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Saddle-point technique for autoionizing states of the lithium atom. III. Low-lying triply excited resonances

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The energy, wave function, and radial parameters of the low-lying triply excited resonances of the lithium atom are calculated using a saddle-point technique. A total of eleven resonances with $^2P^o$, $^4P^e$, $^2D^e$, $^2S^e$, $^2P^e$, and $^2D^o$ symmetries are investigated. These results are used to identify the observed Auger spectra of Rødbro, Bruch, and Bisgaard. If the identifications suggested here are correct, then the agreement between the results of the present work with those of the experiment is excellent. The oscillator strengths and transition energies of these resonances in an optical absorption or emission process are calculated. In order to compute these oscillator strengths, the energies and wave functions of the Li $1s2s2p\,^4P$, $1s2p2p\,^2P$, and $1s2s2s\,^2S$ states are also tabulated. The energies of the two bound states agree to within 0.013 eV with the highly accurate results in the literature. The result for the ^2S resonance agrees with the more recent experiments and lies well within the quoted experimental error.

I. INTRODUCTION

The multiply excited resonant states of a many-electron atomic system are of great interest theoretically as well as experimentally. They correspond to a discrete spectrum of the Hamiltonian that lies in the continua. In many cases, they are degenerate with an infinite number of open channels, coupling with them via the Coulomb interaction. On the other hand, this coupling is usually very weak, once a resonance is formed it behaves as a bounded system until it decays by autoionization or radiation. Nevertheless, the coupling to the continua presents a great challenge to the theorists in finding a proper way to calculate the energy and wave function of these systems.

Experimentally, more of these resonances are being observed due to the development of many high-resolution techniques. For example, in optical spectra measurements, satellites and hypersatellites[1] are observed in x-ray spectra. Two-electron one-photon emission processes have also been reported.[2] Other practical applications of these autoionizing states can be found in the diagnostics of a high-temperature plasma[3] or in populating a certain excited state through Auger decay.

Recently, a high-resolution Auger spectra of lithium was reported by Rødbro *et al.*[4] By using 200-keV Li^+ impinging on CH_4, they obtained many Auger lines which seem to originate from triply excited lithium. The resolution quoted for these lines is ±0.1 eV.

The triply excited resonances of lithium have been investigated theoretically by many authors. For example, the $2s^2 2p\,^2P^o$, $2s\,2p^2\,^4P^e$, $^2D^e$, $^2S^e$, $^2P^e$, and $2p2p2p\,^2D^o$, $^2P^o$ have been calculated by Safronova and Senasheko[5] using a perturbation theory. Other methods include the many-body perturbation technique by Simons *et al.*,[6] the projector-operator method by Nicolaides and Beck,[7] and the expansion method by Ahmed and Lipsky.[8] The theoretical results disagree among themselves and do not lead to a reasonable understanding of the observed spectra.

Recently, a saddle-point technique[9] has been developed to study quantum states with inner-shell vacancies. This method has been applied to the elastic and inelastic scattering region of the lithium atom.[10] Highly accurate results were obtained. In this work, this method will be applied to triply excited lithium systems. As compared with the earlier calculations on the triply excited He^- system,[11] the computer code of the present work is much better in that each angular partial wave is allowed to have a different set of optimized nonlinear parameters and a term selection process is used to keep the size of the wave functions to a reasonable level.

In Sec. II, the method of calculation will be outlined briefly and the results of the calculations will be given. Section III discusses the oscillator strengths for optical absorption to these resonances as well as optical emission from these resonances. The results for the states of lithium $1s2s2p\,^4P$, $1s2p2p\,^2P$, and $1s2s2s\,^2S$ will also be reported in this section. Section IV is a detailed analysis comparing the present work with the reported results of Rødbro *et al.*[4] Section V is a brief summary.

II. COMPUTATIONAL ASPECTS AND RESULTS

The method of computation in this work closely parallels that of Ref. 10. Multiconfiguration basis functions are used in a variational calculation with the nonrelativistic Hamiltonian

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$$H=-\sum_{i=1}^{3}\left(\tfrac{1}{2}\nabla_i^2+\frac{3}{r_i}\right)+\sum_{i<j}^{3}\frac{1}{r_{ij}}. \tag{1}$$

In the LS coupling scheme the angular and spin part of the basis set can be represented by $[(l_1,l_2)^kL_{12},l_3]^SL$. In this notation, the orbital angular momentum l_1 of the first electron couples to the l_2 of the second electron to form a core of angular momentum L_{12} and spin multiplicity k. This core is then coupled to the angular momentum l_3 and the spin of the third electron to form the total angular momentum L and spin multiplicity S.

The configuration of the lowest triply excited state is $2s2s2p$. This configuration can only form a ^2P state. To compute the energy of this resonance, two $1s$ vacancies are built into the total wave function. These two vacancies are assumed to be the same screened hydrogenic orbital

$$\phi_{1s}(\vec{r})=Ne^{-qr}, \tag{2}$$

where N is the normalization factor. The nonlinear parameter q is obtained by maximizing the energy in the variation process.[9] Physically q can be interpreted as the effective nuclear charge seen by the vacancy orbital. Since all three electrons are excited to the $n=2$ level, the screening of the nuclear charge by the electrons which is felt by the vacancy is small. Therefore, one would expect the optimized q to be close to 3. For this ^2P state, q is found to be 2.93. This is different from the doubly excited lithium system where q lies close to 2.5.[10]

A general feature of the low-lying triply excited doublet wave functions is the presence of many degenerate configurations. The implication of this is that the two electron "core" is not well defined. A consequence of this is that the various higher l_1, l_2, and l_3 may couple into different partial waves and each of these partial waves may contribute significantly to the binding energy. This is particularly true in some of the even-parity doublet states. Hence, if one wishes to calculate these resonances to high accuracy, one needs to consider the correlations from all possible angular and spin couplings carefully. In the case of the $2s2s2p\,^2P$ resonance, an eleven partial-wave, 99 term-wave function is used. The energy of this wave function is $-2.249\,69$ a.u., compared with the nonrelativistic ground-state energy of lithium $-7.478\,025$ a.u.,[12] it is higher by 142.272 eV. The conversion 1 a.u. $=27.211\,65$ eV is used.[13] The result of this calculation is given in Table I. It should be noted that the coupling of $2s2s2p\,^2P$ and $2p2p2p\,^2P$ is very strong. The contributions from these two configurations to the normalization are 83% and 14%, respectively. The same two configurations in the second lowest root of the secular equation contribute 21% and 74%, respectively. This latter state is classified as the $2p2p2p\,^2P^o$ resonance.

The second lowest triply excited resonance should correspond to the configuration $2s2p2p$. In the LS coupling, this configuration may couple into $^4P^e$, $^2D^e$, $^2S^e$, and $^2P^e$ states. The lowest state among these symmetries is the $^4P^e$ because the exchange energy of this configuration is large. It contributes significantly to the binding of this system.

For quartet states, the coupling of l_1, l_2, and l_3 is straightforward compared with doublet states. The rate of convergence is also faster. By using an eight partial-wave, 74 term-wave function, the energy is $-2.239\,58$ a.u. This is 142.547 eV above the ground state of lithium. To show the convergence in this calculation, the results are given in Table II.

TABLE I. Energy and wave function of the $2s2s2p\,^2P^o$ resonance of the lithium atom ($q=2.93$). N is the number of linear parameters in the partial wave. α, β, and γ are the nonlinear parameters. ΔE is the contribution to the binding energy when the partial wave is added. $\langle\Psi_i\|\Psi_i\rangle$ is its contribution to the normalization.

	Partial waves	N	α,β,γ	$-\Delta E$ (a.u.)	$\langle\Psi_i\Psi_i\rangle$
1	$[(s,s)\,^1S,p]$	25	1.3, 1.3, 1.25	2.178 110	0.834 33
2	$[(s,p)\,^1P,s]$	14	1.5, 1.65, 0.7	0.001 728	
3	$[(p,p)\,^1S,p]$	10	1.35, 1.35, 1.35	0.044 850	0.138 52
4	$[(s,p)\,^1P,d]$	16	1.1, 1.45, 1.6	0.010 331	0.011 98
5	$[(s,p)\,^3P,d]$	7	1.1, 1.35, 1.6	0.009 879	0.012 18
6	$[(p,d)\,^1P,d]$	9	1.25, 1.7, 1.6	0.002 940	0.002 12
7	$[(d,d)\,^1S,p]$	4	1.6, 1.6, 1.25	0.000 250	
8	$[(s,d)\,^1D,f]$	7	1.5, 1.9, 2.0	0.000 862	0.000 41
9	$[(f,f)\,^1S,p]$	2	2.0, 2.0, 1.25	0.000 103	0.000 04
10	$[(p,p)\,^1D,f]$	2	1.5, 1.5, 1.8	0.000 554	0.000 39
11	$[(s,d)\,^3D,f]$	3	1.5, 1.9, 2.1	0.000 107	0.000 05
	Total	99		2.249 694	

TABLE II. Energy and wave function of the $2s2p2p\,^4P^e$ resonance of the lithium atom ($q=2.85$). For notation see Table I.

	Partial waves	N	α,β,γ	$-\Delta E$ (a.u.)	$\langle\Psi_i\|\Psi_i\rangle$
1	$[(s,p)^3P,p]$	19	1.35, 1.15, 1.35	2.227 960	0.989 96
2	$[(p,p)^3P,s]$	7	1.25, 1.25, 1.3	0.000 062	
3	$[(s,d)^3D,d]$	15	1.20, 1.6, 1.9	0.005 324	0.003 57
4	$[(p,d)^3P,p]$	7	1.35, 1.55, 1.2	0.005 019	0.005 97
5	$[(p,p)^3P,d]$	6	1.35, 1.35, 1.6	0.000 081	
6	$[(s,f)^3F,f]$	9	1.0, 2.1, 2.3	0.000 344	0.000 12
7	$[(d,f)^3P,p]$	8	1.55, 2.05, 1.25	0.000 682	0.000 38
8	$[(p,f)^3F,d]$	3	1.20, 1.9, 1.45	0.000 104	
	Total	74		2.239 58	

It is interesting to note that the binding energy due to the first partial wave in Table II is substantially lower than that of Table I. It is only after the inclusion of the correlation due to other partial waves that the energy of $2s2s2p\,^2P$ becomes lower than that of $2s2p2p\,^4P$. This clearly exhibits the effects of degeneracy, exchange, and correlation on these triply excited levels.

Among the doublets formed by the $2s2p2p$ configuration, the $^2D^e$ resonance is the lowest, followed by $^2S^e$ and $^2P^e$. In order to obtain a reliable energy and wave function, various angular partial waves are considered. For simplicity, the detailed results of these wave functions as given in Tables I and II will not be reported here. This information will be supplied upon request. The energy, the number of partial waves, and the number of linear parameters for these resonances are given in Table III, together with earlier results from the literature for comparison.

In order to make a detailed comparison with the spectra reported in Ref. 4, the second members of $^2S^e$, $^2P^e$, and $^2D^e$ are also computed. The second member of $^2S^e$ can be roughly classified as the $2s2s3s\,^2S^e$ resonance. This is because the $2s2s3s$ configuration contributes 72% to the normalization. Classification is more difficult in the case of $^2P^e$. The partial waves $[(2s2p)^3P,3p]$, $[(2s2p)^1P,3p]$, and $[(2p2p)^3P,3s]$ interact strongly and a simple configuration representation is difficult. Therefore the second resonance will be denoted $^2P^e(2)$. Similarly, $^2D^e(2)$ is used for the second member of the $^2D^e$ resonances. These results are also given in Table III.

Other results included in Table III are the $2p2p2p\,^2P^o$, $2p2p2p\,^2D^o$, and $^4P^e(2)$ resonances. The $2p2p2p\,^4S^o$ is metastable against autoionization. Therefore it will not be considered in this work. Results for this state are available in the literature.[14] As discussed before, the $2p2p2p\,^2P^o$ corresponds to the second lowest root of the $^2P^o$ secular equation. The nonlinear parameters in

TABLE III. The energies of some low-lying triply excited resonances. q is the nonlinear parameter in the vacancy orbitals. L is the number of partial waves. N is the number of linear parameters in the wave function.

						E other calculations (eV)		
Resonances	q	L	N	E (a.u.)	E (eV)[a]	Ref. 5	Ref. 7	Others
$2s2s2p\,^2P^o$	2.93	11	99	−2.249 69	142.272	141.811	142.608	142.661[b] 141.7[c]
$2s2p2p\,^4P^e$	2.85	8	74	−2.239 58	142.547	142.458		
$2s2p2p\,^2D^e$	2.89	10	99	−2.156 15	144.817	143.937		
$2s2p2p\,^2S^e$	2.895	10	82	−2.093 66	146.517	146.414	147.454	
$2p2p2p\,^2D^o$	2.78	12	85	−2.077 39	146.960	146.645		
$2s2p2p\,^2P^e$	3.00	11	104	−2.076 30	146.990	146.769		
$2p2p2p\,^2P^o$	2.93	11	99	−2.003 44	148.972	148.706	149.261	148.5[c]
$2s2s3s\,^2S^e$	2.91	10	82	−1.989 78	149.344		149.048	
$^2P^e(2)$	2.91	9	84	−1.974 30	149.765			
$^4P^e(2)$	2.91	7	73	−1.961 10	150.125			
$^2D^e(2)$	2.92	11	97	−1.956 45	150.251			

[a] Energy relative to the ground state at −7.478 025 a.u. Conversion factor 1 a.u. = 27.211 65 eV.

[b] Reference 6.

[c] Reference 8.

Table I also give an optimized energy for this resonance. The ${}^4P^e(2)$ is the second lowest state of the ${}^4P^e$ symmetry. The reason that this state is calculated is to see whether it has contributed to the spectra of Rødbro *et al.*[4] at 82.06 eV (see Sec. IV). The second lowest ${}^2D^o$ resonance is not calculated. The configuration of this state is $2p2p3p\,{}^2D^o$. The energy of this state is much higher.

To gain more insight into these resonances, some radial expectation values for these states are tabulated. Define

$$\langle r^m\rangle = \tfrac{1}{3}\langle\Psi\,|r_1^m + r_2^m + r_3^m|\Psi\rangle\,. \qquad (3)$$

The results for $m=-1$, $m=1$, and $m=2$ are computed. These values are given in Table IV. Judging from the geometric size of $2s2s3s\,{}^2S^e$, ${}^2P^e(2)$, ${}^4P^e(2)$, and ${}^2D^e(2)$, the presence of the $n=3$ electron is quite apparent.

III. OSCILLATOR STRENGTHS

In recent years, the technique of Auger electron spectroscopy has been greatly improved and high-resolution spectral lines have been obtained in many lithium experiments.[15,16] However, the most accurate experimental results for certain resonances are still likely to be obtained in optical absorption and emission experiments. The fact that the states accessible in these experiments are restricted by the dipole selection rules makes identification of resonances easier. For doubly excited lithium, resolutions of ±0.006 eV have been reported.[17,18] For this reason, the oscillator strengths of these triply excited lithium states are calculated to assess the likelihood of detection in an optical experiment.

In this work, the oscillator strength is computed with the dipole length operator. It is summed over the final states and averaged over the initial states. The summation and average can be easily done with the Wigner-Eckert theorem,[19] so only one matrix element between a particular pair of magnetic substates need be calculated, i.e.,

$$f = \tfrac{2}{3}(E_i - E_f)\frac{|\langle\Psi(L,M)|\vec{\mathrm{r}}|\Psi(L',M')\rangle|^2}{(2L+1)\begin{pmatrix} L & 1 & L' \\ M & m & M'\end{pmatrix}^2}\,, \qquad (4)$$

where $M = m + M'$.

TABLE IV. Radial expectation values for some low-lying triply excited resonances of the lithium atom.

Resonances	$\left\langle\frac{1}{r}\right\rangle$	$\langle r\rangle$	$\langle r^2\rangle$
$2s2s2p\,{}^2P^o$	0.604 08	2.3155	6.4964
$2s2p2p\,{}^4P^e$	0.607 20	2.2487	6.1790
$2s2p2p\,{}^2D^e$	0.590 42	2.3333	6.7362
$2s2p2p\,{}^2S^e$	0.577 26	2.4629	7.7730
$2p2p2p\,{}^2D^o$	0.575 94	2.3101	6.7194
$2s2p2p\,{}^2P^e$	0.577 17	2.3750	7.0858
$2p2p2p\,{}^2P^o$	0.567 24	2.4287	7.6038
$2s2s3s\,{}^2S^e$	0.537 93	3.3241	15.8788
${}^2P^e(2)$	0.512 51	3.6402	21.0624
${}^4P^e(2)$	0.504 68	4.1501	29.9977
${}^2D^e(2)$	0.501 76	4.2652	32.3009

The oscillator strengths calculated here are for both absorption and emission processes associated with these triply excited states. Many of these absorption processes are one-photon two-electron transitions. The lower bound states considered here are $1s1s2s\,{}^2S^e$, $1s1s2p\,{}^2P^o$, $1s2s2p\,{}^4P^o$, and $1s2p2p\,{}^2P^e$. The wave functions for the first two states were tabulated in Ref. 10. The wave functions of the ${}^4P^o$ and ${}^2P^e$ are calculated here. These results are shown in Table V. It should be pointed out that our result for the ${}^2P^e$ state, −5.213 17 a.u., is higher than the upper bound of Bunge[20] by about 0.0125 eV. The result for ${}^4P^o$ in this work is 0.011 eV higher than the result of Ahlenius and Larsson[21] who use r_{ij} explicitly in an elaborate calculation. Since the purpose of this calculation is to obtain a reasonable wave function for computing oscillator strengths rather than to obtain high accuracy for the energy of these bound states, no exhaustive attempt has been made for improvement.

Once a triply excited resonance is formed, it may decay by either an Auger process or by a $2p\to 1s$ transition to a doubly excited resonant state. The resonances involved are $1s2s2s\,{}^2S$, $1s2p2p\,{}^2D$, $[1s(2s2p)^3P]\,{}^2P$, and $[1s(2s2p)^1P]\,{}^2P$. The last three states are calculated in Ref. 10. The ${}^2S$ resonance is calculated in this work, and is given in Table V. The present result, −5.405 22 a.u. (56.404 eV), is somewhat higher than the experimental result of Pegg *et al.* (56.31 ± 0.03 eV) and Ziem *et al.* (56.36 ± 0.01 eV),[15] but it agrees closely with the more recent experiment of Rassi *et al.*[16] (56.395 ± 0.015 eV) and it also lies within the experimental error of Rødbro *et al.* (56.37 ± 0.05 eV).[4] Our result is higher than that of Bhatia and Temkin,[22] but lower than the result of Bhatia.[23]

The results of the oscillator strength calculations and the corresponding transition energies are given in Table VI. It should be pointed out that the transition energies quoted in this table are slightly different from what would be obtained from the positions given in Table III. This is because the conversion factor used in this table is the reduced Rydberg for which 1 a.u. = 27.2095 eV.[13] Notice that in this table the oscillator strength for the

TABLE V. Energy of the $1s2s2p\,^4P^o$, $1s2p2p\,^2P^e$, and $1s2s2s\,^2S^e$ states of the lithium atom (in a.u.). For notation see Table III.

States	q	L	N	E (a.u.)	Accurate theory or experiment (a.u.)
$1s2s2p\,^4P^o$		8	73	−5.367 380	−5.367 802 (Ref. 21)
$1s2p2p\,^2P$		7	62	−5.213 168	−5.213 606 (Ref. 20)
$1s2s2s\,^2S^e$	2.48	10	79	−5.405 22	−5.4053 ± 0.0006 (Ref. 16 quoted in Ref. 4)
					−5.4064 ± 0.0018 (Ref. 4)
					−5.4068 ± 0.0004 (Ref. 15)

same two states differ depending on which state is chosen to be the initial state. The f value of $1s1s2s\,^2S \rightarrow 2s2s2p\,^2P$, 0.0014, in Table VI is almost one order of magnitude larger than the 0.000 18 of Ref. 8.

The emission lines in Table VI are usually referred to as hypersatellites due to the presence of two 1*s* vacancies in the initial state. It can be seen from this table that the energy range of the $2p \rightarrow 1s$ transition is rather broad for different angular and spin symmetries. The $3p \rightarrow 1s$ transition for the $2s2s3s\,^2S^e(2)$, and $^2D^e(2)$ is considered in this table.

IV. COMPARISON WITH THE RESULTS OF RØDBRO, BRUCH, AND BISGAARD

In Ref. 4, Rødbro *et al.* impinge Li^+ (100 to 500 keV) on He and CH_4. They obtain many Auger lines from the Li^+ system. Many lines are also reported in this experiment that are most likely coming from triply excited lithium. For example, part of the spectrum obtained by 200 keV Li^+ on CH_4 are shown in Fig. 1. The lines coming from the Li^+ system are unambiguously identified because accurate experimental and theoretical values are available. However, lines 23, 26, 28, and 32

TABLE VI. Oscillator strengths for optical transitions of low-lying triply excited resonances of the lithium atom. The bound-state energies are from accurate calculations, $1s1s2s\,^2S$ at −7.478 025 a.u. (Ref. 12); $1s2s2p\,^4P$ at −5.367 80 a.u.; $1s1s2p\,^2P$ at −7.410 08 a.u. (Ref. 21); $1s2p2p\,^2P$ at −5.213 606 a.u. (Ref. 20). These energies are converted into eV by using 1 a.u. = 27.2095 eV. The lower doubly excited energies from experiments are $1s2s2s\,^2S$ at 56.395 eV (Ref. 16); $1s2p2p\,^2D$ at 61.062 eV (Ref. 18); $[1s(2s2p)^3P]^2$ at 58.910 eV, and $[1s(2s2p)^1P]^2$ at 60.396 eV (Ref. 17).

	Photoabsorption			Photoemission		
	Transition from	f	Transition energy (eV)	Transition to	f	Transition energy (eV)
$2s2s2p\,^2P^o$	$1s1s2s\,^2S$	1.424(−3)	142.261	$1s2s2s\,^2S$	7.983(−2)	85.866
				$1s2p2p\,^2D$	5.946(−3)	81.199
				$1s2p2p\,^2P$	1.452(−2)	80.647
$2s2p2p\,^4P^e$	$1s2s2p\,^4P$	1.886(−1)	85.117	$1s2s2p\,^4P$	1.886(−1)	85.117
$2s2p2p\,^2D^e$	$1s1s2p\,^2P$	4.501(−4)	142.956	$[1s(2s2p)\,^3P]^2P$	1.375(−1)	85.896
				$[1s(2s2p)\,^1P]^2P$	1.407(−2)	84.410
$2s2p2p\,^2S^e$	$1s1s2p\,^2P$	3.254(−4)	144.656	$[1s(2s2p)\,^3P]^2P$	1.319(−1)	87.596
				$[1s(2s2p)\,^1P]^2P$	1.083(−2)	86.110
$2p2p2p\,^2D^o$	$1s2p2p\,^2P$	1.731(−1)	85.335	$(1s2p2p)\,^2D$	1.195(−1)	85.887
				$(1s2p2p)\,^2P$	1.038(−1)	85.335
$2s2p2p\,^2P^e$	$1s1s2p\,^2P$	6.427(−4)	145.129	$[1s(2s2p)\,^3P]^2P$	1.455(−2)	88.069
				$[1s(2s2p)\,^1P]^2P$	1.601(−1)	86.583
$2p2p2p\,^2P^o$	$1s1s2s\,^2S$	7.848(−4)	148.961	$[1s2s2s]\,^2S$	4.585(−3)	92.566
				$[1s2p2p]\,^2D$	4.794(−2)	87.899
				$[1s2p2p]\,^2P$	7.326(−2)	87.347
$2s2s3s\,^2S^e$	$1s1s2p\,^2P$	9.475(−4)	147.483	$[1s(2s2p)\,^3P]\,^2P$	1.425(−3)	90.423
				$[1s(2s2p)\,^1P]\,^2P$	6.896(−4)	88.937
$^2P^e(2)$	$1s1s2p\,^2P$	1.413(−5)	147.904	$[1s(2s2p)\,^3P]\,^2P$	4.025(−2)	90.844
				$[1s(2s2p)\,^1P]\,^2P$	8.621(−4)	89.358
$^4P^e(2)$	$1s2s2p\,^4P$	4.339(−7)	92.695			
$^2D^e(2)$	$1s1s2p\,^2P$	1.157(−4)	148.391	$[1s(2s2p)\,^3P]\,^2P$	1.419(−4)	91.329
				$[1s(2s2p)\,^1P]\,^2P$	1.109(−2)	89.843

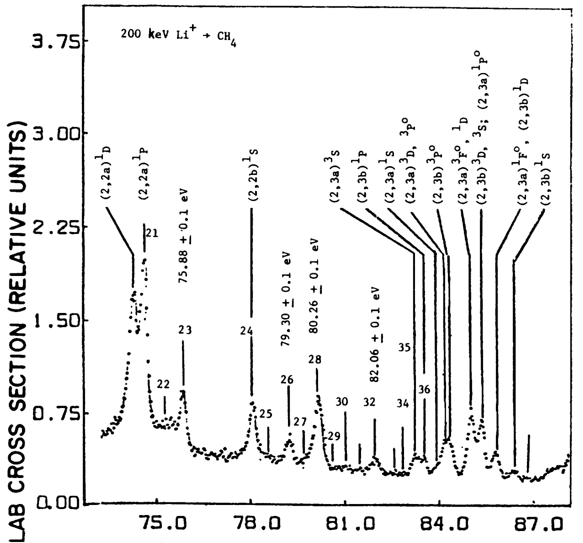

FIG. 1. Auger spectra of Li$^+$→CH$_4$. The Auger lines from Li$^+$ in this figure were identified in Ref. 4.

have well-defined structures, but their origin is not clear at all. The earlier theoretical results from the literature for the triply excited resonances do not help to identify them. In this complicated collision process, resonances of many possible symmetries are formed. Further complications arise by the fact that each resonances may have several decay channels. In order to make an unambiguous identification, it is necessary to be able to calculate all these resonances accurately. This is the prime motivation in carrying out the present work.

The energy carried by an Auger electron depends on the decay channel. In Fig. 1, the principle Auger channels are Li$^+$ $1s2s\,^3S$ at 64.418 eV, $1s2s\,^1S$ at 66.319 eV,[24] $1s2p\,^3P$ at 66.677 eV, and $1s2p\,^1P$ at 67.612 eV.[25] The Auger electron energies corresponding to these channels are tabulated and given in Table VII. Also given in this table are the reported line positions as well as those from private communications.[26] An analysis can be made as to the origin of the spectral lines in Fig. 1 based on this table.

Line 22 is very likely coming from the transition $2s2s2p\,^2P^o \rightarrow 1s2p\,^3P$. Experimentally the line position is quoted at 75.36 ± 0.1 eV. However, the line structure is so flat that the corresponding $^2P^o$ energy cannot be accurately determined by this line alone. The calculated position for line 22 is at 75.595 eV in this work. Although the transition energies of $^2P^o$ at 74.660 eV and 75.953 eV agree well with line 21 at 74.68 ± 0.1 eV and line 23 at 75.88 ± 0.1 eV, respectively, I do not consider them to be the main contributors to these two lines for two reasons. First of all, line 21 is known to come from $2s2p\,^1P^o$ of Li$^+$ and the line corresponds to the decay channel $1s2s\,^3S$ at 77.854 eV is not reported at all. Secondly, Simons *et al.*[6]

TABLE VII. Autoionizing channel energies for some triply excited resonances of the lithium atom (in eV).

Resonances	Energy	Autoionizing channel energy				Observed line[a] number and position	
		$1s2s\,^3S$	$1s2s\,^1S$	$1s2p\,^3P$	$1s2p\,^1P$	21	74.68 ± 0.1
$2s2s2p\,^2P^o$	142.272	77.854	75.953	75.595	74.660	22	75.36 ± 0.1
$2s2p2p\,^4P^e$	142.547			75.870		23	75.88 ± 0.1
						24	78.13 ± 0.1
$2s2p2p\,^2D^e$	144.817	80.399	78.498	78.140	77.195	25[b]	78.7 ± 0.2
						26	79.30 ± 0.1
$2s2p2p\,^2S^e$	146.517	82.099	80.198	79.840	78.905	27[b]	79.9 ± 0.1
$2p2p2p\,^2D^o$	146.960			80.283	79.348	28	80.26 ± 0.1
$2s2p2p\,^2P^e$	146.990			80.313	79.378	29	80.52 ± 0.1
						30[c]	81.2 ± 0.2
$2p2p2p\,^2P^o$	148.972	84.554	82.653	82.295	81.360	31[c]	81.6 ± 0.2
$2s2s3s\,^2S^e$	149.344	84.926	83.025	82.667	81.732	32	82.06 ± 0.1
						35	83.36 ± 0.1
$^2P^e(2)$	149.765			83.088	82.153	36	83.60 ± 0.1
$^4P^e(2)$	150.125			83.448			
$^2D^e(2)$	150.251	85.833	83.932	83.574	82.639		

[a] Rødbro, Bruch, and Bisgaard (Ref. 4). Lines 21, 24, 35, and 36 are associated with Li$^+$ Auger lines.

[b] Poul Dahl (private communication, Ref. 26).

[c] Statistically not significant, Poul Dahl (private communication, Ref. 26).

studied the decay rate of this $^2P^o$ resonance. They found that line 22 should be several times more intense than the other decay channels. Since this line is very weak, and lines 21 and 23 are strong, they must be coming from other sources.

Line 23 is probably mostly due to the $2s2p2p\,^4P^e \rightarrow 1s2p\,^3P$ decay. The calculated decay energy of 75.870 eV agrees well with the experimental result of 75.88 ± 0.1 eV. It should be noted that this is the only principle Auger channel, since others are forbidden by spin and parity symmetry. The formation of this high spin state in this experiment is very likely. The strongest line observed in this energy region is line 19 (not shown in Fig. 1) which comes from the decay of $\mathrm{Li}^+\,^3P^o$.

The other major lines coming from the triply excited states are lines 26, 28, and 32 at 79.30 ±0.1 eV, 80.26 ± 0.1 eV, and 82.06 ± 0.1 eV, respectively. The results in Table VII suggest that lines 26 and 28 may be coming from the symmetry preferred decays:

$$2p2p2p\,^2D^o \rightarrow 1s2p\,^1P + kd \text{ (at 79.348 eV)}, \quad \text{(5a)}$$

$$2p2p2p\,^2D^o \rightarrow 1s2p\,^3P + kd \text{ (at 80.283 eV)}, \quad \text{(5b)}$$

or

$$2s2p2p\,^2P^e \rightarrow 1s2p\,^1P + kp \text{ (at 79.378 eV)}, \quad \text{(6a)}$$

$$2s2p2p\,^2P^e \rightarrow 1s2p\,^3P + kp \text{ (at 80.313 eV)}. \quad \text{(6b)}$$

Theoretically, it is very difficult to determine the relative contributions of reactions (5) and (6) to the observed line intensities. Experimentally, this can be determined by measuring the angular distribution of the Auger electrons, or by a coincidence measurement of the photodecay energy.

Line 32 may be coming from the decay process

$$^2P^e(2) \rightarrow 1s2p\,^1P + kp \text{ (at 82.153 eV)}. \quad \text{(7a)}$$

The other decay channel

$$^2P^e(2) \rightarrow 1s2p\,^3P + kp \text{ (at 83.088 eV)} \quad \text{(7b)}$$

seems to agree with the position of line 34 very well. This line is very weak and the exact position is not quoted in Ref. 4. For the two $^2P^e$ resonances, it is interesting to note that line 28 is more intense than line 26, implying that reaction (6b) is preferred more than (6a) in contrast to the relative strengths of (7a) and (7b). This agrees with the results of the oscillator strength calculation in Table VI where different lower states are preferred in emission for these two $^2P^e$ resonances.

There is some evidence that $2s2p2p\,^2S^e$ is present in the collision process. Lines are reported at all four of the following decay channel positions:

$2s2p2p\,^2S \rightarrow$

$$1s2s\,^3S + ks \text{ (at 82.099 eV vs No. 32 at 82.06} \pm 0.1 \text{ eV)}, \quad \text{(8a)}$$

$$1s2s\,^1S + ks \text{ (at 80.198 eV vs No. 28 at 80.26} \pm 0.1 \text{ eV)}, \quad \text{(8b)}$$

$$1s2p\,^3P + kp \text{ (at 79.840 eV vs No. 27 at 79.9} \pm 0.1 \text{ eV)}, \quad \text{(8c)}$$

and

$$1s2p\,^1P + kp \text{ (at 78.905 eV vs No. 25 at 78.7} \pm 0.2 \text{ eV)}. \quad \text{(8d)}$$

Since experimentally lines 25 and 27 are weak but statistically significant,[26] and reaction (8c) is the only one with an Auger energy falling in the region 79.9 ± 0.1 eV, the presence of $2s2p2p\,^2S^e$ can be assured. However, reactions (8a) and (8b) may not be the major contributors to lines 32 and 28 because of the weakness of lines 27 and 25. Another reason is that judging from the Auger lines from Li^+ in this particular experiment, the lines corresponding to *kp* and *kd* electrons seem to give stronger signals than *ks* electrons.

A very weak line at 80.52 ± 0.1 eV is reported in Ref. 4. This is slightly higher than the decay energy

$$2s2p2p\,^2D^e \rightarrow 1s2s\,^3S + kd \text{ (at 80.399 eV)}. \quad \text{(9a)}$$

The reactions

$$2s2p2p\,^2D^e \rightarrow 1s2s\,^1S + kd \text{ (at 79.498 eV)}, \quad \text{(9b)}$$

$$\rightarrow 1s2p\,^3P + kp \text{ or } kf \text{ (at 78.140 eV)} \quad \text{(9c)}$$

may also contribute to line 25 at 78.7 ± 0.2 eV and line 24 at 78.13 ± 0.1 eV. However, the decay line

$$2s2p2p\,^2D^e \rightarrow 1s2p\,^1P + kp \text{ (at 77.195 eV)} \quad \text{(9d)}$$

is not reported and line 24 may have some contribution from the $\mathrm{Li}^+\,^1S$ resonance. Hence this $^2D^e$ state is a likely product of the collision process, but not necessarily in a large amount.

Another state of interest is the second member of the $^4P^e$ resonances. It is a mixture of $2s2p3p$ and $2p2p3s$. Since its decay mode is more selective due to spin and parity, it is more likely to be observed in an Auger spectrum. In order to make sure this state is not the main contributor to line 32, its energy is also tabulated. The result shows that

$$^4P^e(2)\rightarrow 1s2p\,^3P+kp \text{ (at 83.448 eV)}, \qquad (10)$$

which lies much higher than line 32. In Ref. 4 lines are observed at 83.36 ± 0.1 eV (line 35) and 83.60 ± 0.1 eV (line 36) with significant signals in between. It seems likely that reaction (10) has contributed to the experimental observation.

Lines 30 (81.2 ± 0.2 eV) and 31 (81.6 ± 0.2 eV) are believed not to be statistically significant,[26] but they seem to agree with the decay processes

$$2p2p2p\,^2P^o\rightarrow 1s2p\,^1P+ks \text{ or } kd \text{ (at 81.360 eV)} \qquad (11)$$

and

$$2s2s3s\,^2S^e\rightarrow 1s2p\,^1P+kp \text{ (at 81.795 eV)}. \qquad (12)$$

Line 33 energy lies very close to the decay line

$$2p2p2p\,^2P^o\rightarrow 1s2s\,^1S+kp \text{ (at 82.653 eV)}. \qquad (13)$$

V. SUMMARY

In this work, eleven low-lying triply excited resonances of lithium with $^2P^o$, $^4P^e$, $^2D^e$, $^2S^e$, $^2P^e$, and $^2D^o$ symmetries are investigated. These are not the lowest triply excited resonances since other $^2P^o$ resonances may be lower than some of the higher states considered here. The purpose of this work is to identify the reported spectrum of Rødbro *et al.*[4] It appears that all of the reported lines are accounted for. If the suggested identifications are correct, then excellent agreement has been obtained between the present theoretical calculation and the experiment. This would indicate that the saddle-point technique is a simple but accurate method for highly excited quantum systems. To assess the likelihood of obtaining these triply excited resonances in an optical-absorption experiment or in a coincidence experiment, the oscillator strengths associated with the relevant transitions are also tabulated.

In computing the energy for these highly excited states, it is found that the various possible angular and spin partial waves contribute greatly to the correlation. This should serve as a warning to the many multivacancy theoretical calculations in which continua have not been carefully removed, but good results are seemingly obtained without detailed consideration of correlations. These energies may result from cancellation of errors. The wave functions on the other hand, would still contain large errors.

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