

Explicitly correlated Gaussian calculations of the ${}^2P^o$ Rydberg spectrum of the lithium atom

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Accurate quantum-mechanical nonrelativistic variational calculations are performed for the nine lowest members of the ${}^2P^o$ Rydberg series ($1s^2np^1$, $n = 2, \dots, 10$) of the lithium atom. The effect of the finite nuclear mass is included in the calculations allowing for determining the isotopic shifts of the energy levels. The wave functions of the states are expanded in terms of all-electron explicitly correlated Gaussian functions. The exponential parameters of the Gaussians are variationally optimized with the aid of the analytical energy gradient determined with respect to those parameters. The calculated state energies are compared with the available experimental data. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3698584>]

I. INTRODUCTION

The last two decades have witnessed significant progress in high-precision calculations of energy levels for lithium and lithiumlike ions.^{1–9} We have also contributed to this effort.^{10–12} The 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 $O((m/M)\alpha^5 mc^2)$ and produced results of unprecedented accuracy. Particularly precise have been the calculations involving Hylleraas and Slater¹³ basis functions because they are capable of very well describing the medium and long range electron correlations. They also have the correct behavior at short electron–electron and electron–nucleus distances. An alternative to using Hylleraas functions in expanding wave functions of ground and excited states of small atoms are all-electron explicitly correlated Gaussian (ECG) functions. These functions are at present the only viable alternative to perform high-accuracy calculations for atoms with more than three electrons. Our ECG calculations on the Be atom¹⁴ demonstrated that an uncertainty of about 0.002 cm^{-1} for the transition energies can be achieved, if an extensive variational optimization of the nonlinear parameters of these functions is performed. Even though this is larger than the uncertainties, which have been achieved in calculations with Hylleraas basis functions for three electron systems, the results obtained with Gaussians can always be improved by adding more basis functions and investing more computational effort in the optimization. As of now, while Hylleraas functions have been generally superior in the calculations of two and three electron atomic systems, the field of high-accuracy calculations of four and five-electron atoms have been dominated by Gaussians. However, even for some types of excited states of the three-electron atoms, the calculations

with Gaussians provided the most accurate transition energies available in the literature. A good example here is the lithium atom, for which the Gaussian calculations provided the most accurate available transition energies of 2D Rydberg states.^{11,12} This may be associated with the higher flexibility of Gaussians in describing rich nodal structures of excited-state wave functions. However, it may also be because the use of Hylleraas functions in high-accuracy calculations of states with higher angular and radially excitations has not yet been scrutinized.

In this work we continue our high-accuracy calculations of yet another group of states of the lithium atom. They are the lowest nine ${}^2P^o$ Rydberg states ($1s^2np$, $n = 2, \dots, 10$). The calculations are performed with all-electron ECGs. The NIST Atomic Spectra Database (NIST ASD) (Ref. 15) provides energies (determined with respect to the ${}^2S(1s^22s)$ ground state) of 41 such states located below the ionization threshold among the total of 182 lithium states. This is by far the largest group of states measured for lithium.

In this work, we employ the variational method with a Hamiltonian, which describes the internal electronic state of the atom and which explicitly depends on the mass of atom's nucleus. The calculations, which involve generating an ECG basis for each studied state, are first performed for the most abundant lithium isotope, ${}^7\text{Li}$. Subsequently, the basis sets generated for the nine ${}^2P^o$ states of ${}^7\text{Li}$ are used in the calculations for ${}^6\text{Li}$, as well as in the calculations of the lithium atom with an infinite nuclear mass (${}^\infty\text{Li}$). The purpose of the latter set of calculations is to generate energies that can be directly compared with the results obtained in conventional nonrelativistic calculations, which are usually performed with the infinite-nuclear-mass approach (i.e., by assuming the Born–Oppenheimer approximation). Such calculations were recently performed for the lowest ${}^2P^o$ state of lithium^{5,8} and resulted in the energy value of $-7.410\,156\,532\,650\,66$ hartree and in an estimate for the exact energy of $-7.410\,156\,532\,651\,6(5)$ hartree. These values

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provide a good reference for the calculations with Gaussians performed in this work.

Recently, we performed high-accuracy nonrelativistic calculations with all-electron ECGs for the lowest six $^2S(1s^2ns)$ (Ref. 16) and the lowest nine $^2D(1s^2nd)$ states^{11,12} of the ^7Li atom. The nonrelativistic energies determined with respect to the $^2S(1s^22s^1)$ ground state for most of those states were converged with the accuracy better than 0.01 cm^{-1} . The results of the calculations allowed for refinement of the experimental energies of some highest states in the two series. The refinement concerned the states whose experimental energies have not been measured as accurately as the energies of the bottom four states in each series.

The high accuracy in the present calculations has been achieved by employing large ECG basis sets and by optimizing the nonlinear parameters of Gaussian with a procedure which employs the analytical energy gradient determined with respect to these parameters. The algorithms for calculating the energy and the energy gradient used in the present $^2P^o$ -state calculations, were presented in our previous work.¹⁷ They have been derived using \hat{H}_{int} , which is obtained by rigorously separating the kinetic energy of the center of mass motion from the laboratory frame Hamiltonian. The separation leads to the following form of \hat{H}_{int} 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 vector connecting the nucleus with the i th electron, r_i is its length, r_{ij} is the distance between electrons i and j , m_0 is the nucleus mass ($12\,786.3933m_e$ for ^7Li and $10\,961.898m_e$ for ^6Li , 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. The prime indicates the matrix/vector transpose.

The lithium $^2P^o$ Rydberg series has been experimentally investigated by several workers. The early work of France¹⁸ reported the energies of the lowest 31 $^2P^o$ states including the states studied in this work. In 1959, Johansson¹⁹ remeasured the lithium spectrum and made some refinements to the energies reported by France. For example, the refinement considerably shifted the energy levels corresponding to $n = 6$ and $n = 8$. In 1995, Radziszewski *et al.*²⁰ made further improvement to the accuracy of the state energies of lithium including five lowest $^2P^o$ states considered in this work. In 2010, Oxley and Collins^{21,22} reported very accurate measurements of eight $1s^2np\ ^2P^o$ states with n ranging from 8 to 15. Three lowest of those states are the top states considered in the present work. The above literature survey shows that only recently a complete set of results for the lower part of the $^2P^o$ Rydberg spectrum became available from high-resolution experiments. This is probably the reason why the NIST Atomic Spectra Database¹⁵ still mostly relies on France's experimental results in listing the energy levels of the $^2P^o$ states of lithium,

even though inaccuracies of those results have been known for some time due to the works performed with the use of the quantum defect (QD) method.^{19,23} The QD method has been particularly useful for detecting inaccuracies in energies of $^2P^o(1s^2np)$ Rydberg states with high n values.

II. METHOD

The all-electron explicitly correlated Gaussians used in this work to describe the $^2P^o$ states of the Li atom have the following form¹⁷:

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

where the electron label i_k can vary from 1 to n , 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. To assure that the Gaussians (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. The values of the L_k matrix elements can vary from ∞ to $-\infty$ and A_k is automatically positive definite and the Gaussian is square integrable. Thus the optimization of the elements of matrices L_k can be carried out without any constraints.

The basis set optimization has been carried out separately for each of the nine $^2P^o$ states considered in this work. As mentioned, it was only done for the ^7Li isotope and then the ^7Li basis sets were reused in the ^6Li and $^\infty\text{Li}$ calculations without reoptimization of the nonlinear parameters (i.e., the L_k matrix elements and the i_k electron indices were kept the same for all isotopes). Our previous experience suggests that readjusting the linear expansion coefficients is sufficient to account for the small variation of the total wave function resulting from the change of the nuclear mass.

Generating the basis set for a particular state was initiated with a small, randomly chosen set of functions and involved incremental addition of new functions and variationally optimizing them with the use of the analytic gradient. The new functions were added to the basis set one by one with L_k parameters chosen as a best guess out of several hundred candidates. The parameters of the candidate functions were generated based on the parameters of the functions already included in the set. After each new function was selected, its i_k index and the L_k parameters were optimized. Next the function was checked for any linear dependency with the functions already included in the basis set and, if such linear dependency appeared, the function was rejected and replaced by a new function. After a certain number of new functions (usually a hundred) was added to the basis set following the above procedure, the whole set was reoptimized by cycling over all functions, one by one, and reoptimizing their L_k parameters. After the parameters of a function were reoptimized, the function was again checked for any linear dependency with all other functions in the set and its parameters were reset to their original values if the linear dependency within a certain predefined threshold occurred. The process of growing the basis set continued until a satisfactory level of the energy convergence for each state was reached. This required a smaller number of functions for lower states and larger for higher states, as the

energy convergence slows down with an increasing excitation level.

The threshold for the energy convergence was set based on the convergence of the relative energy of the state determined with respect to ground $^2S(1s^22s)$ state expressed in wavenumbers. As the aim of the present work was to achieve a similar level of precision as typical to the experimental data listed in NIST ASD (i.e., two digits after the decimal point in the transition energies expressed in wavenumbers) the number of Gaussians in the basis set for each state was increased until two digits in the calculated transition energy of the state were converged. This was achieved for all except the last two states considered in this work, i.e., the $1s^29p$ and $1s^210p$ states, where the final energy convergence was slightly lower and the use of a more extended ECG basis would be desirable. However, due to the practical limits related to the computational resources available for this work, we had to stop increasing the basis sets at a certain point. For the same reason we did not go beyond the $1s^210p$ excited state, even though our approach, in principle, allows to do that.

There is also another issue that needs to be addressed in extending the present calculations to higher excited Rydberg states. It is related to the effectiveness of ECGs (2) used in this work to represent states with wave functions having an increasing number of radial nodes. Such nodes require the use of Gaussians whose maxima are shifted away from the nucleus. For example, multiplying Gaussians (2) by $r_{i_k}^{2m}$ factors, where m is a positive power:

$$\phi_k = z_{i_k} r_{i_k}^{2m} \exp[-\mathbf{r}'(A_k \otimes I_3) \mathbf{r}], \quad (3)$$

would generate such functions. We are currently in the process of implementing Gaussians with the following general form:

$$\phi_k = (q1)_{i_{1k}} (q2)_{i_{2k}} (q3)_{i_{3k}} \exp[-\mathbf{r}'(A_k \otimes I_3) \mathbf{r}], \quad (4)$$

where $(q1)_{i_{1k}}$, $(q2)_{i_{2k}}$, and $(q3)_{i_{3k}}$ are either x , y , or z coordinates of electrons i_{1k} , i_{2k} , and i_{3k} . They will be used to calculate F states of small atoms including ^7Li . However, they can also be used to generate the following Gaussians:

$$\phi_k = z_{i_k} r_{i_k}^2 \exp[-\mathbf{r}'(A_k \otimes I_3) \mathbf{r}]. \quad (5)$$

Combining them with Gaussians (2) would generate a basis which is likely to be better suited to describe higher Rydberg P states than functions (2) alone.

Incidentally, the appearance of linear dependencies in the calculations of the lithium 2P states, which has been more frequent for higher states than for lower ones, is a clear indication of the need for additional types of Gaussians in the basis set. The majority of such linear dependencies involve pairs of Gaussians. If, for example, the two Gaussians in a pair differ (a little) only in terms of a single A_k matrix element and this element is the i th diagonal element, then a linear combination of the two Gaussians with linear coefficients of approximately the same magnitude but with opposite signs mimics Gaussian (2) multiplied by r_i^2 . This is a type-(5) Gaussian. 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 certain types of excitations. Thus, linear dependencies, if they form very

frequently during the variational optimization of the nonlinear parameters, may provide an indication of what type of Gaussians need to be added to basis to improve the convergence.

III. RESULTS

While the accuracy currently achievable with ECG basis functions in the calculations of atoms is lower than that one can get with Hylleraas basis functions, the ECG results are sufficiently accurate for the purpose of the present work. For example, our calculation of the ground 2S state of $^\infty\text{Li}$ with 10,000 basis functions yielded the nonrelativistic energy of $-7.478\,060\,323\,81$ hartree.¹⁰ It is off by one is the tenth figure after the decimal point from the best result obtained with 26 520 Hylleraas functions of $-7.478\,060\,323\,910\,134\,843$ hartree.⁸

At the first step of this work we have tested the accuracy of the ECG variational calculations for the lowest $^2P^o$ state of lithium. Such a test is possible due to the availability of recently published very accurate Hylleraas results for this state.⁸ First, a basis set of 7000 ECGs was generated for ^7Li isotope following the procedure described in Sec. II. As the procedure involves incremental addition of subsets of functions, some basis set with smaller sizes were also generated in the process. Next, these basis sets, as well as the 7000-ECGs basis set, were used to calculate the energy of the lowest $^2P^o$ state of $^\infty\text{Li}$. In Table I our results are compared with the results obtained using a similar number of Hylleraas functions, as well as with the those computed with the largest Hylleraas expansion in Ref. 8. The comparison shows that the Hylleraas basis energies are comparable to the ECG results when the number of basis functions is about the same and that ten significant figures of our best 7000 ECG energy are converged.

TABLE I. The convergence of the total nonrelativistic energy (in hartree) for the lowest $^2P^o$ state ($1s^2p^1$) of $^\infty\text{Li}$ atom with the number of ECG basis functions.

Basis	Energy
1000	-7.410 156 457 19
1500	-7.410 156 512 86
2000	-7.410 156 524 50
2500	-7.410 156 528 79
3000	-7.410 156 530 47
3500	-7.410 156 531 20
4000	-7.410 156 531 58
4500	-7.410 156 531 87
5000	-7.410 156 532 09
5500	-7.410 156 532 22
6000	-7.410 156 532 33
6500	-7.410 156 532 39
7000	-7.410 156 532 44
Ref. 8	
3024	-7.410 156 531 219 66
4824	-7.410 156 532 310 89
7440	-7.410 156 532 558 34
30224	-7.410 156 532 650 66
∞	-7.410 156 532 651 6(5)

The convergence of the total energy in the present calculations for the lowest ${}^2P^o$ state is good enough to determine its relative position with respect to the ground 2S state with the precision better than 0.01 cm^{-1} , which was our target for all nine states considered in the present work.

As mentioned previously, higher excited states normally require progressively more basis functions to describe the increasing number of radial nodes in their wave function. Therefore in the present calculations the number of Gaussians has been increased with the excitation level and reached 9500 for the ninth ${}^2P^o(1s^210p)$ state. The energy convergence with the number of ECGs in the basis set for all nine states ($1s^2np$, $n = 2, \dots, 10$) of ${}^7\text{Li}$ is shown in Table II. As one can see, even with the significant increase of the number of basis functions, the highest two states, i.e., the $1s^29p$ and $1s^210p$ states, are not as tightly converged as the lower ones.

In Table III we show differences between the experimental transition energies determined with respect to the ground ${}^2S(1s^22s)$ state and the calculated transition energies for the nine ${}^2P^o$ states. The differences are shown as they converge with the increasing number of the basis functions. The differences account for the effects not included in the present calculations, e.g., the relativistic and QED effects (the contribution of these effects is the negative of the difference). In the table we also show the experimental energies and the energies calculated with the largest number of Gaussians generated for each state in the present work. Upon examination of the convergence patterns one can conclude that the energies of the lowest seven of the nine states are converged to the second figure after the decimal point (as intended). For the top two states the convergence is somewhat worse.

The following observations can be made upon examining the results presented in Table III:

- The energy difference between the experimental frequency value and the calculated result (almost) monotonically increases from the value of -2.85 cm^{-1} for the lowest state to the value of -2.53 cm^{-1} for the $1s^210p$ state. One would expect that this latter value should be closer (or identical) to -2.55 cm^{-1} , which is the result corresponding to $n = \infty$, i.e., to the ${}^7\text{Li}^+$ electron affinity. The reason it is not is related to the mentioned slower convergence of the calculated energy for the $1s^210p$ state which resulted in the experimental-theoretical energy difference not to be as tightly converged as for the lower states. The convergence trend observed here for the ${}^2P^o(1s^2np)$ states is very similar the trends previously observed for the ${}^2S(1s^2ns)$ states¹⁶ and for the ${}^2D(1s^2nd)$ states^{11,12} states of lithium.
- Based on the trend, the experimental-theoretical energy difference for the $1s^26p$ state can be expected to already reach the -2.55 cm^{-1} value. However, with respect to the experimental result of Radziszewski *et al.*²⁰ the difference is smaller and equal to -2.53 cm^{-1} while with respect to the experimental result of Johansson the value of the difference is the expected -2.55 cm^{-1} . This seems to suggest that, in this

TABLE II. The convergence of the total nonrelativistic energies for the lowest ${}^2P^o$ states of ${}^7\text{Li}$ with the number of ECG in the basis set. All values are in hartrees.

Basis	$1s^22p$	$1s^23p$	$1s^24p$	$1s^25p$	$1s^26p$	$1s^27p$	$1s^28p$	$1s^29p$	$1s^210p$
${}^7\text{Li}$	4000	-7.409 557 757 96	-7.336 556 361 97	-7.311 295 097 76	-7.299 694 895 41	-7.293 427 170 03	-7.289 662 221 97	-7.287 225 326 50	-7.285 557 655 56
	4500	-7.409 557 758 24	-7.336 556 362 45	-7.311 295 098 99	-7.299 694 897 90	-7.293 427 175 82	-7.289 662 243 86	-7.287 225 426 91	-7.285 557 960 87
	5000	-7.409 557 758 46	-7.336 556 362 82	-7.311 295 099 85	-7.299 694 899 14	-7.293 427 179 65	-7.289 662 259 59	-7.287 225 494 48	-7.285 558 198 17
	5500	-7.409 557 758 59	-7.336 556 363 05	-7.311 295 100 31	-7.299 694 900 01	-7.293 427 182 19	-7.289 662 271 93	-7.287 225 537 22	-7.285 558 343 47
	6000	-7.409 557 758 60	-7.336 556 363 20	-7.311 295 100 65	-7.299 694 900 64	-7.293 427 183 81	-7.289 662 277 13	-7.287 225 566 29	-7.285 558 458 42
	6500	-7.409 557 758 76			-7.299 694 901 06	-7.293 427 184 72	-7.289 662 281 17	-7.287 225 584 25	-7.285 558 520 88
	7000	-7.409 557 758 81				-7.293 427 185 42	-7.289 662 283 61	-7.287 225 594 03	-7.285 558 563 33
	7500						-7.289 662 285 78	-7.287 225 601 11	-7.285 558 592 88
	8000						-7.289 662 287 34	-7.287 225 607 05	-7.285 558 616 29
	8500							-7.287 225 611 09	-7.285 558 630 54
	9000								-7.284 368 137 45
	9500								-7.284 368 192 21
									-7.284 368 236 16
									-7.284 368 269 71
${}^6\text{Li}^a$		-7.409 458 110 32	-7.336 457 285 19	-7.311 196 253 21	-7.299 596 169 23	-7.293 328 519 60	-7.289 563 662 58	-7.287 127 013 59	-7.285 460 052 05
∞Li^a		-7.410 156 532 44	-7.337 151 707 93	-7.311 889 059 38	-7.300 288 164 88	-7.294 020 052 93	-7.290 254 908 09	-7.287 818 068 01	-7.286 150 973 21

^aCalculated with the largest basis set generated for the particular state of ${}^7\text{Li}$.

TABLE III. Experimental and calculated nonrelativistic transition energies of the lowest nine $2P^o$ states of ${}^7\text{Li}$ determined with respect to the ground ${}^2S(1s^22s)$ state^a and the convergence of the difference between the experimental transition energies and the calculated energies with the number of ECGs. All values are in cm^{-1} .

	$1s^22p$	$1s^23p$	$1s^24p$	$1s^25p$	$1s^26p$	$1s^27p$	$1s^28p$	$1s^29p$	$1s^210p$	$1s^2\infty p$
Experiment										
France ¹⁸	14 903.81	30 925.38	36 469.55	39 015.56	40 390.84	41 217.35	41 751.63	42 118.27	42 379.16	
Johansson ¹⁹	14 903.906 ^b	30 925.632	36 469.79	39 015.71	40 391.31	41 217.58				
Radziszewski <i>et al.</i> ²⁰	14 903.899 6 ^c	30 925.625 3 ^d	36 469.784 3 ^e	39 015.714 6 ^f	40 391.290 ^g					
Oxley & Collins ²¹									42 379.498	
Oxley & Collins ²²							41 752.397	42 118.249		
Reference 15										43 487.15
Calculated	14 901.05	30 923.00	36 467.21	39 013.16	40 388.76	41 215.06	41 749.85	42 115.71	42 376.97	43 484.60
Difference ^h	Basis									
	4000	-2.85	-2.62	-2.57	-2.55	-2.52	-2.51	-2.48	-2.32	-1.58
	4500	-2.85	-2.62	-2.57	-2.56	-2.52	-2.51	-2.51	-2.39	-1.93
	5000	-2.85	-2.62	-2.58	-2.56	-2.53	-2.51	-2.52	-2.44	-2.14
	5500	-2.85	-2.62	-2.58	-2.56	-2.53	-2.51	-2.53	-2.47	-2.26
	6000	-2.85	-2.62	-2.58	-2.56	-2.53	-2.52	-2.54	-2.50	-2.35
	6500	-2.85			-2.56	-2.53	-2.52	-2.54	-2.51	-2.41
	7000	-2.85				-2.53	-2.52	-2.54	-2.52	-2.46
	7500						-2.52	-2.54	-2.53	-2.49
	8000						-2.52	-2.54	-2.53	-2.50
	8500							-2.55	-2.54	-2.52
	9000									-2.53
	9500									-2.53
										-2.55 ⁱ

^aCalculated relative to the ground $1s^22s^1$ state of Li. $E({}^7\text{Li}) = -7.477\,451\,930\,7$ hartree taken from Ref. 24.

^bGravity center of the ${}^2P_{1/2}$ and ${}^2P_{3/2}$ states with energies 14 903.654 and 14 903.990 cm^{-1} , respectively.

^cGravity center of the ${}^2P_{1/2}$ and ${}^2P_{3/2}$ states with energies 14 903.648 130(14) and 14 903.983 468(14) cm^{-1} , respectively.

^dGravity center of the ${}^2P_{1/2}$ and ${}^2P_{3/2}$ states with energies 30 925.553 0 and 30 925.649 4 cm^{-1} , respectively.

^eGravity center of the ${}^2P_{1/2}$ and ${}^2P_{3/2}$ states with energies 36 469.754 2 and 36 469.794 3 cm^{-1} , respectively.

^fGravity center of the ${}^2P_{1/2}$ and ${}^2P_{3/2}$ states with energies 39 015.698 8 and 39 015.719 9 cm^{-1} , respectively.

^gGravity center of the ${}^2P_{1/2}$ and ${}^2P_{3/2}$ states with energies 40 391.283 and 40 391.295 cm^{-1} , respectively.

^hCalculated with respect to the most recent experimental result.

ⁱEnergy 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 Ref. 12).

case, Johansson's result is perhaps more accurate than Radziszewski's *et al.* result.

- For the $1s^27p$ state the experimental-theoretical energy difference is -2.52 cm^{-1} instead of the expected -2.55 cm^{-1} . The calculated energy for this state is converged much better than 0.01 cm^{-1} . The experimental-theoretical energy difference is calculated with respect to the result of Johansson,¹⁹ as Radziszewski *et al.* did not measure this state. The slightly lower than expected energy difference seems to suggest that there might be a small inaccuracy of the order of -0.03 cm^{-1} in Johansson's result (this was the highest state measured in his experiment).
- For the $1s^28p$ state the best available experimental results is that of Oxley and Collins.²² The experimental-theoretical energy difference for this state is right where it should be at -2.55 cm^{-1} . One should note a significant difference between the experimental energies for this state reported by Oxley and Collins²² and by France.¹⁸ A similar large energy difference also appears for the $1s^27p$ state.

- For the $1s^29p$ and $1s^210p$ states the experimental-theoretical energy differences are, as mentioned, not completely converged. However, as one can see in Table III, with inclusion of more basis functions in the calculations for these states, the differences should converge to values very close to the expected -2.55 cm^{-1} .

For completeness of the present computational work, in Table IV we also show commonly computed expectation values of the powers of the interparticle distances and Dirac delta-functions (contact densities). As expected, upon increasing the excitation level both the average nucleus–electron and electron–electron distances rapidly increase. There are some slight differences between the values of the average distances for ${}^6\text{Li}$ and ${}^7\text{Li}$. Due to the reduced mass of the electron being slightly smaller for ${}^6\text{Li}$ than for ${}^7\text{Li}$, both nucleus–electron and electron–electron distances are slightly longer for the former system. For example, for the highest $1s^210p$ state considered in the present calculations, the expectation values of r_{ne} for ${}^7\text{Li}$ and ${}^6\text{Li}$ are 49.587 03 and

TABLE IV. Expectation values of some low positive and negative powers of the interparticle distances and Dirac δ -functions. All values are in atomic units.

Isotope	State	$\langle 1/r_{ne}^2 \rangle$	$\langle 1/r_{ee}^2 \rangle$	$\langle 1/r_{ne} \rangle$	$\langle 1/r_{ee} \rangle$	$\langle r_{ne} \rangle$	$\langle r_{ee} \rangle$	$\langle r_{ne}^2 \rangle$	$\langle r_{ee}^2 \rangle$	$\langle \delta(\mathbf{r}_{ne}) \rangle$	$\langle \delta(\mathbf{r}_{ee}) \rangle$
⁷ Li	² S(1s ² 2p)	9.965 409	1.421 675	1.879 488	0.698 759	1.957 221	3.470 853	9.316 964	18.684 89	4.557 526	0.177 393
	² S(1s ² 3p)	9.954 327	1.378 225	1.830 211	0.599 596	4.408 927	8.354 911	56.50 759	113.043 1	4.563 874	0.177 743
	² S(1s ² 4p)	9.951 867	1.367 909	1.813 225	0.565 478	7.861 757	15.254 39	190.905 3	381.830 9	4.565 465	0.177 832
	² S(1s ² 5p)	9.951 023	1.364 289	1.805 440	0.549 858	12.314 85	24.157 86	481.576 6	963.170 2	4.565 818	0.177 876
	² S(1s ² 6p)	9.950 657	1.362 703	1.801 240	0.541 435	17.768 07	35.062 88	1 017.592	2 035.300	4.566 012	0.177 891
	² S(1s ² 7p)	9.950 473	1.361 902	1.798 719	0.536 381	24.221 41	47.968 73	1 908.029	3 816.074	4.565 976	0.177 924
	² S(1s ² 8p)	9.950 369	1.361 454	1.797 088	0.533 114	31.674 96	62.875 29	3 281.991	6 563.995	4.565 334	0.177 959
	² S(1s ² 9p)	9.950 305	1.361 188	1.795 973	0.530 880	40.129 78	79.784 56	5 288.883	10 577.78	4.564 367	0.178 108
	² S(1s ² 10p)	9.950 262	1.361 019	1.795 177	0.529 285	49.587 03	98.698 82	8 098.424	16 196.86	4.563 019	0.178 186
	⁶ Li	² S(1s ² 2p)	9.965 145	1.421 642	1.879 464	0.698 752	1.957 237	3.470 879	9.317 111	18.685 18	4.557 345
² S(1s ² 3p)		9.954 063	1.378 193	1.830 187	0.599 589	4.408 971	8.354 992	56.508 67	113.045 3	4.563 694	0.177 736
² S(1s ² 4p)		9.951 603	1.367 877	1.813 201	0.565 471	7.861 842	15.254 55	190.909 3	381.839 0	4.565 285	0.177 825
² S(1s ² 5p)		9.950 759	1.364 257	1.805 416	0.549 852	12.314 99	24.15 813	481.587 3	963.191 6	4.565 638	0.177 869
² S(1s ² 6p)		9.950 393	1.362 671	1.801 216	0.541 428	17.768 28	35.063 28	1 017.615	2 035.246	4.565 832	0.177 884
² S(1s ² 7p)		9.950 209	1.361 870	1.798 695	0.536 375	24.221 69	47.969 28	1 908.073	3 816.161	4.565 796	0.177 918
² S(1s ² 8p)		9.950 106	1.361 422	1.797 064	0.533 107	31.675 31	62.875 98	3 282.065	6 564.143	4.565 154	0.177 953
² S(1s ² 9p)		9.950 041	1.361 156	1.795 949	0.530 873	40.130 17	79.785 33	5 288.992	10 578.00	4.564 186	0.178 102
² S(1s ² 10p)		9.949 999	1.360 987	1.795 153	0.529 279	49.587 40	98.699 54	8 098.564	16 197.14	4.562 838	0.178 180
[∞] Li		² S(1s ² 2p)	9.967 000	1.421 872	1.879 635	0.698 802	1.957 121	3.470 696	9.316 079	18.683 16	4.558 612
	² S(1s ² 3p)	9.955 913	1.378 419	1.830 357	0.599 636	4.408 662	8.354 424	56.500 93	113.029 8	4.564 960	0.177 783
	² S(1s ² 4p)	9.953 451	1.368 102	1.813 370	0.565 516	7.861 249	15.253 42	190.880 8	381.782 0	4.566 550	0.177 871
	² S(1s ² 5p)	9.952 606	1.364 481	1.805 585	0.549 896	12.314 02	24.156 25	481.512 0	963.041 2	4.566 902	0.177 915
	² S(1s ² 6p)	9.952 240	1.362 896	1.801 384	0.541 472	17.766 85	35.060 48	1 017.452	2 034.920	4.567 096	0.177 931
	² S(1s ² 7p)	9.952 056	1.362 094	1.798 863	0.536 418	24.219 74	47.965 42	1 907.764	3 815.543	4.567 060	0.177 964
	² S(1s ² 8p)	9.951 953	1.361 647	1.797 232	0.533 150	31.672 86	62.871 14	3 281.546	6 563.106	4.566 418	0.177 999
	² S(1s ² 9p)	9.951 888	1.361 380	1.796 117	0.530 916	40.127 45	79.779 95	5 288.230	10 576.47	4.565 450	0.178 148
	² S(1s ² 10p)	9.951 846	13.612 11	1.795 321	0.529 321	49.584 85	98.694 50	8 097.585	16 195.18	4.564 102	0.178 226

49.587 40 a.u., respectively. The corresponding values for the r_{ee} expectation values are 98.698 82 and 98.699 54 a.u., respectively. Also, for the same reason, the expectation values of the contact terms, $\delta(\mathbf{r}_{ne})$ and $\delta(\mathbf{r}_{ee})$, are slightly larger for all considered states of ⁷Li than of ⁶Li.

IV. SUMMARY

Accurate nonrelativistic variational calculations have been performed for the nine lowest members of the ²P^o 1s²np series of the lithium atom. For all these nine states experimental transition energies relative to the ground ²S(1s²2s) state are known with precision better than two significant figures after the decimal point. The analysis of the trend of the experimental-theoretical energy differences for these states leads to a suggestion that, perhaps, the most recently obtained energies of two of the states (1s²6p and 1s²7p) may be slightly inaccurate (by 0.03–0.02 cm⁻¹). Thus our theoretical predictions can provide a guide for more accurate remeasurements of the energies of these states.

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