemented by acting with a projection operator on each basis function. In constructing this operator we use the so-called spin-free formalism involving standard Young operators as described, for example, in Ref. [17]. For 2S states of lithium, the Young operator can be chosen as $\hat{Y} = (\hat{1} + \hat{P}_{23})(\hat{1} - \hat{P}_{12})$, where 1, 2, and 3 are electron labels, and \hat{P}_{ij} permutes the spatial coordinates of the i th and j th electron. As the internal Hamiltonian (1) commutes with all electron permutations, in the calculation of the overlap and Hamiltonian matrix elements, \hat{Y} needs to be only applied to the *ket* basis function (as $\hat{Y}^\dagger \hat{Y}$).

As mentioned, the basis set optimization has been carried out separately for each of the nine 2S states considered in this work. The optimization was only done for the ${}^7\text{Li}$ isotope. In the calculations for the ${}^6\text{Li}$ isotope, as well as for ${}^\infty\text{Li}$, the ${}^7\text{Li}$ basis sets were used without reoptimization of the nonlinear parameters. Because the change in the total wave function is quite small when the mass of the nucleus is varied, it is sufficient to adjust only the linear coefficient of the basis functions.

The final basis set for each of the considered states have been generated in a basis set growing process. It starts with a small set of randomly chosen functions and involves incremental addition of new functions. The new functions are added to the basis set one by one and their nonlinear L_k parameters are variationally optimized using the analytic gradient of the energy. The initial values of these parameters are obtained from randomly perturbing the parameters of the functions already included in the set and selecting the function which lowers the energy the most when added to the basis. After a certain number of functions (usually 100) is added to the basis set, all functions in the set are reoptimized. The reoptimization involves cycling over all functions, one by one, several times and reoptimizing them with the gradient-based approach.

An important issue in the optimization is preventing linear dependencies between the basis functions to form when their exponential parameters are optimized. Linear dependencies are undesirable because they may cause the precision of the calculation to decrease and, in extreme cases, the results (energy) become unphysical. There are several reasons why linear dependencies may appear in variational calculations. The most common one is that the basis functions are not perfectly well suited for expanding the eigenfunctions of the atomic Schrödinger equation (for example, due to their incorrect cusp and long-distance behavior). The variational procedure may try to generate clusters of basis functions that mimic functions which better describe those features. For

example, forming a linearly dependent ECG pair, where the two ECGs differ only in terms of one A_k matrix element, is effectively generating the first derivative of the Gaussian with respect to that element. If, for example, this element is the first element on the diagonal of A_k , the derivative is equal to the original Gaussian multiplied by \mathbf{r}_1^2 . As such function vanishes at $\mathbf{r}_1 = 0$, it may help to describe the behavior of the wave function near the nucleus-electron contact point. In a similar way functions approximating products of Gaussians by squares of the interelectron distances, \mathbf{r}_{ij}^2 , can be generated. Such functions can help better describe the interelectronic cusps. Thus, certain deficiencies of basis functions can cause linear dependencies to appear in the calculation.

In view of the above, a procedure has to be devised to prevent linear dependencies to form in the basis set in the variational optimization of the ECG exponential parameters, because if they do form, the efficiency of the energy minimization usually significantly decreases and numerical noise appears in the energy. As in the majority of cases only ECG pairs become linearly dependent, after a new function is added to the basis set and its exponential parameters are optimized, it is checked for linear dependency with every function already included in the set. If linear dependency is noticed, the function is rejected and replaced by another function. The process continues until the added function, after optimization, does not show linear dependency with any other function in the basis set. A similar procedure is also applied in the cyclic reoptimization of the functions. If after reoptimization of a function linear dependency is found, the parameters of the functions are reset to their values before the reoptimization.

The basis set growing process continues until a certain target level of the energy convergence is reached. As this target level was about the same for all considered states, more ECGs had to be generated for higher states than for lower ones. In the present calculations the target convergence level was set to assure that two digits after the decimal point of the transition energy (expressed in wave numbers) for each state determined with respect to the ground state were converged.

III. CALCULATIONS OF THE ENERGIES OF THE 2S STATES FOR ${}^7\text{Li}$ AND ${}^6\text{Li}$

In the calculations of atoms with ECGs one can hardly expect to reach the level of the energy convergence that is achievable with Hylleraas functions. While in principle very well optimized ECG functions are as good (if not better) as the Hylleraas functions in describing the atomic wave function, the generation of very extended and at the same time thoroughly optimized ECG basis sets is an extremely demanding computational task. For example, our best results obtained for the ground, first-excited, and second-excited 2S states of ${}^\infty\text{Li}$ with 6500 ECGs for the first two states and with 7000 ECGs for the third state of $-7.478\,060\,323\,89$, $-7.354\,098\,421\,39$, and $-7.318\,530\,845\,92$ hartree are off by about 2, 5, and 8 in the 11th digit after the decimal point, respectively, from the best results obtained with 34 020 Hylleraas functions of $-7.478\,060\,323\,910\,146\,894$, $-7.354\,098\,421\,444\,364\,045$, and $-7.318\,530\,845\,998\,906\,901$ hartree [9]. For the seventh excited state, which was the highest state considered in

TABLE II. The convergence of the total variational nonrelativistic finite-nuclear-mass energies (in hartrees) of the $1s^2ns$, $n = 2, \dots, 10$ 2S 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 state.

Basis	$1s^22s$	$1s^23s$	$1s^24s$	$1s^25s$	$1s^26s$	$1s^27s$	$1s^28s$	$1s^29s$	$1s^210s$
${}^7\text{Li}$									
5000	-7.47745193073	-7.35350048810							
5500	-7.47745193074	-7.35350048814							
6000	-7.47745193075	-7.35350048817	-7.31793584244	-7.30295779383					
6500	-7.47745193076	-7.35350048819	-7.31793584249	-7.30295779400					
7000			-7.31793584252	-7.30295779409	-7.29526634559				
7500			-7.31793584254	-7.30295779415	-7.29526634611				
8000					-7.29526634634				
8500						-7.29079946342			
9000						-7.29079946461			
9500						-7.29079946763			
10000						-7.29079946808			
10500							-7.28797724198	-7.28608110814	
11000							-7.28797724403	-7.28608113258	-7.28474604479
11500							-7.28797724539	-7.28608114383	-7.28474607248
12000							-7.28797724640	-7.28608114739	-7.28474610081
12500									-7.28474611908
${}^6\text{Li}$	-7.47735068135	-7.35340097942	-7.31783682131	-7.30285897567	-7.29516763131	-7.29070081262	-7.28787862852	-7.28598255468	-7.28464754405
${}^\infty\text{Li}$	-7.47806032389	-7.35409842139	-7.31853084592	-7.30355157905	-7.29585951046	-7.29139227334	-7.28856982584	-7.28667357553	-7.28533844092
${}^\infty\text{Li}$ [7]	-7.478060323910097	-7.35409842144266	-7.3185308459903	-7.3035515792190	-7.2958595108083	-7.291392274160	-7.288569832747	-7.28667358671	
${}^\infty\text{Li}$ [9]	-7.478060323910146894	-7.354098421444364045	-7.318530845998906901						

TABLE III. Calculated nonrelativistic energies (in cm^{-1}) of the $1s^2ns$, for $n = 3, \dots, 10$ and $n = \infty$, 2S states of ^7Li determined with respect to the ground 2S ($1s^22s$).^a Energies of ^6Li and $^\infty\text{Li}$, as well as the $^6\text{Li}/^7\text{Li}$ isotope shifts, are also shown.

	Basis	$1s^23s$	$1s^24s$	$1s^25s$	$1s^26s$	$1s^27s$	$1s^28s$	$1s^29s$	$1s^210s$	$1s^2\infty s^b$
^7Li	5000	27 204.20								
	5500	27 204.20								
	6000	27 204.20	35 009.73	38 297.04						
	6500	27 204.20	35 009.73	38 297.04						
	7000		35 009.73	38 297.04	39 985.11					
	7500		35 009.73	38 297.04	39 985.11					
	8000				39 985.11					
	8500				39 985.11	40 965.48				
	9000					40 965.48				
	9500					40 965.48				
	10 000					40 965.48	41 584.89	42 001.04		
	10 500						41 584.89	42 001.04		
	11 000						41 584.89	42 001.03	42 294.05	
	11 500						41 584.89	42 001.03	42 294.05	
	12 000								42 294.04	
12 500								42 294.04		
										43 484.60
^6Li		27 203.82	35 009.25	38 296.50	39 984.56	40 964.91	41 584.31	42 000.45	42 293.45	43 484.00
Isotopic shift from ^7Li		-0.38	-0.49	-0.53	-0.56	-0.57	-0.58	-0.58	-0.59	-0.60
$^\infty\text{Li}$		27 337.72	35 012.67	38 300.24	39 988.46	40 968.90	41 718.41	42 004.54	42 297.56	42 581.01

^aCalculated relative to the ground 2S $1s^22s$ 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 [19].

^bEnergy difference between the ground 2S $1s^22s$ state of Li and the ground 1S $1s^2$ state of 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 [20]).

the previous calculations [7], our $^\infty\text{Li}$ energy obtained with 11 500 ECGs of $-7.286\,673\,575\,53$ hartree is off from the best previous result of $-7.286\,673\,586\,71$ hartree by 1 in the eighth place after the decimal point. A similar accuracy can be expected of the energy of the eighth excited state, whose energy obtained in our calculations with 12 500 ECGs is $-7.285\,338\,440\,92$ hartree. This state has never been calculated before. Even though the accuracy of the energy in the ECG calculations noticeably decreases with the increasing excitation level, the accuracy achieved in the present calculations is sufficient for the purpose of the present study.

In order to extrapolate the energies of the 2S $1s^2ns$, $n = 2, \dots, 10$ states of ^7Li to higher n values these energies have to be very well converged. Therefore, in the first part of the present work significant computational effort has been invested in generating and optimizing the basis sets for the nine considered states. The energies obtained for the states are shown in Table II. The energies for ^6Li and $^\infty\text{Li}$ computed with the largest basis set generated for the particular states are also shown in Table II.

The results from Table II are used to generate the relative energies of the $n = 3, \dots, 10$ states of ^7Li determined with respect to the ground 2S $1s^22s$ state. They are presented in Table III. The convergence of these relative energies with the number of the basis function is shown. As one can see, for all considered states, except, perhaps, for the last $n = 10$ state, 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 [12,13] 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 values [14] converges to a constant equal to -2.58 cm^{-1} . This happens because the dominant (by far the largest) contribution to the calculated or 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 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 $n = \infty$. To see if a similar trend occurs for the 2S states the differences between the calculated (nonrelativistic) energies and the experimental energies for the $n = 3, \dots, 6$ 2S states of ^6Li and ^7Li are determined and shown in Table IV. As one can see, while these differences also clearly show convergence to the value corresponding to $n = \infty$, the value at $n = 6$ is

TABLE IV. Shifts (in cm^{-1}) of the calculated energies of the $1s^2ns$, for $n = 3, \dots, 6$ and $n = \infty$ 2S states of ^7Li and ^6Li with respect to the experimental energies taken from Ref. [15]. For $n = 7, \dots, 10$ the shifts are determined by extrapolating the $n = 3, \dots, 6$ and $n = \infty$ shifts.

n	^7Li	^6Li
3	-1.8980	-1.8978
4	-2.2979	-2.2976
5	-2.4264	-2.4255
6	-2.472	-2.469
7	-2.5069	-2.5059
8	-2.5223	-2.5216
9	-2.5313	-2.5308
10	-2.5370	-2.5366
∞	-2.5511	-2.5511 ^a

^aFor the experimental $n = \infty$ energy corresponding to ^6Li used in the calculation of this shift the experimental $n = \infty$ energy of ^7Li of $43\,487.150 \text{ cm}^{-1}$ (see Table I) plus the calculated isotopic shift of -0.60 cm^{-1} (see Table III) is used.

still somewhat lower than the value at $n = \infty$. Therefore, to predict the values of the shifts between the experimental and calculated energies for the states with $n = 7, \dots, 10$, which we will need in the next step of this work, we apply an extrapolation. This extrapolation, which is based on the values of the difference for $n = 3, \dots, 6$ and $n = \infty$, results in the values for the difference for the $n = 7, \dots, 10$ states of ${}^6\text{Li}$ and ${}^7\text{Li}$ also shown in Table IV. By adding these values to our best calculated energies for these states, predictions for the experimental energies of these states are generated. These predictions together with the experimental energies for the $n = 3, \dots, 6$ states are employed in the quantum-defect extrapolation procedure (described next) to predict energies of ${}^6\text{Li}$ and ${}^7\text{Li}$ for the value of n up to 30.

IV. 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 principal quantum number to take into account the fact that the inner (core) electrons do not entirely screen with their charges the charge of the nucleus in the interaction of the nucleus with the Rydberg electron [18]. 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 multielectron atoms in Rydberg states with a low value of the orbital angular momentum, there is some 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 two quantum-defect-like extrapolation formulas (called models 1 and 2). They express relative energies of $2S$ $1s^2ns$ states of ${}^7\text{Li}$ with respect to the ground $1s^22s$ state as a function of n . Model 1 is equivalent to (3) and model 2 includes an additional n -dependent higher-order correction term. The general formulas for the two models are

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

and

$$\text{Model 2: } E(n) = a_2 - \frac{b_2}{(n - c_2 + d_2n^2)^2}, \quad (5)$$

where a_1, b_1, c_1, a_2, b_2 , etc., are adjustable parameters. The parameters are determined by fitting the energies of the $n = 3, \dots, 10$ and $n = \infty$ states of ${}^7\text{Li}$. The first four of those energies ($n = 3, \dots, 6$) are the experimental values taken from Ref. [15] (see Table I; as each line is a doublet, an average of the two line frequencies is used), while the next four ($n = 7, \dots, 10$) are obtained from the refinement procedure described above. The $n = \infty$ limit is the experimental energy of ${}^7\text{Li}^+$ ($n = \infty$; IE = 43 487.150 cm^{-1} [14]). The fitting resulted in the following $E(n)$ expressions for the two models (in cm^{-1}):

$$\text{Model 1: } E(n) = 43\,487.150 - \frac{109\,569.357\,225\,05}{(n - 0.405\,172\,165\,284\,388)^2} \quad (6)$$

and

$$\text{Model 2: } E(n) = 43\,487.150 - \frac{109\,126.118\,895\,334}{(n - 0.409\,316\,209\,061\,811 - 0.000\,175\,095\,119\,657\,704n^2)^2}. \quad (7)$$

Expressions (6) and (7) are used to determine the energies of the $2S$ $1s^2ns$ Rydberg series for $n = 11, \dots, 30$. The results are shown in Table V.

Next, the approach is used for $2S$ $1s^2ns$ states of ${}^6\text{Li}$ with only one difference. The energy corresponding to $n = \infty$ used in the extrapolation is not the experimental energy of ${}^6\text{Li}^+$, but the energy obtained by adding the calculated isotopic shift of 0.60 cm^{-1} (shown in Table III) to the experimental energy of ${}^7\text{Li}^+$. The calculated shift value should provide a very good estimate for the experimental shift because the missing contributions from the differences in the relativistic correction (the so-called recoil corrections) and the QED correction between ${}^6\text{Li}$ and ${}^7\text{Li}$ can be expected to be very small. The procedure renders the energy of ${}^6\text{Li}^+$ (this value is equivalent to the energy of the ${}^6\text{Li}$ $2S$ $1s^2ns$ for $n = \infty$) equal to 43 486.55 cm^{-1} . This value is used in the ${}^6\text{Li}$ extrapolants for methods 1 and 2, which have the following form:

$$\text{Model 1: } E(n) = 43\,486.547 - \frac{109\,567.963\,017\,694}{(n - 0.405\,171\,143\,268\,452)^2} \quad (8)$$

and

$$\text{Model 2: } E(n) = 43\,486.547 - \frac{109\,124.897\,586\,163}{(n - 0.409\,313\,628\,571\,568 - 0.000\,175\,028\,793\,281\,85n^2)^2}. \quad (9)$$

TABLE V. The energies (in cm^{-1}) of the Rydberg $1s^2ns$, $n = 3, \dots, 30$, states for ${}^6\text{Li}$ and ${}^7\text{Li}$ obtained from the two quantum-defect-like formulas (models 1 and 2) discussed in the text. The energies are given with respect to the ${}^2S\ 1s^2s$ ground states of the respective isotopes. The columns marked “data” contain the energies used in the fitting of models 1 and 2.

n	${}^7\text{Li}$			${}^6\text{Li}$		
	Model 1	Model 2	Data	Model 1	Model 2	Data
3	27213.60	27207.74	27205.71	27213.99	27208.12	27206.10
4	35007.89	35009.46	35011.54	35008.38	35009.95	35012.03
5	38296.82	38298.58	38298.93	38297.35	38299.12	38299.46
6	39986.21	39987.31	39987.03	39986.77	39987.87	39987.59
7	40967.27	40967.75	40967.42	40967.84	40968.32	40967.99
8	41587.01	41587.02	41586.83	41587.59	41587.60	41587.41
9	42003.31	42003.00	42002.98	42003.90	42003.58	42003.56
10	42296.38	42295.82	42295.99	42296.96	42296.41	42296.57
11	42510.44	42509.73		42511.03	42510.32	
12	42671.55	42670.72		42672.14	42671.32	
13	42795.83	42794.93		42796.43	42795.52	
14	42893.71	42892.75		42894.30	42893.35	
15	42972.17	42971.18		42972.76	42971.77	
16	43036.02	43035.01		43036.62	43035.61	
17	43088.68	43087.66		43089.28	43088.26	
18	43132.62	43131.60		43133.22	43132.20	
19	43169.66	43168.65		43170.26	43169.25	
20	43201.18	43200.17		43201.78	43200.77	
21	43228.22	43227.22		43228.82	43227.82	
22	43251.59	43250.60		43252.19	43251.20	
23	43271.93	43270.96		43272.53	43271.56	
24	43289.74	43288.78		43290.34	43289.38	
25	43305.41	43304.47		43306.02	43305.07	
26	43319.29	43318.36		43319.89	43318.96	
27	43331.63	43330.72		43332.23	43331.32	
28	43342.66	43341.76		43343.26	43342.36	
29	43352.55	43351.66		43353.15	43352.26	
30	43361.45	43360.58		43362.05	43361.18	
∞	43486.55	43486.55	43486.55	43487.15	43487.15	

They are used to predict the energy levels of the ${}^6\text{Li}\ 2S\ 1s^2ns$ Rydberg series for $n = 11, \dots, 30$. The results are shown in Table V.

Naturally, the model with the larger number of free parameters (model 2) provides the best fit to the original data (energies of the $n = 3, \dots, 10$ and $n = \infty$ states) in Table V. The maximal discrepancy between the energies of $n = 12, \dots, 30$ states predicted with the two models are of the order of $1.0\ \text{cm}^{-1}$. Due to the somewhat higher flexibility of model 2, the values obtained using it are probably more reliable than the values obtained with model 1. This flexibility is likely needed more to predict the energies of the 2S Rydberg states than to predict states where the Rydberg electron has a nonzero angular momentum (i.e., the 2P , 2D , etc., states), because the s Rydberg electron, particularly for low n value, overlaps more and interacts stronger with the core electrons than p , d , etc., Rydberg electrons. This interaction may require that the simple quantum-defect formula, Eq. (3), is corrected by an additional term such as the one which differentiates model 1 from model 2. We believe that the accuracy of the present predictions is sufficient for them to be useful in guiding the experimental

measurements of yet unmeasured 2S energy levels of ${}^6\text{Li}$ and ${}^7\text{Li}$.

V. SUMMARY

An approach which combines high-accuracy quantum-mechanical (QM) calculations, the experimental data, and the quantum-defect extrapolation formulas has been employed to predict the energies of ${}^2S\ 1s^2ns$ Rydberg states of the ${}^6\text{Li}$ and ${}^7\text{Li}$ isotopes. The QM 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 $n = 11, \dots, 30$. The predicted energy values can guide experimental measurements of these quantities.

ACKNOWLEDGMENT

We are grateful to the University of Arizona Research Computing Center for the use of their computer resources.

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