$^4P^o$ series of lithium

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The term energies of the lowest ten doubly excited $^4P^o$ terms of neutral lithium are calculated by using the restricted variational method with a full core plus correlation. Relativistic and mass-polarization effects are included as the first-order perturbation to the nonrelativistic energy. Our results support the assignments for the observed lines at 3619 Å and at 4885 Å as the decay from the term $1s2p3s\,^4P^o$. This term is identified as the seventh member in the $^4P^o$ series, and its energy is almost degenerate with that of the eighth member, being only 24 cm^{-1} apart. To facilitate unambiguous closed loop analyses in comparisons with experiment, precision calculations are also carried out to determine the relative term values for $1s2p2p\,^4P$ at 26 915.7(5) cm^{-1} and for $1s2s3d\,^4D$ at 42 778.4(4) cm^{-1}, which agree well with the experimental data of 26 915.16(6) cm^{-1} and 42 778.3 cm^{-1}, respectively. Our results suggest that the transition $1s2s3d\,^4D - 1s2p3s\,^4P^o$ should be at 8500.5 Å.

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I. INTRODUCTION

In building up the quartet system of neutral lithium, particular efforts have been made to locate the spectroscopic term which is dominated by the configuration $1s2p3s$. For neutral lithium, this is the only quartet term of the type $1s2pnl$ ($n > 2$) which dives below the $1s2s\,^3S$ threshold [1]; thus it is metastable against autoionization but merges in and perturbs the $1s2snp\,^4P^o$ Rydberg series. Its low principal and angular momentum quantum numbers make it appropriate to account for some observed transition lines. This term was first involved for assigning the line at 3618 Å as the transition to $1s2p2p\,^4P$ by Berry *et al.* [2]. This assignment was not reconfirmed either experimentally or theoretically until the lines at 3619 Å and 4885 Å were observed and classified as the transitions $1s2p2p\,^4P - 1s2p3s\,^4P^o$ and $1s2s3s\,^4S - 1s2p3s\,^4P^o$, respectively [3,4]. By combining with the corresponding observed lines to the lowest quartet $1s2s2p\,^4P^o$, a closed loop check is now possible. As a result, the relative term value for $1s2p3s\,^4P^o$ is determined to be 54 540(1) or 54 536(1) cm^{-1}, depending on the decay route [5], and is illustrated in Fig. 1.

On the theoretical side, no definite conclusion has been reached on the position of the $1s2p3s$ term in the $^4P^o$ series. The pioneer work by Holøien and Geltman [6] found that the second and third member of the $^4P^o$ series, $^4P^o(2)$ and $^4P^o(3)$, can both be linear combinations of $1s2p3s$ and $1s2s3p$ due to the strong interaction between these two configurations. The studies by Lunell and Beebe [7] and Lunell [8] found no such strong interac-

tion and their Hartree-Fock calculations showed $1s2p3s$ should lie above $^4P^o(5)$. The configuration-interaction calculation by Glass [9] provided better term energies and indicated that the term $1s2p3s\,^4P^o$ cannot appear below $^4P^o(4)$. The calculation performed by Larsson and Crossley [10] showed that $^4P^o(5)$ should be responsible
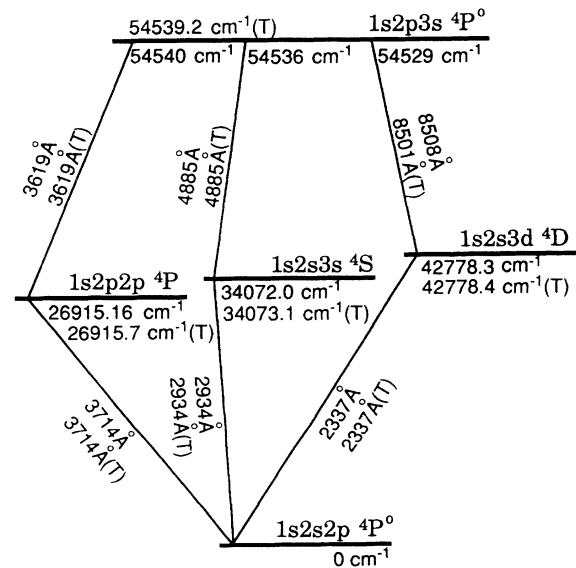

FIG. 1. Schematic diagram (not to scale) showing the three alternative term values 54 540 cm^{-1}, 54 536 cm^{-1}, and 54 529 cm^{-1} for $1s2p3s\,^4P^o$ from observed lines. The notation (T) indicates our present theoretical result.

for the configuration $1s2p3s$. Bunge's fine calculation [11] stopped at $^4P^o(4)$ where he was concerned of the increasing contribution which may come from a perturber at a higher position and denoted it by $^4P^o(?)$.

Using a model-potential method, Fairley and Laughlin [12] studied the radiative properties of $1s2snl$ and $1s2pnl$ quartet terms and obtained energy differences in agreement with experimental observations to within a few cm^{-1}. Their transition wavelength for $1s2s3d\,^4D - 1s2p3s\,^4P^o$ is at 8518 Å and they found that $1s2p3s\,^4P^o$ is the seventh member in the $^4P^o$ series. It seems to coincide with the line at 8517.369 Å observed by Herzberg and Moore [13] in the gas discharge spectroscopy. Yet this line has never been found in beam-foil experiments [1,14] where doubly-excited states are abundantly populated. Hence, it is considered as caused by an impurity and no satisfactory assignment in the quartet system had been made. If the calculation of Ref. [12] is precise, the lines at 3619 Å and 4885 Å can no longer be assigned to the transitions with the upper term $1s2p3s$. Instead, Mannervik [15] suggested that the line at 8508 Å observed by Bukow and Heine [16] should be the transition $1s2s3d\,^4D - 1s2p3s\,^4P^o$. However, this assignment does not agree with Fairley and Laughlin's calculation [12]. Furthermore, it reduces the term value of $1s2p3s\,^4P^o$ to 54 529(4) cm^{-1} [5] when it is combined with the transition $1s2s2p\,^4P^o - 1s2s3d\,^4D$ at 2337 Å [13]. This relative term value is much lower than the other alternative values 54 540(1) and 54 536(1) cm^{-1} mentioned above (Fig. 1).

To resolve the discrepancy discussed above, a precise theoretical study on the $^4P^o$ series is needed. In a previous work [17], the Rayleigh-Ritz variational method with Slater-type orbitals is shown to be able to obtain a $1s2s2p\,^4P^o$ term energy with an accuracy of a few cm^{-1}. Recently, the method of full core plus correlation (FCPC) has been developed by Chung [18] for systems whose core wave functions are not strongly perturbed by the outer electrons. This method has been applied to systems with a $1s1s\,^1S$ core. The recently developed restricted variational (RV) method by Chung and Zhu [19,20] are also shown to be very useful in computations where a large nonorthogonal basis set is used to saturate the functional space. These methods have been shown to give very accurate results for the ground or excited states of various symmetries, $^{2S+1}L^\pi$, for three- and four-electron systems [19–21]. In this work, they will be applied to explore higher excited $^4P^o$ terms of the lithium atom. In these systems, most of the states will have a $1s2s\,^3S$ core.

II. THEORY

The Hamiltonian and the perturbation operators considered in this work are the same as those of Ref. [17]. They will not be repeated here. The variational wave function of the higher $^4P^o$ terms is constructed with the FCPC method [18] in the LS-coupling scheme. It is composed of a $1s2s\,^3S$ two-electron wave function, ψ_{3S}, with the p-electron orbital and other three-electron partial waves, ϕ_Ω, as given by

$$\psi(1,2,3) = \mathcal{A}\left(\psi_{3S}(1,2)\sum_i d_i r_3^i e^{-\gamma r_3} Y_{1M}\chi(3)\right.$$
$$\left. + \sum_\Omega \phi_\Omega(1,2,3)\right), \qquad (1)$$

where $\mathcal{A}$ is the antisymmetrization operator. The partial wave ϕ_Ω is given by

$$\phi_\Omega(1,2,3) = \sum_{mnk} C_{mnk}\, \mathcal{R}_{mnk}(r_1,r_2,r_3)$$
$$\times \mathcal{Y}_{LM}(\hat{r}_1,\hat{r}_2,\hat{r}_3)\,\chi(123), \qquad (2)$$

with the basis function given by

$$\mathcal{R}_{mnk}(r_1,r_2,r_3) = r_1^m r_2^n r_3^k e^{-\alpha r_1} e^{-\beta r_2} e^{-\gamma r_3}, \qquad (3)$$

$$\mathcal{Y}_{LM}(\hat{r}_1,\hat{r}_2,\hat{r}_3) = \sum_{m_1,m_2,\mu,m_3} \langle l_1 m_1 l_2 m_2 | L_{12}\mu\rangle$$
$$\times \langle L_{12}\mu l_3 m_3 | LM\rangle$$
$$\times Y_{l_1 m_1}(\hat{r}_1)Y_{l_2 m_2}(\hat{r}_2)Y_{l_3 m_3}(\hat{r}_3), \qquad (4)$$

and $\chi(123)$ denoting a quartet spin function. Here m, n, and k are non-negative integers, and Ω represents the angular coupling $[(l_1,l_2)\,^3L_{12},l_3]\,^4L$ together with the set of nonlinear parameters (α,β,γ), which differ for each partial wave. The "core" wave function, ψ_{3S}, is the two-electron analogs of ϕ_Ω. The FCPC method has the advantage that it reduces the matrix size in the computations [18]. The core is prepared by minimizing the lowest eigenvalue of the nonrelativistic Hamiltonian matrix $\langle\psi_{3S}|H_0|\psi_{3S}\rangle$ and may not necessarily be very precise. Then it is frozen and put into Eq. (1). The nonrelativistic term energy of $^4P^o(n)$ is calculated by minimizing the lowest nth eigenvalue of the matrix $\langle\psi|H_0|\psi\rangle$. The minimizing procedures for both the two- and the three-electron calculations are implemented by adjusting the nonlinear parameters in each partial wave and by systematically increasing the number of partial waves in a manner of improving the angular correlation, radial expansion, and core relaxation.

However, with the constraints of finite precision of a computer and computing resources, the size of the trial wave function may not be enlarged at one's will. The numerical instability due to the linear dependence among the basis functions arises when too many terms of $\mathcal{R}_{mnk}$ in Eq. (3) are used to saturate the radial expansion of the functional space spanned by various couplings from a given set of angular momenta $[l_1,l_2,l_3]$. The RV calculation is an effective method to partially overcome this difficulty.

After a sufficiently accurate wave function ψ in Eq. (1) is obtained, which contains the dominant partial waves, it is fixed and treated as a single term, ψ_B. It will be referred to as the *basic wave function* in the restricted variational wave function, ψ_{RV}, which is given by

$$\psi_{RV}(123) = C_B\psi_B(123) + \psi_S(123), \qquad (5)$$

with

$$\psi_S(123) = \mathcal{A} \sum_S \phi_S(123) , \qquad (6)$$

where C_B is the expansion coefficient and ϕ_S takes the same form as ϕ_Ω in Eq. (2) except different sets of linear and nonlinear parameters. Thereafter, the partial waves for saturation purpose or of higher angular components join in the calculation as ϕ_S. The same procedure for obtaining the eigenvalue of ψ_B is repeated for $\psi_{\rm RV}$ except that the variation is restricted to those linear and nonlinear parameters in ψ_S. As a result, the overlap between the basis function in ψ_B and ψ_S does not cause any problem of linear dependence [19].

The reduced-mass corrections are considered, when converting the energy from a.u. to cm^{-1}, by using the value 109 728.731 for the Rydberg constant. In this work, no explicit calculations are carried out for the QED effects. However, for lithium, these effects could contribute as much as 1.25 cm^{-1} to the transition energy. To estimate these contributions, we use the results of Drake [22]. We assume that the QED contribution comes mainly from the Li^+ core and the contribution from the third electron with $n > 2$ is very small. Drake has calculated the QED contribution to the ionization potential of Li^+ $1s2s\,^3S$ to be -1.01 cm^{-1} and of $1s2p\,^3P^o$ to be $+0.24$ cm^{-1} [22]. Hence, the QED contribution to the Li I quartet transition energies will be

$$\Delta E_{\rm QED}(1s2snl - 1s2pn'l') = -1.01 - 0.24$$
$$= -1.25\,\text{cm}^{-1} \quad (n, n' > 2). \qquad (7)$$

For $1s2s2p\,^4P^o$, the core is not well defined. We take the average of the contributions of $1s2s\,^3S$ and $1s2p\,^3P^o$. Therefore,

$$\Delta E_{\rm QED}(1s2s2p - 1s2snl) = (-1.01 + 0.24)/2 + 1.01$$
$$= 0.63(20)\,\text{cm}^{-1} \quad (n > 2). \qquad (8)$$

In this case, an uncertainty of 0.2 cm^{-1} is assumed.

III. RESULTS AND DISCUSSIONS

A. The term energy of $1s2s2p\,^4P^o$

Strictly speaking, a variational calculation using finite basis set gives only upper bounds to the exact eigenvalues

of the Hamiltonian. In a previous work [17], the nonrelativistic term energy upper bound, $-5.367\,999$ a.u., was reported for $1s2s2p\,^4P^o$ with the value of $-5.368\,001(2)$ a.u. suggested for the exact nonrelativistic term energy. The extrapolated quantity, $-0.000\,002(2)$ a.u., is the expected difference if the basis set in the calculation were large enough to simulate a complete set. It is empirical in nature since no formulas of extrapolation were available. Presently, a more effective improvement is possible by using the restricted variational (RV) method [19].

In this work, we extend the 812-term wave function in Ref. [17] to 988 terms. The upper bound is improved by about 0.9 μa.u. to $-5.367\,999\,9$ a.u. This wave function is used as the basic wave function for the RV calculation. Following the same procedure as in Refs. [19] and [20], we carried out an RV calculation for 21 groups of mutually orthogonal $[l_1, l_2, l_3]$. The total number of terms participating in the RV calculation is 2 519. The total energy improvement obtained for the 21 groups is -5.480 μa.u. Since the RV procedure limited the flexibility of the coupling between ψ_S and ψ_B, which may further lower the energy, we add -0.5 μa.u. contribution to the energy and assign a possible uncertainty of 0.5 μa.u. Hence, the total nonrelativistic energy becomes $-5.368\,005\,9(5)$ a.u. By combining with the relativistic and mass polarization corrections -610.2 μa.u. from Ref. [17], the energy of $1s2s2p\,^4P^o$ becomes $-5.368\,616\,1(5)$ a.u.

A closed loop analysis will be made in Sec. III D to compare the transition energies involving $1s2p3s\,^4P^o$ with experimental results. The three intermediate terms in the closed loops are $1s2s3s\,^4S$, $1s2p2p\,^4P$, and $1s2s3d\,^4D$, whose transitions to $1s2s2p\,^4P^o$ have been well studied by experiment. The energy of $1s2s3s\,^4S$ has been calculated in Ref. [17] to be $-5.213\,358(1)$ a.u. The energies of $1s2p2p\,^4P$ and $1s2s3d\,^4D$ are calculated in this work. These results together with that of $1s2s2p\,^4P^o$ are given in Table I. For $1s2s3d\,^4D$, the FCPC wave function is used with the same $1s2s\,^3S$ core as that of the $1s2snp\,^4P^o$ $(n > 2)$ series. The basic wave function contains 596 terms. For $1s2p2p\,^4P$, no core wave function is assumed. The basic wave function of this ^4P term contains 625 terms, but the energy convergence is much slower than the other quartet terms considered in the present work. We have included high angular components up to the $[0, 9, 9]$ and $[7, 8, 1]$ in our calculation. The combined contribution of these two components to the energy is -0.61 μa.u. Hence, we estimate that the total contribution of the higher angular momentum components not included in the computation should be no less than -0.7 μa.u.

TABLE I. Term energies (in μa.u.) of $1s2s2p\,^4P^o$, $1s2p2p\,^4P$, and $1s2s3d\,^4D$ for neutral lithium. Here H_1 is the mass polarization, H_2 the mass variation, H_3 the Darwin term, and H_4 the orbit-orbit interaction.

Term	Nonrelativistic energy			Perturbative corrections			
	$E_{\rm upperbound}$	$\Delta_{\rm RV}$	$E_{\rm nonrel}$	$\langle H_1 \rangle$	$\langle H_2 + H_3 \rangle$	$\langle H_4 \rangle$	$E_{\rm total}$
$1s2s2p\,^4P^o$	$-5\,367\,999.9$	$-6.0(5)$	$-5\,368\,005.9(5)$	-15.4	-604.0	9.2	$-5\,368\,616.1(5)$
$1s2p2p\,^4P$	$-5\,245\,390.3$	$-14.2(10)$[a]	$-5\,245\,404.5(10)$	-27.43	-552.8	18.2	$-5\,245\,966.5(10)$
$1s2s3d\,^4D$	$-5\,173\,072.1$	$-8.5(5)$	$-5\,173\,080.6(5)$	1.20	-611.5	0.2	$-5\,173\,690.8(5)$

[a]Includes an estimated -0.7 μa.u. from higher-l angular components.

B. Term values of the $^4P^o$ series

The present study will pursue an accurate energy for $^4P^o(n)$, then locate the perturbing term $1s2p3s\,^4P^o$ submerged in the energy spectrum. The FCPC method is used to construct the trial wave function from which the energy eigenvalue and the perturbative corrections are obtained. It is followed by the RV method to give the nonrelativistic term energy. Beginning with $^4P^o(2)$, the calculation proceeds upwards until two terms beyond the one which can be recognized as the perturber. There are nine terms involved, namely $^4P^o(n)$, $n = 2$–10.

The ^3S core wave function prepared for the present calculation contains 51 terms in five partial waves, $[l,l]\,^3S$ for $0 \le l \le 4$, and gives the eigenenergy of $-5.110\,719$ a.u., which is to be compared with the nonrelativistic energy of $-5.110\,727$ a.u. derived from Accad et al. [23]. The inaccuracy of the core is compensated by the three-electron partial waves of the type $[l,l,1]$ in the FCPC and the RV calculations. The number of terms in each of the final FCPC wave function of $^4P^o(n)$ ranges from 452–657. In the succeeding RV calculations there are 21 groups of mutually orthogonal $[l,l,1]$ and $[0,l,l+1]$ with $0 \le l \le 10$ considered for each $^4P^o(n)$. The details of the energy convergence and RV results are not given. They will be supplied to the interested reader upon request. The results together with those perturbative corrections are collected in Table II, where the values of Δ_{RV} contain the RV results and the additional contributions estimated for the relaxation of the basic wave function as described in Sec. III A. These contributions are -0.5 μa.u. for $n = 2$–7 and -0.3 μa.u. for $n = 8$–10. In Table II, the best previous values available from other theoretical works are also presented. These previous upper bounds, $E_{upperbound}$, are improved in the present calculation. The estimated energy of $^4P^o(2)$ in Bunge [11] agrees with that of the present work excellently. His results for $^4P^o(3)$ and for $^4P^o(4)$ are slightly higher than the energies obtained in this work.

Along the $^4P^o$ series, the trends of the perturbative contributions are disturbed at the seventh and the eighth members, which are possible candidates of the perturber. The two terms are only 24 cm^{-1} apart such that quadruple precision computations (128-bit storage for a floating point number) and noniterative type algorithm are necessary to resolve them in the eigenvalue problem.

The predicted relative term value, $T\big(^4P^o(n)\big)$, to the ground quartet $1s2s2p\,^4P^o$ can be determined by

$$T\big(^4P^o(n)\big) = E_{total}\big(^4P^o(n)\big) - E_{total}(1s2s2p\,^4P^o) \quad (9)$$

with $E_{total}(1s2s2p\,^4P^o) = -5.368\,616\,1$ a.u. given in Sec. III A. The results are presented and compared with experiment in Table III. For the term $^4P^o(7)$, the predicted relative term value, $54\,539.2(4)$ cm^{-1}, is to be compared with $54\,529(4)$, $54\,536(1)$, and $54\,540(1)$ cm^{-1} for $1s2p3s\,^4P^o$ from experiment [5]. The experimental values span a range of 16 cm^{-1}, which is comparable to the difference between $^4P^o(7)$ and $^4P^o(8)$. Therefore, no conclusion on the identification of these lines can be drawn before the radiative and electron-configurational characteristics of $^4P^o(7)$ and $^4P^o(8)$ are clarified. This will be done in Sec. III C. The configuration assignments from Sec. III C are used to estimate the QED corrections to the relative term values in Table III by Eq. (8).

C. The term $1s2p3s\,^4P^o$ and the $1s2snp\,^4P^o$ Rydberg series

Current experimental assignments imply that, in the transitions to $1s2s3s\,^4S$, $1s2p2p\,^4P$, and $1s2s3d\,^4D$, the perturbing term, $1s2p3s\,^4P^o$, should has the strongest intensities among its neighboring terms in the $^4P^o$ series. We, therefore, calculate the absorption oscillator strength f and the emission rate R (in sec^{-1}) for $^4P^o(n)$. The results are presented in Table IV. The transition probability for $1s2s3d\,^4D - \,^4P^o(7)$ is 1.01×10^6 sec^{-1}, which is close to the value of 1.4×10^6 sec^{-1} calculated by Fairley and Laughlin [12]. It can be seen that the term $^4P^o(7)$ has larger transition probabilities than $^4P^o(8)$ for all three transitions considered and is the appropriate candidate for $1s2p3s\,^4P^o$ from the radiative aspect.

TABLE II. Term energies (in μa.u.) of $^4P^o(n)$ for neutral lithium, $n = 2$–10. Here H_1 is the mass polarization, H_2 the mass variation, H_3 the Darwin term, and H_4 the orbit-orbit interaction.

Term	Nonrelativistic energy			Perturbative corrections			
	$E_{upperbound}$	Δ_{RV}	E_{nonrel}	$\langle H_1 \rangle$	$\langle H_2 + H_3 \rangle$	$\langle H_4 \rangle$	E_{total}
$^4P^o(2)$	$-5\,187\,272.09$	$-7.2(5)$	$-5\,187\,279.3(5)$	-1.57	-613.39	1.32	$-5\,187\,892.9(5)$
	$-5\,187\,236^a$		$-5\,187\,278(9)^a$				
$^4P^o(3)$	$-5\,149\,729.94$	$-6.2(5)$	$-5\,149\,736.1(5)$	0.32	-614.97	0.25	$-5\,150\,350.5(5)$
	$-5\,149\,692^a$		$-5\,149\,722(4)^a$				
$^4P^o(4)$	$-5\,134\,473.29$	$-3.4(5)$	$-5\,134\,476.7(5)$	0.86	-615.17	-0.08	$-5\,135\,091.1(5)$
	$-5\,134\,422^a$		$-5\,134\,454(5)^a$				
$^4P^o(5)$	$-5\,126\,706.35$	$-8.2(5)$	$-5\,126\,714.6(5)$	1.09	-615.31	-0.21	$-5\,127\,329.0(5)$
$^4P^o(6)$	$-5\,122\,218.44$	$-4.6(5)$	$-5\,122\,223.0(5)$	1.20	-615.35	-0.27	$-5\,122\,837.5(5)$
$^4P^o(7)$	$-5\,119\,514.24$	$-8.0(5)$	$-5\,119\,522.2(5)$	-20.68	-564.48	12.25	$-5\,120\,095.2(5)$
$^4P^o(8)$	$-5\,119\,376.97$	$-1.6(3)$	$-5\,119\,378.6(3)$	-0.59	-611.15	0.74	$-5\,119\,989.6(3)$
$^4P^o(9)$	$-5\,117\,486.50$	$-1.2(3)$	$-5\,117\,487.7(3)$	1.30	-615.41	-0.33	$-5\,118\,102.1(3)$
$^4P^o(10)$	$-5\,116\,149.12$	$-2.8(3)$	$-5\,116\,151.9(3)$	1.32	-615.43	-0.36	$-5\,116\,766.4(3)$

^{a}Reference [11].

TABLE III. Relative term values (in cm^{-1}) of $1s2s3s\,^4S$, $1s2p2p\,^4P$, $1s2s3d\,^4D$, and $^4P^o(n)$, $n = 2$–10 for neutral lithium. The term values are relative to $1s2s2p\,^4P^o$.

Term	T_{calc}	QED corr.	T This work	Assignment	Experiment[a]
$^4P^o(2)$	39 661.1(2)	0.6(2)	39 661.7(4)	$1s2s3p\,^4P^o$	39 655(4)[b]
$^4P^o(3)$	47 900.0(2)	0.6(2)	47 900.6(4)	$1s2s4p\,^4P^o$	
$^4P^o(4)$	51 248.8(2)	0.6(2)	51 249.4(4)	$1s2s5p\,^4P^o$	
$^4P^o(5)$	52 952.3(2)	0.6(2)	52 952.9(4)	$1s2s6p\,^4P^o$	
$^4P^o(6)$	53 937.9(2)	0.6(2)	53 938.5(4)	$1s2s7p\,^4P^o$	
$^4P^o(7)$	54 539.8(2)	−0.6(2)	54 539.2(4)	$1s2p3s\,^4P^o$	54 529(4)[c]
					54 536(1)[d]
					54 540(1)[e]
$^4P^o(8)$	54 562.9(1)	0.6(2)	54 563.5(3)	$1s2s8p\,^4P^o$	
$^4P^o(9)$	54 977.2(1)	0.6(2)	54 977.8(3)	$1s2s9p\,^4P^o$	
$^4P^o(10)$	55 270.3(1)	0.6(2)	55 270.9(3)	$1s2s10p\,^4P^o$	
$^4P(1)$	26 916.3(2)	−0.6(3)	26 915.7(5)	$1s2p2p\,^4P$	26 915.16(6)
$^4S(1)$	34 072.5(4)[f]	0.6(2)	34 073.1(6)	$1s2s3s\,^4S$	34 072.0
$^4D(1)$	42 777.8(2)	0.6(2)	42 778.4(4)	$1s2s3d\,^4D$	42 778.3

[a]Reference [5].
[b]Based on the observed lines at 1680 and 5033 Å.
[c]Based on the observed lines at 2337 and 8508 Å.
[d]Based on the observed lines at 2934 and 4885 Å.
[e]Based on the observed lines at 3714 and 3619 Å.
[f]Reference [17].

The fine-structure splittings of $1s2p3s\,^4P^o$ and of $1s2snp\,^4P^o$ should be quite different if we consider them as resulting from the $1s2p\,^3P^o$ core with a $3s$ electron and from the $1s2s\,^3S$ core with an np electron, respectively. It is obvious that the main contributions should come from the two core electrons. Larger splittings are expected from the term dominated by the $1s2p\,^3P^o$ core. Table V presents the first-order perturbative contributions to the total term energy for the $J = 5/2$ level of $^4P^o(n)$ calculated in the LSJ scheme and their fine-structure splittings. The perturbation operators are the same as in Ref. [24]. It is clear that $^4P^o(7)$ can be discerned definitely from the $1s2snp$ Rydberg series and it can be named $1s2p3s$ with reasonable certainty. The splittings of $^4P^o(8)$ are also orders of magnitude larger than that of $^4P^o(6)$ and $^4P^o(9)$. It suggests a certain amount of mixing between the configurations $1s2p3s$ and $1s2s8p$ as was anticipated by Mannervik [15]. In calculations using configuration wave functions as the basis functions, the mixing should have an important effect on the results. Fairley and Laughlin [12] have located $1s2p3s\,^4P^o$ as the seventh member, however they reported that it interacts only very weakly with the $1s2snp\,^4P^o$ Rydberg series.

The term energies and the configuration assignments in Table III for the $1s2snp$ series can also be studied through the quantum defect analysis using the Ritz formula [25],

$$I_n = \frac{\mathfrak{R}}{(n + \mu + \alpha I_n)^2} = \frac{\mathfrak{R}}{n^{*2}},\qquad (10)$$

where α and μ are constants, $\mathfrak{R}$ is the Rydberg constant, and n^* is the effective quantum number of $1s2snp$. The nonrelativistic ionization potential I_n is obtained from the term energy of this work and the $1s2s\,^3S$ series limit $-5.110\,727$ a.u. [23]. Figure 2 presents the

quantum defects for the series, which shows that, excluding $^4P^o(7)$, the term energies of the other eight terms studied in this work can be appropriately described by the Ritz formula as in a Rydberg series with $1s2s8p$ being slightly perturbed. The linear least-square fit gives $\alpha = -2.732 \times 10^{-5}$ and $\mu = -0.3971$, which can be used in the extrapolation for higher $^4P^o$ term energies.

D. Transitions involving $^4P^o$ terms

In recent experimental works [2–4,15], the three observed lines at 3619, 4885, and 8508 Å are tentatively
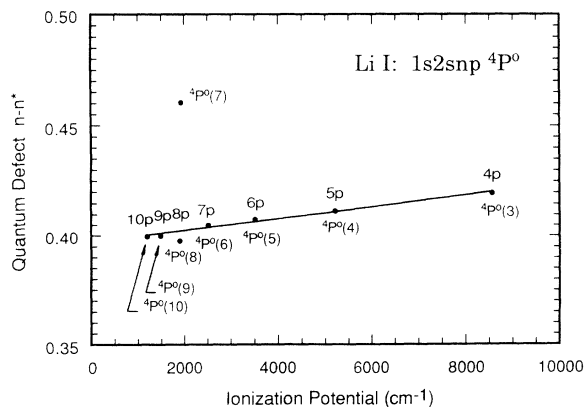

FIG. 2. Quantum-defect diagram for the $1s2snp$ Rydberg series by using the Ritz formula. The straight line is fitted for np, where $n = 4$, 5, 6, 7, 9, and 10. The diagram also shows the point for $^4P^o(7)$ if it were assigned as $1s2s8p$.

TABLE IV. Absorption oscillator strengths, f, and emission rates, R (in sec^{-1}), of the transitions between $^4P^o(n)$ and $1s2s3s\,^4S$, $1s2p2p\,^4P$, and $1s2s3d\,^4D$ for neutral lithium, $n = 1$–10.

Term	$1s2s3s\,^4S$		$1s2p2p\,^4P$		$1s2s3d\,^4D$	
	f	R	f	R	f	R
$^4P^o(1)$	6.37×10^{-2}	1.48×10^8	3.59×10^{-1}	1.73×10^8	3.35×10^{-1}	2.45×10^8
$^4P^o(2)$	9.51×10^{-1}	6.61×10^6	6.69×10^{-6}	7.26×10^2	4.26×10^{-1}	1.66×10^6
$^4P^o(3)$	5.12×10^{-3}	2.18×10^5	8.83×10^{-5}	2.59×10^4	7.58×10^{-2}	2.21×10^6
$^4P^o(4)$	5.35×10^{-3}	3.51×10^5	8.07×10^{-5}	3.19×10^4	1.15×10^{-2}	9.17×10^5
$^4P^o(5)$	3.67×10^{-3}	2.91×10^5	4.61×10^{-5}	2.08×10^4	4.30×10^{-3}	4.95×10^5
$^4P^o(6)$	2.91×10^{-3}	2.56×10^5	5.34×10^{-6}	2.60×10^3	2.00×10^{-3}	2.77×10^5
$^4P^o(7)$	2.87×10^{-1}	2.67×10^7	1.41×10^{-1}	7.16×10^7	6.55×10^{-3}	1.01×10^6
$^4P^o(8)$	1.38×10^{-2}	1.29×10^6	1.37×10^{-2}	7.01×10^6	3.66×10^{-3}	5.64×10^5
$^4P^o(9)$	5.15×10^{-4}	5.00×10^4	1.58×10^{-4}	8.29×10^4	8.93×10^{-4}	1.48×10^5
$^4P^o(10)$	4.91×10^{-4}	4.90×10^4	7.84×10^{-5}	4.21×10^4	5.93×10^{-4}	1.03×10^5

assigned as the transitions from $1s2p3s\,^4P^o$ to $1s2p2p\,^4P$, $1s2s3s\,^4S$, and $1s2s3d\,^4D$, respectively. The present study determines the term values which give the aerial transition wavelengths in excellent agreement with the first two lines; but the large discrepancy for the third line leaves the assignment for the relatively weak line at 8508 Å in doubt (see Fig. 1). However, the present calculation shows that it cannot be replaced by the line at 8517.369 Å observed by Herzberg and Moore [13] (see Sec. I). In fact, our results show that the $1s2s3d\,^4D$ − $1s2p3s\,^4P^o$ transition occurs at about 8500.5 Å. It should be mentioned that the mass-polarization and relativistic contributions are crucially important for these identifications. If only nonrelativistic energies were considered, our results for the relative term value of $^4P^o(7)$ would be 54 531.0 cm^{-1}, which would favor the assignment [15] of the line at 8508 Å for the transition $1s2s3d\,^4D$ − $1s2p3s\,^4P^o$.

One may predict a line at 4879 Å and a line at 3616 Å arising from the transitions from $1s2s8p\,^4P^o$ to $1s2s3s\,^4S$ and $1s2p2p\,^4P$, respectively, using the term values in Table III since Table IV has shown these transition probabilities are not too small. However, the two lines were not reported in the experiments [3–5,26]. It is possible that the line at 4879 Å was blended by the intense line of Li II at 4881 Å, and the line at 3616 Å was not resolved from the relatively stronger line of the corresponding transition from $1s2p3s\,^4P^o$ at 3619 Å.

IV. CONCLUSION

The purpose of this work is to establish firmly the position of the lithium $1s2p3s\,^4P^o$ within the $^4P^o$ series. In doing this we have calculated the energies for the ten lowest members of the $^4P^o$ symmetry. The identification is made by studying the transition rates, quantum defects, and fine structures. In all these studies, they show clearly that $1s2p3s$ is the seventh lowest member in the series, which is in accord with the study of Fairley and Laughlin [12]. It lies very closely to the eighth member, $1s2s8p\,^4P^o$, and perturbs the energy of this term. Nevertheless, the perturbation is sufficiently weak such that both terms retain their $1s2p3s$ and $1s2s8p$ characteristics.

In order to make closed loop analyses, we have also calculated the term energies of $1s2p2p\,^4P$ and $1s2s3d\,^4D$. The results are predicted to well within 1 cm^{-1}. To our knowledge, these are the most reliable theoretical results to date.

As for the current status of the quartet system of neutral lithium, the optical study of the beam-foil spectrum has satisfactorily established the ^4S and ^4D series with the transitions $^4P^o(1)$ − $1s2sns\,^4S$, $n = 3$–6, and the transitions $^4P^o(1)$ − $1s2snd\,^4D$, $n = 3$–10. However, little has been known for excited $^4P^o$ terms. As the high-resolution and infrared measurements have been proposed, we hope the present study will stimulate further theoretical and experimental works.

TABLE V. First-order perturbative contributions (in a.u.) of spin-orbit (SO), spin-other-orbit (SOO), and spin-spin (SS) interactions and fine structure splittings (in cm^{-1}) of $^4P^o(n)$ for neutral lithium, $n = 2$–10.

Term	Perturbative contribution for the $J = 5/2$ level			Level splitting	
	$\langle H_{SO} \rangle$	$\langle H_{SOO} \rangle$	$\langle H_{SS} \rangle$	$\Delta E_{3/2-1/2}$	$\Delta E_{5/2-3/2}$
$^4P^o(2)$	1.841×10^{-6}	1.880×10^{-7}	-1.961×10^{-6}	-0.397	0.162
$^4P^o(3)$	6.558×10^{-7}	6.676×10^{-8}	-6.941×10^{-8}	-0.140	0.0592
$^4P^o(4)$	3.097×10^{-7}	3.143×10^{-8}	-3.266×10^{-8}	-0.0659	0.0284
$^4P^o(5)$	1.720×10^{-7}	1.753×10^{-8}	-1.812×10^{-9}	-0.0366	0.0159
$^4P^o(6)$	1.111×10^{-7}	1.130×10^{-8}	-1.171×10^{-9}	-0.0236	0.0102
$^4P^o(7)$	1.633×10^{-5}	1.378×10^{-6}	-1.647×10^{-6}	-2.75	1.46
$^4P^o(8)$	1.378×10^{-6}	1.165×10^{-7}	-1.381×10^{-7}	-0.231	0.127
$^4P^o(9)$	4.634×10^{-8}	4.757×10^{-9}	-4.825×10^{-9}	-0.00981	0.00452
$^4P^o(10)$	3.222×10^{-8}	3.349×10^{-9}	-3.371×10^{-9}	-0.00694	0.00313

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