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Absolute term energy of core-excited doublet states of lithium

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Thirteen core-excited lithium doublet states of the ^2P, $^2P^o$, ^2D, and $^2D^o$ symmetries are calculated with a multiconfiguration-interaction wave function. A variation method is used for the bound states whereas the saddle-point and saddle-point complex-rotation methods are used for the autoionizing states. A restricted variation method is used for the saturated wave functions. Fine structures, relativistic corrections, and mass polarization corrections are calculated. The quantum electrodynamic corrections are also estimated. The absolute term energy is predicted with an uncertainty which is much smaller than that in the literature. Among these core-excited states, ten doublet-doublet transitions and one doublet-quartet transition have been measured. The largest error bar for the transition energy has been 6.2 cm^{-1} whereas others range from 0.5 to 3.3 cm^{-1}. Our predicted transition wavelengths agree with the experiment for 10 of the 11 transitions. The only discrepancy is about 2 cm^{-1}. In the case where there is a disagreement between different experiments, our results show a clear preference in the comparison. The transition rates calculated in this work suggest that other spectral lines may also be observed in future experiments.

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I. INTRODUCTION

Recently, a comprehensive review of multiply excited atomic systems was given by Mannervik [1]. In the early 1970's, many activities were undertaken in the study of core-excited doublets of lithium. The experiment of Ederer, Lucatorto, and Madden [2] reported the first observation of the core-excited LiI $^2P^o$ resonances with synchrotron radiation. The fact that these resonances were measured with high precision has stimulated considerable interest. Some of these resonances were also observed later in electron spectra with a larger error bar [3–5]. Other core-excited doublets were also observed in optical spectra by Berry, Pinnington, and Subtil [6], Buchet, Buchet-Poulizac, and Berry [7], and Andersen *et al.* [8]. The interest in lithium core-excited states continued into the late 1970's, for example, the high-resolution Auger spectroscopy of Rødbro, Buch, and Bisgaard [9] and Rassi, Pejcev, and Ross [10]. High-precision optical spectra were also reported by McIlrath and Lucatorto [11], Cantú *et al.* [12] and more recently, Meyer *et al.* [13].

Using the data from Refs. [2,11, and 12], the absolute term energy (T) of many of the lithium core-excited doublets can be determined. However, the most precise measurement in these experiments quoted an uncertainty of 23 cm^{-1} (3 meV). In an effort to substantially reduce the experimental uncertainty, Mannervik and Cederquist [14] took a more elaborate approach. They use the $1s2s2p\ ^4P^o$ term energy determined in their experiment together with the $1s2s2p\ ^4P^o$–$1s2p2p\ ^2P$ transition energy observed in Willison *et al.* [15] to determine the T of this ^2P state accurately. They also use optical emission spectroscopy to measure the transitions between the core-excited bound-bound and bound-autoionizing states [16, 17]; the most accurate datum quoted an uncertainty of 0.5 cm^{-1}. To our knowledge, this is the most accurate datum for transitions involving a three-electron autoionizing system. Using these results, Mannervik and Cederquist determine the absolute T's for many lithium doublets. The uncertainty of these energy ranges from 6 to 8 cm^{-1} [18].

The transitions observed in the optical emission spectra involve twelve core-excited doublets, three ^2P, and $^2D^o$ bound states, and three $^2P^o$, and ^2D autoionizing states, respectively. Theoretically, the most accurate calculation on these core-excited bound states has been done by Bunge [19] and Jáuregui and Bunge [20]. In their work, the uncertainties of the nonrelativistic energy are predicted to about 3–7 cm^{-1}.

The accurate calculation of the three-electron autoionizing states is more challenging. Although the saddle-point method [21] and the saddle-point complex-rotation method [22] provided powerful tools for these states, the methods have not been carried out to their potential partly due to the limited computation resources in the past. Early applications of the saddle-point method on the lowest lithium ^2D and $^2P^o$ autoionizing states give results which are 0.01 and 0.02 eV higher than the experiment [23]. Although these "saddle-point energies" are improved somewhat in a later work [24], Mannervik [1] points out that these results still differ substantially from high-precision experimental data. Other theoretical calculations on lithium resonances include Bhatia [25], Wakid, Bhatia, and Temkin [26], and Nicolaides and Aspromallis [27]. More recently, Jaskólska and Woźnicki use the saddle-point method with correlated-coordinate wave functions [28,29]. Their energies are more accurate than the earlier theoretical works. How-

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ever, they did not calculate the width, shift, and relativistic corrections of these resonances. This makes an unambiguous comparison with precise experiment difficult.

In the last few years, computation resources have been much improved. Large-scale computation can now be carried out on a compact workstation. This further stimulated the development of new numerical techniques to fully utilize these resources. The restricted variation method [30] is one of these methods. It is an effective method of saturating the functional space with large numbers of basis functions but it avoids numerical instability. This method has been successfully applied to some three- and four-electron atomic systems [30,31]. It will be used in this work.

The absolute *T*'s of quantum states are important quantities in constructing the atomic data tables and Grotrian diagrams. In establishing these term energies for the doublets, Mannervik and Cederquist [18] relied on their measured $1s2s2p\,^4P^o$ ionization potential (IP). However, a recent accurate calculation of $1s2s2p\,^4P^o$IP shows substantial disagreement with the reported experimental result [32]. Hence, it would be very meaningful to calculate explicitly the absolute *T*'s of these doublet states and to compare them with those suggested in Ref. [18]. In the existing atomic data tables [33–35], the entries for each state are made with the fine structure resolved *T*'s. In Mannervik and Cederquist [18], center of gravity energies are given. In this work, the fine structures of the doublets will be calculated for future data tables.

The precision of experimental results in the autoionizing states raises some interesting questions. It is well known that an autoionizing state is the result of the interaction of a discrete state with one or more continua. In general, the line shape involving an autoionizing state could be asymmetric with a Fano profile parameter [36]. However, in Cederquist and Mannervik [16,17], "the recorded spectra were analyzed by a peak-fitting program in which the lines are approximated with a Gaussian line profile. The program gives also the opportunity of folding the Gaussian with a Lorentzian profile." Since the maximum intensity spectral line position does not always coincide with the theoretical "resonance" position [36], one may question the validity of such an experimental procedure. This question is especially relevant when the width of the resonance is orders of magnitude larger than the quoted experimental uncertainty. For example, the error bar for the $1s2p2p\,^2D-[(1s2p)\,^2P,3d\,]^2D^o$ and $[1s(2s2p)\,^3P\,]^2P^o-1s2p2p\,^2P$ transitions is about 1 cm^{-1}, whereas the widths of the ^2D and $^2P^o$ states are measured to be about 86 and 21 cm^{-1}, respectively [16,17].

In the experiment of Ederer, Lucatorto, and Madden [2] and Cantú *et al.* [12], most line positions agree with each other, the only exception being the position of $[1s(2s2p)\,^1P\,]^2P^o$ state. It is, therefore, important to know which experimental result is more accurate. This autoionizing state is conspicuously missing in the optical emission spectra. What is the reason for this absence? These should be interesting questions to look into. There are also other experimental discrepancies in the literature. For example, the transitions at 2846(2) and 4590 Å in Berry, Pinnington, and Subtil [6] are at 2850.3(5) and 4585.4(1) Å in Cederquist and Mannervik [16]. Which results are better? An accurate calculation may be able to resolve these discrepancies.

We will try to answer the questions raised in previous paragraphs. In making accurate calculations, it is always difficult to estimate the theoretical uncertainty. In this work, we hope to carry out a calculation such that the nonrelativistic energy is accurate to well within 1 cm^{-1}. By including the relativistic and QED correction, we hope to determine the absolute term energy to about 1 cm^{-1}. The calculations are carried out in atomic units, but in order to make a definitive comparison with experiment, the results are converted into cm^{-1}. The reduced Rydberg constant used is 1 Ry = 109 728.731 cm^{-1}.

II. THEORY

The *LS* coupling scheme is adopted in the computation. The nonrelativistic Hamiltonian H_0 and the Pauli-Breit perturbation operators [37] H_1 (P^4 kinetic-energy correction), H_2 (Darwin term), H_3 (electron-electron contact term), H_4 (mass polarization), H_5 (orbit-orbit interaction), $H_{\rm so}$ (spin-orbit), and $H_{\rm soo}$ (spin-other-orbit) are the same as those in Wang, Zhu, and Chung [38], they will not be repeated here. We use the conventional Slater orbital configuration interaction (CI) basis functions. The explicit expression of the wave function is given in Chung [23].

The conventional variation method is used to obtain the basic wave functions for the six bound states considered in this work. The corresponding energy E_b and wave function $\Psi_b(1,2,3)$ are obtained by solving the secular equation from

$$\delta E_b=\delta\frac{\langle\Psi_b|H_o|\Psi_b\rangle}{\langle\Psi_b|\Psi_b\rangle}=0\ . \tag{1}$$

We use a large and flexible wave function for this Ψ_b. The wave function contains 464–699 linear parameters and 63–84 nonlinear parameters. These parameters are optimized to obtain the lowest energy. A good Ψ_b is important when it is used to carry out the restricted variation calculation. We construct a more accurate wave function as

$$\Psi(1,2,3)=d_o\Psi_b+\sum_i d_i\Phi_i(1,2,3)\ . \tag{2}$$

The *d*'s are linear parameters which can be determined by a new variation calculation in which the Ψ_b from Eq. (1) is restricted to being a single term, Φ_i's are basis functions similar to those of Ψ_b but with different nonlinear parameters. The advantage of Ψ is that if the basis function in Φ_i is very similar to that in Ψ_b, no numerical instability will occur [30].

For the seven autoionizing states, the saddle-point method is used [21,39]. The energy $E_{\rm sdl}$ obtained from the basic wave function is the saddle-point energy. It is a closed-channel approximation of the autoionizing (resonance) state. To calculate the true resonance energy, we need to include the open-channel continuum. The open-channel wave function in real coordinate space is not square integrable. In order to use square integrable wave functions, the saddle-point complex-rotation method [40,22] is used. The complex eigenvalue obtained is defined to be $E_{\text{res}} - i\frac{\Gamma}{2}$ where Γ is the width of the resonance. The difference $E_{\text{res}} - E_{\text{sdl}}$ is the "shift" of the resonance from the saddle-point energy.

The mass polarization is a kinematic effect coming from the center of mass coordinate transformation [37]. We can easily include this as a part of H_0 and recalculate the wave function. This wave function is employed to calculate the relativistic corrections for the Pauli-Breit operators [37] with first-order perturbation theory. The higher-order relativistic effect of lithium is much smaller than 0.01 cm^{-1}. They will not be considered in this work.

Although the nuclear charge of lithium is considered to be small. The QED effect cannot be neglected. This can be seen from the results of Drake [41]. He calculated the contribution of the QED effect to the IP of the Li^+ two-electron systems and obtained -8.938, -0.775, -1.013, -0.016, and $+0.238$ cm^{-1} for the $1s^2$, $1s2s\ ^1S$, $1s2s\ ^3S$, $1s2p\ ^1P$, and $1s2p\ ^3P$, respectively. The contribution of QED to the $1s^22s$ IP is approximately -0.4 μa.u. (0.08 cm^{-1}) [42], which suggests that the QED from the $3p$, or $3d$ electrons in lithium should be negligible. Hence, the QED contributions to the absolute T's of lithium core-excited states should range approximately from -7.9 to -9.2 cm^{-1}.

To calculate the QED correction for the three-electron core-excited states is very difficult. No such attempts will be made in this work. The IP (excluding QED) of the Li $1s^22s$ is calculated accurately to be 0.198 1582 a.u. [42]. Using the $1s^2$ relativistic energy, $-7.280\,5197$ a.u. from Pekeris [43], the $1s^22s$ relativistic energy becomes 7.478 677 9 a.u. To determine the absolute T, we subtract this energy from the relativistic energy of the core-excited states. The QED contribution to the absolute T's can be estimated from Drake's results [41]. For example, for $[(1s2p)\,^3P,3d\,]^2D^o$, it is

$$-8.938-0.08-0.238=-9.26(20)\text{cm}^{-1} . \tag{3}$$

Where 0.08 is the QED contribution for $2s$ in $1s^22s$. A possible uncertainty of 0.20 cm^{-1} is quoted. The same correction will also be used for other states with a $(1s2p)^3P$ core. The correction for systems with a $(1s2s)\,^3S$ core is

$$-9.02+1.013=-8.01(20)\text{cm}^{-1} . \tag{4}$$

For $[1s(2s2p)\,^3P]^2P^o$ and $[1s(2s2p)\,^1P]^2P^o$, no well defined core is present. We take the average of $1s2s\ ^1S$, $1s2s\ ^3S$, $1s2p\ ^1P$, and $1s2p\ ^3P$ to give

$$-9.02+0.22=-8.80(30)\text{cm}^{-1} . \tag{5}$$

In this case, a 0.30 cm^{-1} uncertainty is quoted. For $1s2p2p\ ^2P$ and ^2D states, a correction of $-9.02(30)\text{cm}^{-1}$ is adopted.

III. COMPUTATIONAL ASPECT

The conventional variation method is used to calculate an accurate but not yet saturated "basic" wave function for the six bound states and seven autoionizing states of interest. Double-precision arithmetics is used. Two spin doublet functions and all possible couplings of the orbital angular momenta l_1, l_2, and l_3 $(l \le 8)$ which give the correct total angular momentum L are considered. We try to use a flexible wave function with a large number of linear and nonlinear parameters. For each normalized wave function, we examine the sum

$$S=\sum_{i=1}^{N} \langle C_i\phi_i | C_i\phi_i \rangle , \tag{6}$$

where C_i is the coefficient of the basis function ϕ_i. Since Slater-type orbital basis functions are not mutually orthogonal, S could be greater than unity. A very large number of terms in a particular angular component may give an S which is larger than unity by many orders of magnitude. This implies that there will be a loss of significant figures in the normalized wave function. We need a reliable Ψ_b for the restricted variation calculation. Hence, we limit the size of our basic function by requiring that S be much less than one thousand.

Thirteen states are investigated in this work. We will only present the detailed results for the $^2P^o$ as an example. The detailed results for other states will be supplied to the interested reader upon request. The energy convergence for the four $^2P^o$ basic wave functions are given in Table I. The angular components, the number of linear and nonlinear parameters used, are also given in this table. The notation $[l_1l_2l_3]$ represents the various possible couplings of l_1, l_2, and l_3. In this work, we classify the six bound states as $1s2p2p\ ^2P$, $[(1s2p)\,^3P,3p\,]^2P$, $^2P(3)$, $[(1s2p)^3,3d\,]^2D^o$, $[(1s2p)^3,4d\,]^2D^o$, and $^2D^o(3)$. This is consistent with the classification in Bunge and Jáuregui [19,20]. The classifications for the seven autoionizing states are $[1s(2s2p)\,^3P]^2P^o$, $[1s(2s2p)\,^1P]^2P^o$, $[(1s2s)\,^3S,3p\,]^2P^o$, $[(1s2s)\,^3S,4p\,]^2P^o$, $[1s2p2p]^2D$, $[(1s2s)^3S,3d\,]^2D$, and $[(1s2s)\,^3S,4d\,]^2D$. They are also consistent with the classification in earlier works [2,11].

The next step is to carry out the restricted variation calculation. We try to saturate the functional space using a large number of linear parameters (a few hundred for each $[l_1l_2l_3]$) and a sufficient number of nonlinear parameters in Ψ. These parameters are optimized. We do one restricted variation calculation for each $[l_1l_2l_3]$ and record the corresponding energy improvement which is the new energy subtracted from E_b, the energy of the basic wave function. The results of energy improvements for the $^2P^o$ states are given in Table II as an example. These improvements are all very small. This is important. The total energy improvement for each state is obtained by summing the individual $[l_1l_2l_3]$ results. Note that the final energy obtained in this manner is no longer an upper bound to the true eigenvalue.

To show that these improvements are additive, we take the wave functions from the three largest improvements of each bound state and put them together into one wave function. We use this wave function to carry out a re-

TABLE I. Nonrelativistic energy convergence of the basic wave function of the core-excited $^2P^o$ states of lithium (in μa.u.). N is the number of linear parameters, N' is the number of the nonlinear parameters. $[l_1l_2l_3]$ is the angular component.

	$[1s(2s2p)^3P]^2P^o$			$[1s(2s2p)^1P]^2P^o$			$[1s2s\,^3S,3p]^2P^o$			$[1s2s\,^3S,4p]^2P^o$		
$q=$	2.470			2.526			2.468			2.509		
	N	N'	$-\Delta E$	N	N'	$-\Delta E$	N	N'	$-\Delta E$	N	N'	$-\Delta E$
[001]	195	15	5 303 097.95	187	21	5 225 593.98	176	12	5 178 641.48	188	12	5 147 517.12
[012]	156	15	8 029.38	196	24	29 878.75	166	15	4 009.92	156	15	863.39
[111]	69	9	1393.47	77	9	1291.85	62	9	1092.10	91	9	1187.15
[023]	74	15	367.99	100	15	953.30	101	9	131.62	65	9	33.00
[221]	77	15	173.37	62	18	204.67	47	9	77.65	52	9	74.51
[034]	50	9	76.76	55	18	232.26	45	6	27.89	20	6	6.35
[331]	20	6	28.08	18	6	21.11	13	3	8.88	13	3	8.96
[045]	24	9	22.56	27	6	78.31	20	6	8.26	20	6	1.97
[056]	8	6	6.06	20	6	33.43	10	3	2.62	8	3	0.48
[067]	4	3	2.28	17	3	17.51	10	3	1.21			
[078]				17	3	9.70						
[441]	12	3	7.39	13	3	5.45	7	3	1.65	13	3	1.90
[551]	12	3	2.95	7	3	1.21	7	3	0.42	7	3	0.42
[661]				7	3	0.52						
[113]	3	3	5.12	10	6	22.76	13	3	2.46			
[232]				20	6	5.86						
Total	704	111	5 313 212.36	833	147	5 258 350.67	677	84	5 184 006.15	633	78	5 149 695.27

stricted variation calculation (note that the new energy obtained in this way gives the lowest upper bound in this work) and compare the new improvement with the sum of the three individual improvements. This is done for all six bound states. We found that the discrepancies are only 0.55%, 0.33%, 0.19%, 0.29%, 0.26%, and 0.72% for the $1s2p2p\,^2P$, $[(1s2p)^3P,3p]^2P$, $^2P(3)$, $[(1s2p)^3P,3d]^2D^o$, $[(1s2p)^3P,4d]^2D^o$, and $^2D^o(3)$, respectively. They are too small to be significant. Hence, to sum the individual improvements in Table II for the total improvement is probably appropriate. However, there are other sources which may lead to uncertainty in the predicted energy.

Although we try to saturate the functional space, we are never certain that the entire functional space is completely saturated. We have also tried to make the energies in Table II small by including basis functions as much as possible in the basic wave function (provided it

TABLE II. Restricted variation calculation for the core-excited $^2P^o$ states of lithium. (in μa.u.).

	$-\Delta E$ (improvement)			
	$[1s(2s2p)^3P]^2P^o$	$[1s(2s2p)^1P]^2P^o$	$[(1s2s)^3S,3p]^2P^o$	$[(1s2s)^3S,4p]^2P^o$
[001]	6.38	8.75	6.90	5.78
[012]	7.92	7.13	6.31	5.24
[111]	4.93	3.48	3.06	2.47
[023]	8.08	9.54	6.70	1.98
[221]	6.63	6.84	3.71	3.34
[034]	5.56	6.40	4.54	1.37
[045]	5.21	8.12	3.08	0.70
[056]	6.05	5.74	2.49	0.69
[067]	3.87	2.64	1.46	0.60
[331]	7.01	6.14	1.41	2.21
[441]	4.38	3.56	0.74	0.79
[551]	2.14	2.26	0.33	0.45
[661]	2.51	1.31	0.29	0.33
[113]	3.47	0.70	0.18	0.47
[124]	0.86	1.57	0.24	0.06
[135]		0.28		
[232]	1.46	0.36	0.82	0.30
[342]	0.32	0.46	0.14	
[078]		1.37		
[452]		0.46		
Sum	76.77	77.99	42.39	26.75
Uncertainty	3.07(307)	3.12(312)	1.70(170)	1.07(107)
Total	79.84(307)	81.11(312)	44.09(170)	27.82(107)

satisfies the criterion mentioned before). A large energy improvement in the restricted variation calculation is an indication of the degree of difficulty in reaching saturation. Thus, we estimate the possible remaining error by the size of the total improvements in Table II. For each 25 μa.u., we assign a possible remaining error of 1(1) μa.u. For example, the sum of the improvements for the $[(1s2s)\,^3S,3p\,]^2P^o$ is -42.39 μa.u. The corresponding estimated error is $-1.7(17)$ μa.u. The largest improvement is the -77.99 μa.u. for $[1s(2s2p)\,^1P\,]^2P^o$, the estimated error is $-3.12(312)$ μa.u. Of course, this error does not include the possibility that some angular components are left out of Tables I and II, especially those with higher orbital momentum l. The contribution of these components needs to be extrapolated separately.

The advantage of the CI-Slater orbitals is that the matrix elements are easy to evaluate. However, unlike the Hylleraas wave function [44], which accounts for the contributions of high l effectively, these contributions must be computed for each $[l_1l_2l_3]$ in the Slater CI wave function. Since the energy convergence of these $[l_1l_2l_3]$ components could be very slow, an effective method of extrapolation is needed.

In this work, we will use the same extrapolation method which is successful in Refs. [31,38,42, and 45]. Namely, we compare the convergence pattern of the three-electron system with that of the Li^+ $1s1s$ state. Since we know the exact result of Li^+ from Pekeris [43], the three-electron result can be computed. To avoid extensive discussion, we will not present the details of this extrapolation. They will be supplied to the interested reader upon request.

IV. COMPLEX-ROTATION CALCULATION

In the preceding section, the energies obtained for the autoionizing states are the saddle-point energies. The interaction of the saddle-point wave function with the continuum shifts the energy to the resonance energy. It also gives the Auger width. The radiative widths of the lithium resonances considered in this work are very small and they are negligible. To calculate the shift and width, we use a complex-rotation method. To check the stability of the calculated shift and width, three different $1s1s$ target state wave functions are tried. They contain 21, 33, and 47 terms. The energy and wave function for the 21-term and 47-term target states are given in Table III. The width and shift of the resonances are extremely stable with respect to the three wave functions. For example, the shift of the $[1s(2s2p)\,^3P\,]^2P^o$ changes from 267.77 μa.u. to 267.70 μa.u. and the width changes from 120.65 μa.u. to 120.44 μa.u. when we replace the 21-term target state with the 47-term target state.

The stabilities of the shifts and widths are also investigated by varying the nonlinear parameter and the number of terms in the open channel, or the rotation angle θ in the complex scaling. The results are found to be stable with respect to these variations.

In Table IV, we present the results of complex rotation calculation. The widths are compared with the theoretical and experimental data in the literature [16,24,25,27,46–49]. Although the methods of this work are similar to that of Davis and Chung [24], the closed-channel wave functions are much improved. The widths of three states are reduced slightly. The $1s2p2p\ ^2D$ width in this work, 10.63 meV, agrees well with the experimental result of 10.5(3) meV [16,48]. However, the results for $[1s(2s2p)\,^3P\,]^2P^o$ and $[(1s2s)\,^3S,3d\,]^2D$ are outside of the quoted experimental uncertainty [16,49]. The predicted width for $[1s(2s2p)\,^3P\,]^2P^o$, 3.277 meV, agrees well with the 3.2(6) meV of Pedrotti [47], where a larger error bar is quoted.

V. RESULTS AND DISCUSSION

If we combine the energy of the basic wave function, the improvement from the restricted variation calculation, and the extrapolated higher l contributions, we obtain the nonrelativistic energy of the core-excited systems. They can be compared with the most accurate theoretical data in the literature. This comparison is given in Table V. For the six lithium bound states, the most accurate nonrelativistic energies were calculated by Bunge [19] and by Jáuregui and Bunge [20]. Their $[(1s2p)\,^3P,3d\,]^2D^o$ energy, $-5.089\,291(13)$ a.u. [20], agrees remarkably well with the $-5.089\,292\,7(7)$ a.u. in this work. In Ref. [20], an extrapolated correction, $\Delta E_{\mathrm{STO}} = -69(13)$ μa.u., due to the truncation of Slater-type orbitals (STO) is included. For $[(1s2p)\,^3P,3d\,]^2D^o$, this correction makes the final result extremely accurate. However, if the results of the present work are reliable, the ΔE_{STO} could be substantially underestimated for $^2D^o(3)$ and overestimated for $[(1s2p)\,^3P,4d\,]^2D^o$ in this reference. In fact, their $[(1s2p)\,^3P,4d\,]^2D^o$ upper bound, $-5.061\,562$ a.u., is highly accurate and agrees well with our E_b, -5.061570 a.u. But their predicted energy,

TABLE III. The Li^+ $1s1s$ target states used in the complex-rotation calculation. Energy in μa.u., α,β are the nonlinear parameters.

	47-term ψ_{1s1s}				21-term ψ_{1s1s}			
$[ll]$	N	α	β	$-\Delta E_{[ll]}$	N	α	β	$-\Delta E_{[ll]}$
[00]	16	3.695	4.146	7 252 382.09	9	3.436	3.704	7 252 105.97
[11]	12	5.436	6.331	23 286.28	6	4.601	6.051	23 002.02
[22]	9	5.924	9.206	2 662.19	4	6.588	6.420	2 610.03
[33]	6	8.311	10.027	631.88	2	7.508	9.573	495.18
[44]	4	8.825	13.344	184.87				
Total	47			7 279 147.31	21			7 278 213.21

TABLE IV. The shift and width of the autoionizing states of lithium.

	$^2P^o$				^2D		
	$1s(2s2p)\,^3P$	$1s(2s2p)\,^1P$	$(1s2s)\,^3S,3p$	$(1s2s)\,^3S,4p$	$1s2p2p$	$(1s2s)\,^3S,3d$	$(1s2s)\,^3S,4d$
Shift (μa.u.)	267.7	−14.96	4.32	2.55	76.2	11.2	4.01
Width (μa.u.)	120.44	353.31	7.36	1.60	390.57	36.85	11.16
Width (meV)	3.277	9.614	0.200	0.0436	10.63	1.003	0.304
Ref. [24]	3.71	10.01	0.172		11.00	1.11	
Ref. [46]	3.07	11			123		
Ref. [25]	7	11	0.021		5	0.75	
Ref. [27]	3.42				10.0		
Expt:							
Ref. [16]	2.6(1)				10.5(3)		
Ref. [49]						0.89(4)	
Ref. [47]	3.2(6)						

−5.061 629(13) a.u., is lower than our −5.061 594(1) a.u. For $^2D^o(3)$, our upper bound, −5.053 853 a.u. is much lower than the −5.053 668(20) a.u. predicted in Ref. [20]. Our predicted nonrelativistic energy is −5.053 884(2) a.u.

For the ^2P states, all three E_b's in this work are lower than the suggested energies in Bunge [19]. The predicted uncertainty in the present work is also an order of magnitude smaller than that of Ref. [19]. This is largely due to the improvement of computation resources. The results of Refs. [19 and 20] must be considered as remarkably accurate and they were not exceeded for over a decade.

Recently, Jaskólska and Woźnicki [28,29] used a correlated-coordinate saddle-point method for autoionizing states of lithium. Their results for $^2P^o$ and ^2D states are significantly improved over that of Davis and Chung [24]. They attribute the improvement to the use of correlated-coordinate wave functions. The wave function in Davis and Chung contains about 100 terms and the wave function in Jaskólska and Woźnicki [28,29] contains 200–500 terms. In this work, the number of terms in the basic wave functions for the seven autoionizing states ranges from 630 to 833 terms. The corresponding energy E_b's are substantially lower than the energies in Jaskólska and Woźnicki [28,29] for each of the seven states (see Table V). This shows that for core-excited states, the advantage of the correlated wave function over the Slater orbital wave function is limited. One obvious advantage of the correlated wave function is that we can remove the uncertainty due to the higher-l extrapolation. However, the results in Table V show that this uncertainty is very small. The disadvantage of the correlated wave function is that the relativistic corrections cannot be calculated easily and the method cannot be easily extended to a four- or five-electron systems. If these two difficulties can be overcome, the most ideal wave function will probably be a combined CI-Hylleraas wave function as demonstrated in the recent calculation of Pipin and Bishop [50].

The relativistic energies for the core-excited states are obtained by summing the nonrelativistic energy, the shift, the relativistic and mass polarization corrections. They are given in Table VI. The nuclear mass for ^{7}Li is taken from Wapstra and Audi [51]. As mentioned before, the relativistic energy of the lithium $1s^22s$ state is

TABLE V. Nonrelativistic energy ($-E$) for the core-excited states of lithium and comparison with the best theoretical results in the literature. (in μa.u., ΔE_r is the energy improvement from the restricted variation method. The shift of the autoionizing states is not included.)

	$E_{\text{upper bound}}$	E_b	ΔE_r	$\delta E_{\text{higher } l}$	E (total)	Other work	Ref. no.
Bound states							
$1s2p2p\,^2P$	5 213 702	5 213 684.73	35.03(135)	12.8(3)	5 213 733.5(18)	5 213 650(20)	[19]
$[(1s2p)\,^3P,3p\,]^2P$	5 104 364	5 104 346.87	24.61(95)	2.8(4)	5 104 374.3(13)	5 104 290(30)	[19]
$^2P(3)$	5 070 284	5 070 264.77	33.13(127)	7.25(20)	5 070 305.2(15)	5 070 120(30)	[19]
$[(1s2p\,)^3,3d\,]^2D^o$	5 089 285	5 089 277.86	14.56(56)	0.30(10)	5 089 292.7(7)	5 089 291(13)	[20]
$[(1s2p\,)^3,4d\,]^2D^o$	5 061 584	5 061 570.39	22.84(88)	0.25(10)	5 061 593.5(10)	5 061 629(13)	[20]
$^2D^o(3)$	5 053 853	5 053 835.88	34.51(133)	13.8(10)	5 053 884.2(23)	5 053 668(20)	[20]
Autoionization states							
$[1s(2s2p)\,^3P\,]^2P^o$		5 313 212.36	79.84(307)	20.0(7)	5 313 312.2(38)	5 312 936	[28]
$[1s(2s2p)\,^1P\,]^2P^o$		5 258 350.67	81.11(312)	39.5(19)	5 258 471.3(50)	5 257 499	[28]
$[(1s2s)\,^3S,3p\,]^2P^o$		5 184 006.15	44.09(170)	7.0(5)	5 184 057.2(22)	5 183 842	[28]
$[(1s2s)\,^3S,4p\,]^2P^o$		5 149 695.27	27.82(107)	1.7(2)	5 149 724.8(13)	5 149 599	[28]
$[1s2p2p\,]^2D$		5 234 137.89	74.93(288)	23.1(11)	5 234 235.9(40)	5 233 789	[29]
$[(1s2s)\,^3S,3d\,]^2D$		5 166 434.43	35.53(137)	5.4(8)	5 166 475.4(22)	5 166 187	[29]
$[(1s2s)\,^3S,4d\,]^2D$		5 142 193.65	23.85(92)	2.7(4)	5 142 220.2(13)	5 141 919	[29]

−7.478 677 9 a.u. This energy is used to compute the (relativistic) T's of the core-excited states. The final results for the T's are obtained by including the QED corrections mentioned in Sec. II.

The absolute T's given by Mannervik and Cederquist [18], and Jáuregui and Bunge [20] are given in Table VI for comparison. Also given in this table are the absolute T's from the experiments of Ederer, Lucatorto, and Madden [2], and Cantú *et al.* [12]. Using the results from the spin-orbit and spin-other-orbit computation, we also obtain the fine structure resolved T's. These results should be very useful for future atomic data tables.

TABLE VI. Relativistic energy ($-E$) and absolute term energy (T) for the core-excited states of lithium (in μa.u. unless otherwise indicated).

	$[(1s2p)^3,3d]^2D^o$	$[(1s2p)^3,4d]^2D^o$	$^2D^o(3)$	$1s2p2p\ ^2P$	$[(1s2p)\,^3P,3p]^2P$
$-E_{\text{nonrel}}$	5 089 292.7(7)	5 061 593.5(10)	5 053 884.2(23)	5 213 733.5(18)	5 104 374.3(13)
Mass polarization	−23.472	−23.063	17.902	12.081	−18.779
P^4 and Darwin	−550.81	−551.40	−556.04	−558.70	−554.07
e-e contact	0.0056	0.039	1.70	1.57	0.27
Orbit-orbit	13.46	13.26	−8.52	−3.16	11.51
$-E_{\text{relativistic}}$	5 089 853.6(7)	5 062 154.7(10)	5 054 429.1(23)	5 214 281.6(18)	5 104 935.4(13)
T_{Rel}	2 388 824.3(7)	2 416 523.2(10)	2 424 248.8(23)	2 264 396.3(18)	2 373 742.5(13)
T_{Rel}(cm^{-1})	524 245.33(15)	530 324.05(22)	532 019.50(50)	496 938.67(40)	520 935.51(29)
QED Corr. (cm^{-1})	−9.26(20)	−9.26(20)	−9.02(30)	−9.02(30)	−9.26(20)
T this work (cm^{-1})	524 236.07(35)	530 314.79(42)	532 010.48(80)	496 929.65(70)	520 926.25(49)
Ref. [18] (cm^{-1})	524 229(6)	530 310(7)	531 995(8)	496 921(6)	
Ref. [20] (cm^{-1})	524 235.5(30)	530 306.1(30)	532 058.8(45)	496 927.5	
$T_{J=L+1/2}$ (cm^{-1})	524 235.95(35)	530 314.74(42)	532 010.58(80)	496 930.85(70)	520 925.67(49)
$T_{J=L-1/2}$ (cm^{-1})	524 236.26(35)	530 314.86(42)	532 010.33(80)	496 927.25(70)	520 927.41(49)
Splitting (cm^{-1})	−0.3224	−0.1199	0.2542	3.603	−1.745

	$[1s(2s2p)\,^3P]^2P^o$	$[1s(2s2p)\,^1P]^2P^o$	$[(1s2s)\,^3S,3p]^2P^o$	$[(1s2p)\,^3S,4p]^2P^o$	$^2P(3)$
$-E_{\text{nonrel}}$	5 313 312.2(38)	5 258 471.3(50)	5 184 057.2(22)	5 149 724.8(13)	5 070 305.2(15)
Shift	267.7(2)	−15.0(2)	4.3(1)	2.5(1)	
Mass polarization	10.189	−8.5654	0.91987	0.95973	−7.2538
P^4 and Darwin	−591.90	−584.04	−608.94	−612.04	−554.01
e-e contact	5.83	3.72	0.31	0.23	0.74
Orbit-orbit	−4.99	6.65	0.001	0.016	5.02
$-E_{\text{relativistic}}$	5 313 625.3(40)	5 259 068.5(52)	5 184 660.7(23)	5 150 333.1(14)	5 070 860.7(15)
T_{Rel}	2 165 052.6(40)	2 219609.4(52)	2 294 017.2(23)	2 328 344.8(14)	2 407 817.2(15)
T_{Rel} (cm^{-1})	475 136.96(87)	487 109.85(114)	503 439.20(50)	510 972.65(30)	528 413.46(33)
QED Corr. (cm^{-1})	−8.80(30)	−8.80(30)	−8.01(20)	−8.01(20)	−9.02(30)
T this work (cm^{-1})	475.128.16(117)	487 101.05(144)	503 431.19(70)	510 964.64(50)	528 404.44(63)
Ref. [18] (cm^{-1})	475 119(6)				
Ref. [2] (cm^{-1})	475 150(45)	487 140(24)	503 449(25)	511 012(78)	
Ref. [12] (cm^{-1})	475 127(23)	487 094(24)	503 423(25)	511 012(26)	
$T_{J=L+1/2}$ (cm^{-1})	475 128.97(117)	487 100.48(144)	503 430.77(70)	510 964.46(50)	528 404.64(63)
$T_{J=L-1/2}$ (cm^{-1})	475 126.54(117)	487 102.19(144)	503 432.02(70)	510 965.00(50)	528 404.04(63)
Splitting (cm^{-1})	2.438	−1.709	−1.248	−0.5486	0.6019

	$[1s2p2p]^2D$	$[(1s2s)\,^3S,3d]^2D$	$[(1s2s)\,^3S,4d]^2D$
$-E_{\text{nonrel}}$	5 234 235.9(40)	5 166 475.4(22)	5 142 220.2(13)
Shift	76.2(2)	11.2(2)	4.0(1)
Mass polarization	−19.338	1.4383	1.6011
P^4 and Darwin	−562.04	−611.82	−614.57
e-e contact	0.74	0.13	0.07
Orbit-orbit	8.71	0.078	−0.287
$-E_{\text{relativistic}}$	5 234 731.7(42)	5 167 074.3(24)	5 142 829.4(14)
T_{Rel}	2 243 946.2(42)	2 311 603.6(24)	2 335 848.5(13)
T_{Rel} (cm^{-1})	492 450.75(95)	507 298.67(52)	512 619.39(28)
QED Corr. (cm^{-1})	−9.02(30)	−8.01(20)	−8.01(20)
T this work (cm^{-1})	492 441.73(122)	507 290.66(72)	512 611.38(48)
Ref. [17] (cm^{-1})	492 435(6)	507 285(6)	512 605(7)
$T_{J=L\|1/2}$ (cm^{-1})	492 439.52(122)	507 290.48(72)	512 611.32(48)
$T_{J+L-1/2}$ (cm^{-1})	492 444.01(122)	507 290.93(72)	512 611.47(48)
splitting (cm^{-1})	−5.482	−0.4518	−0.1423

The transition wavelengths between the core-excited states have been measured to high precision [6,8,16,17,52]. They can also be calculated from the T's in Table VI. To gain a better understanding of the observed spectra, we have also calculated the dipole-length emission rates. These results are given in Table VII. If longer than 2000 Å, the wavelength in air is quoted. The index of refraction is 1.000 293. The most accurate experimental wavelengths are also given in the table for comparison.

The radiative transition between the autoionizing states is too weak to be detected. Among the possible transitions in Table VII, ten have been observed. Six of the predicted wavelengths fall within the corresponding experimental uncertainties of 0.5–2.9 cm^{-1}. The most precise experimental data is the $[1s(2s2p)\,^3P]^2P^o$-$1s2p2p\,^2P$ transition at 4585.4(1) Å [16]. This error bar corresponds to 0.5 cm^{-1}. Our prediction, 4585.5 Å, is within the experimental uncertainty. One should not forget that the predicted $[1s(2s2p)\,^3P]^2P^o$ energy has an uncertainty of 1.17 cm^{-1}. In spite of this, the agreement shown in Table VII is still quite convincing. All six transitions correspond to decays of bound states to autoionizing states. The calculated resonance position verifies the experiment to about 1 cm^{-1} level. These results, 4585.4(1), 3144.3(1) and 2639.2(2) Å, are particularly remarkable in view of the fact that the calculated $1s2p2p\,^2D$ and $[1s(2s2p)\,^3P]^2P^o$ halfwidths are 42.90 and 13.22 cm^{-1}, respectively. For the $[(1s2s)\,^3S,3p]^2P^o$, $[(1s2s)\,^3S,4p]^2P^o$, and $[(1s2s)\,^3S,4d]^2D$, the halfwidths are 0.808, 0.176, and 1.224 cm^{-1}. The agreement between theory and experiment should be expected. The saddle-point energies of these states are within 1 cm^{-1} of their resonance energies.

The predicted wavelengths for two other transitions, 3661.07 and 2994.47 Å, are barely (less than 0.8 cm^{-1}) outside of the error bar of 3660.9(1) [16] and 2994.1(3) Å [52]. But, if we consider the uncertainty in the predicted energy, we must conclude that the theory agrees with experiment. The predicted 2849.72 Å is also 0.8 cm^{-1} off the uncertainty of 2850.3(5) Å [16] but it is more than 21 cm^{-1} away from the 2846(2) Å of Ref. [6]. Hence, the theory favors the result of Cederquist and Mannervik [16]. The experimental uncertainty in 2850.3(5) Å is 6.2 cm^{-1}. This datum shows that the calculated $^2D^o(3)$ energy is too high. However, the computation for this state is at least as straightforward as that of the lower state, $1s2p2p\,^2P$. It seems unlikely that the calculated energy could be too high by 7 cm^{-1}. We hope that this error bar can be reduced in future experiments to clarify the situation.

The only disagreement between theory and experiment in Table VII is for the $[(1s2s)\,^3S,3d]^2D$-$[(1s2p)\,^3S,3d]^2D^o$, which is also a bound-to-autoionizing transition. The calculated wavelength is 5899.57 Å, whereas it is 5900.3(2) Å in Cederquist and Mannervik [17]. They correspond to 16945.4 and 16943.3(6) cm^{-1}, respectively. The uncertainty in the predicted energy is 0.35 cm^{-1} for the upper state and 0.72 cm^{-1} for the lower state. Hence, the predicted transition energy is definitely larger than that of the experiment. This means that either the predicted $[(1s2p)\,^3S,3d]^2D^o$ energy is too high or the $[(1s2s)\,^3S,3d]^2D$ energy too low. Since the computation for $[(1s2p)\,^3S,3d]^2D^o$ is the most straightforward among the thirteen states and the other transitions, 3661.07 and 3144.29 Å, all suggests that its energy is not too high. The only conclusion we can draw is that the predicted $[(1s2s)\,^3S,3d]^2D$ energy is too low. This is puzzling because in the saddle-point method it is much more likely to obtain an energy that is too high rather

TABLE VII. Transition rates and wavelengths between the core-excited doublets of lithium. The first number is the transition rate (sec^{-1}), the second number is the wavelength in Å. The number with a parenthesis is the wavelength from experiment [16,17,52].

	$[1s2p2p]^2P$	$[1s2p\,^3P,3p]^2P$	$^2P(3)$	$[1s2p2p]^2D$	$[1s2s\,^3S,3d]^2D$	$[1s2s\,^3S,4d]^2D$
$[1s(2s2)^3P]^2P^o$	9.652×10^7 4585.50 4585.4(1)	1.624×10^5 2182.86	5.566×10^6 1877.01	8.154×10^3 5774.12	7.585×10^7 3108.30	4.211×10^7 2667.08
$[1s(2s2p)^1P]^2P^o$	1.127×10^6 10171.4	3.430×10^7 2955.51	1.521×10^7 2420.40	6.175×10^5 18718.7	3.458×10^7 4951.59	1.406×10^7 3918.83
$[(1s2s)\,^3S,3p]^2P^o$	2.660×10^3 15376.5	4.560×10^7 5714.22 5713.8(6)	1.630×10^4 4003.11	6.815×10^6 9096.96	3.525×10^6 25902.7	1.845×10^7 10899.8
$[(1s2s)\,^3S,4p]^2P^o$	6.938×10^3 7122.96	1.183×10^6 10035.6	1.612×10^7 5732.33 5731.8(6)	5.810×10^6 5397.14	2.203×10^6 27210.5	1.157×10^6 60708.3
$[1s2p\,^3P,3d]^2D^o$	4.070×10^7 3661.07 3660.9(1)	1.628×10^6 30204.3	9.869×10^5 23983.2	1.062×10^8 3144.29 3144.3(1)	1.231×10^7 5899.57 5900.3(2)	1.358×10^3 8599.86
$[1s2p\,^3P,4d]^2D^o$	4.583×10^6 2994.47 2994.1(3)	2.654×10^6 10648.2	7.980×10^5 52331.1	4.642×10^7 2639.63 2639.6(2)	3.547×10^6 4342.00	1.722×10^7 5646.97 5646.4(6)
$^2D^o(3)$	1.594×10^8 2849.72 2850.3(5)	1.205×10^6 9019.18	3.877×10^5 27723.1	2.279×10^7 2526.51	1.897×10^6 4044.15	2.380×10^6 5153.37

than too low. The calculated width for this state is 1.003 meV (8.08 cm^{-1}). It also disagrees with the experiment of 0.89(4) meV.

Table VII provides some interesting information. For example, it also predicts the $[1s(2s2p)\,^3P]^2P^o$-$[1s2p3p]^2P$ at 2183 Å as in Jáuregui and Bunge [20]. However, the transition rate is only 1.6×10^5/sec. It is too weak to be observed. Cederquist and Mannervik [16] examine the 2183 Å line in their spectrum and conclude that it does not involve an autoionizing state. Our result supports their conclusion. The transition to the $[1s(2s2p)\,^1P]^2P^o$ state has not been reported in the optical-emission spectrum. Since the transition rates of $[1s(2s2p)^1P]^2P^o$-$[1s2p\,^3P,3p]^2P$ and $[1s(2s2p)\,^1P]^2P^o$-$^2P(3)$, are very close to those of the $[(1s2s)\,^3S,3p]^2P^o$-$[1s2p\,^3P,3p]^2P$, and $[(1s2s)\,^3S,4p]^2P^o$-$^2P(3)$, we suggest that it should be possible to observe these transitions. The lines will be much broader due to the large width of the lower state (see Table IV). Another transition that can be observed is the $1s2p2p\,^2D-^2D^o$ (3). In this case, the transition rate is slightly smaller than that of the 2850 Å line and the line is also broader due to the autoionizing state.

The main object of the present work is to determine the absolute *T*'s of the core-excited doublets. The results of Table VII suggest that the relative accuracies of the thirteen *T*'s predicted in this work are about the same. To compare with other estimates, we note that the lowest two *T*'s in Ref. [18], 475 119(6) and 496 921(6) cm^{-1}, are lower than the 475 128.2(12) and 496 929.7(7) cm^{-1} in this work. The main reason for this discrepancy could come from the extrapolated $1s2s2p\,^4P^o$ IP in Mannervik and Cederquist [14]. They have used this IP and the $1s2s2p\,^4P^o$-$1s2p2p\,^2P$ energy (33 871(2)cm^{-1} [15,18]) to determined the *T* of the $1s2p2p\,^2P$ and, thereafter, the rest of the core-excited doublets. Using our $1s2p2p\,^2P$ relativistic energy, −5.214 281 6(18) a.u., and the $1s2s2p\,^4P^o$ energy from Hsu, Chung, and Huang [32], we obtain a transition energy of 33 870 cm^{-1} which agrees with the experiment. Hence, the transitions derived from the *T*'s in this work are consistent with the precise experimental data.

The three *T*'s of ^2D predicted in this work are all within the uncertainty quoted in Mannervik and Cederquist [18]. For $^2D^o$ states, the largest discrepancy between our *T*'s and those of Ref. [18] is for $^2D^o$ (3). Their result, 531 995(8) cm^{-1}, is 16(8) cm^{-1} lower than the 532 010.5(8) cm^{-1} predicted in this work. Since it is relatively easy to calculate the energy of this state to high precision, it seems unlikely that the prediction could be off by this much.

Jáuregui and Bunge [20] predicted the *T* for the $[(1s2p)\,^3P,3d]^2D^o$ at 524 235 .5(30) cm^{-1}. The agreement with our prediction, 524 236.1(4) cm^{-1}, is truly remarkable. By consulting with precise experimental data, they have also "assumed" the *T*'s of the $1s2p2p\,^2P$ and ^2D to be 496 927.5 and 492 443 cm^{-1}, which are also extremely close to our predictions of 496 929.7(7) and 492.441.7(12) cm^{-1}. However, their predictions of $[(1s2p)^3,4d]^2D^o$ [at 530 306.1(30) cm^{-1}] and $^2D^o(3)$ [at 532 058.8(45) cm^{-1}] are not very close to our *T*'s at 530 314.8(4) and 532 010.5(8) cm^{-1}.

In principle, the *T*'s of the lithium core-excited doublets can be determined directly from the experiments of Refs. [2 and 11–13]. But as pointed out by Mannervik

TABLE VIII. Wavelengths for transition between the $1s^22l$ states and the core-excited doublets of lithium (in Å).

Transition	This work	Experiment	Ref. No.	MCT (derived) [53]
$1s^22s-[1s(2s2p)\,^3P]^2P^o$	210.470	210.47(1)	[12]	210.474(3)
		210.46(2)	[2]	
		210.5(1)	[54]	
$1s^22s-[1s(2s2p)\,^1P]^2P^o$	205.296	205.30(1)	[12]	
		205.28(1)	[2]	
$1s^22s-[(1s2s)\,^3S,3p]^2P^o$	198.637	198.64(1)	[12]	
		198.63(1)	[2]	
$1s^22s-[(1s2s)\,^3S,4p]^2P^o$	195.708	195.69(1)	[12]	
		195.69(3)	[2]	
$1s^22p-1s2p2p\,^2D$	209.407	209.39(2)	[11]	209.410(3)
		209.40(3)	[13]	
$1s^22p-[(1s2s)\,^3S,3d]^2D$	203.092	203.09(2)	[11]	
		203.06(7)	[13]	
$1s^22p-[(1s2s)\,^3S,4d]^2D$	200.921	200.89(2)	[11]	
		200.85(7)	[13]	
$1s^22p-1s2p2p\,^2P$	207.458	207.44(2)	[11]	207.462(3)
		207.45(5)	[54]	
		207.53(1)	[12]	
$1s^22p-[(1s2p)\,^3P,3p]^2P$	197.620	197.62(2)	[11]	
$1s^22p-^2P(3)$	194.742	194.74(2)	[11]	
$1s^23d-[(1s2p)\,^3P,3d]^2D^o$	202.859	202.88(10)	[54]	202.862(3)
$1s^23d-[(1s2p)\,^3P,4d]^2D^o$	200.388			200.390(3)
$1s^23d-^2D^o(3)$	199.709	199.6(1)	[54]	199.716(3)

and Cederquist [18], the error bars in these experiments are 23 cm^{-1} or larger. They are, therefore, not suitable for high-precision T's. Mannervik, Cederquist, and Träbert [53] have also derived the transition wavelength of the Li $1s^2 2l$ to the core-excited doublets to high precision using the available experimental data. We will use our prediction to make a critical comparison with these results. Using the excitation energy of $1s^2 2p$ and $1s^2 3d$ at 14 903.89 and 31 283.10 cm^{-1} [34], these transition wavelengths are computed. These results are given in Table VIII. The wavelengths of Mannervik, Cederquist, and Träbert [53] are extremely close to our result.

In the reported ${}^2P^o$ energies of Ederer, Lucatorto, and Madden [2] and Cantú *et al.* [12], all the energies overlap except one, the $[1s(2s2p)\,{}^1P]^2P^o$. This state has not been observed in the optical emission spectra. In Table VIII, it shows that our prediction, 205.296 Å, agrees well with the 205.30(1) Å of Cantú *et al.* For the lowest three ${}^2P^o$ states, our prediction agrees with Cantú *et al.* perfectly. But their 207.53(1) Å disagrees with the 207.458 Å in this work. The result in Mannervik, Cederquist, and Träbert [53] is 207.462(3) Å. Our agreement with McIlrath and Lucatorto [11] is almost perfect except one state, the $[(1s2s)\,{}^3S,4d]^2D$.

VI. CONCLUSION

In this work, we have computed the energy for thirteen lithium core-excited doublet states. The purpose of this work is to establish their absolute term energy and to verify the observed high-precision optical emission spectra. The estimated uncertainty in the predicted term energy is about 1 cm^{-1}. This is much smaller than the previous estimates in the literature. The reason we can obtain this accuracy is because we have used a restricted variation method to saturate the functional space for energy and a quantitative method to determine the energy contribution from the higher-l angular components.

Seven of the spectral lines observed in the optical emission spectra are decays from bound states to autoionizing states [16,17]. Three of them involve resonances whose halfwidths are more than one order of magnitude larger than the quoted experimental uncertainty. Since the Fano profile parameter of the lines is not measured, one may question whether the experiment is measuring the true resonance positions. Six of the seven transitions calculated in this work are within the experimental error. This gives unambiguous support to the experimental data analysis. There is still one disagreement, however, for the $[(1s2s)\,{}^3S,3d]^2D$-$[(1s2p)\,{}^3P,3d]^2D^o$. The prediction differs with experiment by about 2 cm^{-1}, whereas the halfwidth of this ${}^2D$ is about 4 cm^{-1}. It would be extremely helpful if we could pinpoint the source of this discrepancy. It should be mentioned that the agreement on the Auger widths is not as satisfactory. Of the three measured widths, only one agrees with our calculation. The other two widths are *smaller* than the prediction by about 10–20%. The fact that the experimental result gives a longer lifetime is not expected. More high-precision experimental and theoretical studies are needed to clarify the situation.

For transitions between the $1s^2 2l$ and the core-excited doublets, the calculated wavelengths agree with the experiment of Cantú *et al.* [12], Ederer, Lucatorto, and Madden [2], and with McIlrath and Lucatorto [11] in most cases.

Judging from the calculated transition rates, more bound-autoionizing transitions may be observed in the future. These lines are weaker than the reported ones and they are broader. Nevertheless, a careful search may locate these lines in the spectra.

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