

Doubly Excited States in Lithium*

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Doubly and triply excited states of lithium are considered in an effort to identify the energy levels responsible for the several narrow lines present in the optical spectrum of that element which are not classifiable in the normal singly excited spectra of that atom. Since most of these states are coupled to continuum states through the electrostatic interaction of the electrons and will thus have extremely short lifetimes, a majority of the multiply excited states can be excluded from consideration in identifying these narrow lines. The observed narrow spectral lines can be plausibly identified on the basis of screening-theory estimates of the energies.

THE line spectrum of lithium shows at least three narrow-line complexes in and near the visible region which are not classifiable in the normal one-electron spectra of that element. States of that atom for which more than one electron are simultaneously excited have been considered in an attempt to identify the energy levels responsible for the lines. Since all such levels are subject to autoionization, only those levels whose lifetimes are sufficiently long to produce the observed narrow lines need be considered. Section 1 describes the configurations involved and their coupling to continuum states. Section 2 describes the energy-level calculations, Sec. 3 contains comparisons with the data and discussion and Sec. 4 makes a brief comment on doubly excited states of Li^+ . It is concluded that: (1) States in which three electrons are simultaneously excited cannot provide narrow lines; (2) a classification of the observed lines is as follows:

- $1s2s2p\ ^4P - 1s2p^2\ ^4P$ at 2934 Å;
- $1s2s2p\ ^4P - 1s2s3s\ ^4S$ at 2337 Å;
- $1s2p^2\ ^4P - 1s2p3s\ ^4P$ at 3714 Å;
- $1s2s3p\ ^4P - 1s2p3p\ ^4P$ at 4607 Å;

(3) new lines are predicted due to transitions between the doubly excited levels.

1. SELECTION OF CONFIGURATIONS

It can easily be seen on a qualitative basis that all states of neutral lithium in which two or three electrons are simultaneously excited have energy levels above the first ionization potential (5.39 eV); since the first excited state of Li II , $1s2s\ ^3S_1$, lies 59 eV above the first ionization potential, the addition of one weakly bound electron to a parent ion consisting of an excited state of the ion should produce a state whose energy lies ~ 5 eV below that of the parent.

Since all of these states which lie in the continuum can undergo Auger transitions, their lifetimes will be decreased below the natural radiative lifetime; in most cases the Auger transitions will dominate and the

lifetime will depend on the strength of the coupling to the continuum. If we write the Hamiltonian for the system as

$$H = \sum_i \left(\frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right) + \sum_{i>j} \frac{e^2}{r_{ij}}$$

the coupling to the continuum will occur via the electrostatic interaction of the electrons. For the electrostatic interaction, it has been estimated¹⁻³ that the autoionization lifetime of a doubly excited state is of the order of 10^{-14} to 10^{-15} sec, almost independent of the particular system considered. Lines involving such states would have natural widths much too great to be distinguishable from background (the higher excited states have longer autoionization lifetimes, varying as the cube of the principal quantum number, but for optically observable states the electrostatic autoionization lifetime is still short compared with the natural or radiative lifetime).

Table I shows the multiply excited configurations and associated states in pure LS coupling. The selection

TABLE I. Pure LS coupling.

Configuration	Parity	Possible levels	Levels not coupled to $1s^2kl$ continua via electrostatic interaction	Levels not coupled to $1s2s^kl$ or $1s2p^kl$ continua via electrostatic interaction
$1s2s^2$	(+)	2S		
$1s2s2p$	(-)	$^2P, ^2P, ^4P$	4P	4P
$1s2s3s$	(+)	$^2S, ^2S, ^4S$	4S	4S
$1s2s3p$	(-)	$^2P, ^2P, ^4P$	4P	4P
$1s2s3d$	(+)	$^2D, ^2D, ^4D$	4D	4D
$1s2snl (n > 3)$	(-) ⁱ	$^2nl^i$	4l	4l
$1s2p^2$	(+)	$^2S, ^2P, ^2D, ^4P$	$^2P, ^4P$	$^2P, ^4P$
$1s2p3s$	(-)	$^2P, ^4P$	4P	4P
$1s2p3p$	(+)	$^2S, ^2P, ^2D$	2P	
	(+)	$^4S, ^2P, ^2D$	$^4S, ^4P, ^4D$	$^2P, ^4P$
$1s2p3d$	(-)	$^2P, ^2D, ^2F$	2D	
	(-)	$^4P, ^2D, ^2F$	$^4P, ^4D, ^4F$	$^2D, ^4D$
$1s2pnl (n > 3)$	(-) ⁱ⁺¹	$^2nl \pm 1, l$	$^2l, ^4l \pm 1, ^4l$	$^2l, ^4l$
$n1snln'l'$ ($n \geq 3, n' > 4$)	(-) ^{i+i'}			none (All are definitely above 68 eV)
$n'l'n'l''$ ($n'', n', n > 1$)	(-) ^{i+i'+i''}			none (All are definitely above 92 eV)

* Levels arising from $1s3l3l'$ and $1s3l4l'$ are omitted. These are all expected to lie above $1s2s$ and $1s2p$ (see text).

* Supported in part by the National Science Foundation and by the Research Committee of the Graduate School through funds supplied by the Wisconsin Alumni Research Foundation.

¹ E. Holgøien, *Physica Norvegica* 1, 56 (1961).

² G. Wentzel, *Z. Physik* 43, 524 (1927).

³ T. Y. Wu, *Phys. Rev.* 66, 291 (1944).

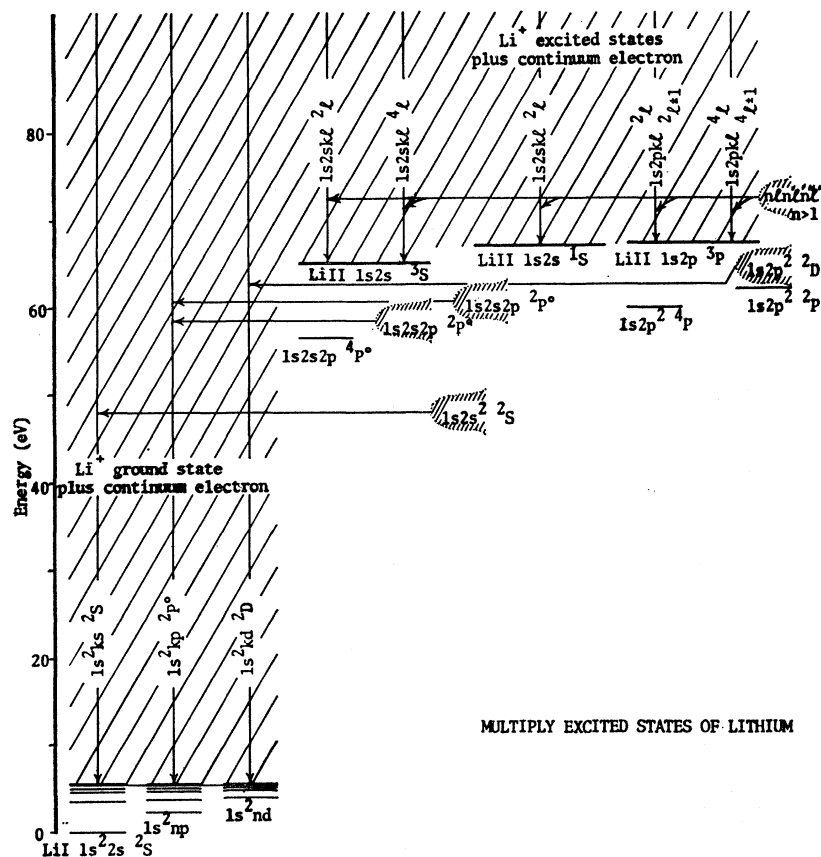


Fig. 1. Three-electron energy levels in lithium (not to scale). Normal singly excited levels are preceded by spectral symbol designation.

rules for autoionization transitions via the electrostatic repulsion in pure LS coupling are quite simple: $\Delta S=0$, $\Delta L=0$, $\Delta J=0$, and no parity change. Final states which consist of the ion ground state plus a free electron are $1s^2 kl \ ^2l$ continuum states, i.e., doublets whose parity is $(-)^l$. Column 3 shows those doubly excited states which are not coupled to a $1s^2 kl$ continuum state. Of course, the $\Delta S=0$ rule makes all quartet states metastable with respect to transitions to the $1s^2 kl$ continuum states.

It is necessary to keep in mind that all multiply excited states are coupled to the $1s^2 kl$ continuum by some interaction. Consider the $1s^2 s^2 p \ ^4P_{5/2, 3/2, 1/2}$ states, for example. The $^4P_{3/2}$ and $^4P_{1/2}$ states are coupled to the $1s^2 s^2 p \ ^2P_{3/2, 1/2}$ states by the spin-orbit interaction and thus to the $1s^2 kp \ ^2P$ continuum state. The $^4P_{5/2}$ state, however, can only couple to $1s^2 kp \ ^2P$ via a spin-other-spin interaction. Pietenpol⁴ gives a rough theoretical estimate of 10^{-6} sec for the $^4P_{5/2}$ lifetime. A $^2P-^4P$ mixing coefficient of 10^{-3} to 10^{-4} (approx spin-orbit energy values) makes the Auger lifetime of the $^4P_{3/2, 1/2}$ on the order of 10^{-6} or 10^{-7} sec. These values may, however, be large enough to permit narrow lines to be observed in transitions involving these states. Thus, the primary consideration in line identification is assumed to be the electrostatic interaction.

Quartet continuum states occur only at energies above

those of the excited states of the ion. Figure 1 indicates this graphically. The continuum states associated with the ion $1s^2 s$ configuration have parity $(-)^l$ and the $1s^2 pkl$ states have parity $(-)^{l+1}$. Any multiply excited state whose energy lies above both the $1s^2 s$ and $1s^2 p$ energies is electrostatically coupled to one of these continua, and its lifetime is correspondingly shorter. A lower bound on the energy levels will then indicate how many configurations must be considered.

Bazley⁵ has developed a procedure which can be used for this purpose. Since the Hamiltonian can be written as $H=H_0+V$, $H_0=\sum (p_i^2/2m - Ze^2/r_i)$, $V=\sum_{i>j} e^2/r_{ij}$, and the operator V is positive definite,

he has used the fact that the eigenvalues of H form an ordered set (as do those of H_0 ; $\langle H \rangle_\alpha > \langle H_0 \rangle_\alpha$ for all α), to define projections of V on a finite set giving successively better lower bounds. That is, the operator $H^{(n)}=H_0+p^{(n)}V$ also has the property $\langle H^{(n)} \rangle_i < \langle H \rangle_i$ (ordered set); here $p^{(n)}V$ is the projection of V on n eigenstates of H_0 .

Using this technique, one can easily show that no triply excited state can participate in narrow line radi-

ation. Here, $H_0=\sum_{i=1}^3 [(p_i^2/2m) - (Ze^2/r_i)]$. For the lowest

⁴ J. L. Pietenpol, Phys. Rev. Letters **7**, 64 (1961).

⁵ N. W. Bazley, Phys. Rev. **120**, 144 (1960).

triply excited configuration $2s^22p$, we have

$$\langle H_0 \rangle = \sum_i \frac{Z^2}{2n_i^2} = -\frac{9}{2}(\frac{1}{4} + \frac{1}{4} + \frac{1}{4}) \\ = -3.375 \text{ atomic units (a.u.) or } 92 \text{ eV}$$

above the Li I ground state, and well above the $1s2p^3P$ level. Thus all configurations $nl'n'l''l''(n, n', n'' > 1)$ will auto-ionize via the electrostatic interaction and will be severely broadened. Similarly all $1sln'l'$ states ($n \geq 3, n' > 4$) must lie above 68 eV and are of no interest here. Probably only configurations of the types $1s2snl$ and $1s2pnl$ have states with lifetimes long enough to participate in narrow-line radiation.

Even without exact calculations, general considerations are informative. Configurations of the type $1s2snl$ provide quartet states whose energies converge from below to that of the parent $1s2s^3S$ term of the ion, and would thus be well-defined states. Quartet levels from $1s2pnl$ configurations, on the other hand, have energies approaching $1s2p^3P$ at 66.6 eV; most of these lie above $1s2s^3S$ and all such states with $L=l\pm 1$ will be broadened (others will have opposite parity). The above technique could be used to reduce even further the number of states to be considered, but it would require extensive calculations. We begin instead with those listed explicitly in column 4 of Table I.

2. ENERGY LEVELS

Because all the states to be considered are excited states, it was felt that hydrogenic wave functions would provide quick and reasonable estimates; Layzer⁶ has developed a Z -dependent screening theory which should be applicable here. The method is based on the theorem that the eigenvalues of the Hamiltonian operator

$$H = \sum_i \left(\frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right) + \sum_{i>j} \frac{e^2}{r_{ij}}$$

TABLE II. Doubly excited states.

Configuration	Levels	Energy ^a		Screening parameters ^b	
		a.u.	eV		
$1s2s2p$	$4P$	2.0405	55.47	$\sigma_{2s} = 0.7517$	$\sigma_{2p} = 1.4342$
$1s2s3s$	$4S$	2.2388	61.11		$\sigma_{3s} = 1.6106$
$1s2s3p$	$4P$	2.2556	61.75		$\sigma_{3p} = 1.2240$
$1s2s3d$	$4D$	2.2744	61.80		$\sigma_{3d} = 1.8500$
limit $(1s2s)^3S$		2.3461	63.80		
$1s2p^2$	$4P$	2.1957	59.67	$\sigma_{2p} = 1.2291$	
$1s2p3s$	$4P$	2.3188	63.17	$\sigma_{2p} = 0.9029$	$\sigma_{2s} = 1.6223$
$1s2p3p$	$4D$				
	$4P$	2.3534	63.99		$\sigma_{3p} = 1.9064$
	$4S$				
$1s2p3d$	$4F$				
	$4D$	2.3674	64.40		$\sigma_{3d} = 1.9578$
limit $(1s2p)^3P$		2.4283	66.04		

^a Referred to Li I ground state -7.478 a.u.

^b σ_{1s} for all of these is 0 (external screening was neglected).

⁶ David A. Layzer, Ann. Phys. (N. Y.) 8, 271 (1959); 17, 177 (1962).

TABLE III. Comparisons.^a

Levels	Energy (eV)				Experimental
	Present calculation	Other calculations			
$(1s2s2p)^4P$	55.47	56.0 ^b	55.54 ^c	57.99 ^d	56 ^e
$(1s2p^2)^4P$	59.67			61.35 ^d	
Li II $(1s2s)^3S$	63.80				64.4 ^f
Li II $(1s2p)^3P$	66.04				66.6 ^f
Li I $(1s^2s)^2S$	0.19				0.0 ^f

^a b, c, d, and e are all quoted from Ref. 10.

^b E. Holmøen (private communication).

^c S. Manson (private communication).

^d Ta-You Wu and S. T. Shen, Chinese J. Phys. 5, 150 (1944).

^e P. Feldman, Ref. 10.

^f Natl. Bur. Std. (U.S.) Circ. 469, (1948).

have the form

$$E = W_2 Z^2 + W_1 Z + W_0 + O(Z^{-1}).$$

The screening theory gives a first-order perturbation method for evaluating the W 's (neglecting the terms of order Z^{-1} or less) and thus gives the screening parameters σ , for writing $E = \sum - (Z - \sigma_i)^2 / 2n_i^2$. The screening theory, even neglecting external screening, has been shown to give reasonable values for low-lying states belonging to $Z < 10$.⁷

To test the applicability of the theory to lithium and to doubly excited states, the Li I ground-state energy and the He $2p^2^3P$ energy were evaluated. Reference 1 gives a value of -1.40151 Ry for the $2p^2$ contribution to the He $2p^2^3P$ energy in a multiconfiguration variational calculation. The screening theory gives -1.398 Ry. The Li I ground state is also given within 0.19 eV $\sim 0.1\%$. The screening theory does give more accurate results for configurations involving closed shells and subshells, however; this is a consequence of the way in which the σ 's are obtained (note that in the He $2p^2^3P$ example the value is a true upper bound and the individual electronic wave functions are truly orthogonal, i.e., this is the same result as would be given by a variational calculation).

To illustrate the ease of calculation the energy of the $1s2s2p^4P$ levels will be evaluated explicitly: there is only one configuration having these principal quantum numbers, L, S , and parity. According to Chap. 6 of Ref. 8 (and using the notation used there) the diagonal value of $\sum_{i>j} e^2/r_{ij}$ is given by $(0^+0^+1^+)$. Thus

$$W_1[1s2s2p^4P] = F^0(1s2s) - G^0(1s2s) + F^0(1s2p) \\ - \frac{1}{3}G^1(1s2p) + F^0(2s2p) - \frac{1}{3}G^1(2s2p).$$

⁷ According to this theory,⁸ σ_i are given by

$$\sigma_i = (n_i^2/q_i)[W_1(q_1q_2 \dots q_i) - W_1(q_1q_2 \dots q_{i-1})],$$

where n_i is the principal quantum number of the i th electron, q_i is the number of electrons in the i th shell and W_i 's are the eigenvalues of $V = \sum_{i>j} e^2/r_{ij}$ evaluated for all states having the same

principal quantum numbers L, S , and parity, and using H-like functions, $Z=1$.

⁸ E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, England, 1951).

TABLE IV. Lines from doubly excited states.

Observed ^a	No. of components	Transition	Calculated		Transition probability (sec ⁻¹)	Probable energy range
			Energy without configuration interaction	Energy including configuration interaction		
2337 Å (5.31 eV)	3	(1) (1s2s2p) ⁴ P - (1s2s3s) ⁴ S	5.41 eV (2292 Å)	5.64 eV (2198 Å)	3.3 × 10 ⁷	6.2-5.0 eV
2934 Å (4.22 eV)	3	(2) (1s2s2p) ⁴ P - (1s2p ³) ⁴ P	4.20 eV (2951 Å)		5.9 × 10 ⁹	4.8-3.6 eV
3714 Å (3.34 eV)	6	(3) (1s2p ²) ⁴ P - (1s2p3s) ⁴ P	3.39 eV (3657 Å)	3.50 eV (3542 Å)	1.4 × 10 ⁶	4.1-2.9 eV
4607 Å (2.69 eV)	1	(4) (1s2s3p) ⁴ P - (1s2p3p) ⁴ P	2.65 eV (4661 Å)	2.24 eV (5535 Å)	3.6 × 10 ⁸	2.8-1.6 eV
1420 Å (8.72 eV)		(5) (1s2s2p) ⁴ P - (1s2p3p) ⁴ P	8.52 eV (1455 Å)		7.7 × 10 ⁶	9.1-7.9 eV
		(6) (1s2s3s) ⁴ S - (1s2p3s) ⁴ P	2.18 eV (5687 Å)	1.95 eV (6357 Å)	6.7 × 10 ⁷	2.5-1.35 eV
9572 Å (1.30 eV)		(7) (1s2p3s) ⁴ P - (1s2p3p) ⁴ P	0.94 eV (13,189 Å)	0.72 eV (17,219 Å)		1.3-0.1 eV
		(8) (1s2s3p) ⁴ P - (1s2s3p) ⁴ P	0.64 eV (19,679 Å)	0.48 eV (25,829 Å)		1.2-0.0 eV
		(9) (1s2s2p) ⁴ P - (1s2s3d) ⁴ D	6.33 eV (1959 Å)	6.38 eV (1943 Å)	8.8 × 10 ⁹	7.0-5.8 eV
		(10) (1s2p ²) ⁴ P - (1s2p3d) ⁴ D	4.57 eV (2713 Å)	4.73 eV (2621 Å)	1.4 × 10 ⁹	5.3-4.1 eV
		(11) (1s2s3d) ⁴ D - (1s2p3d) ⁴ D	2.60 eV (4768 Å)	2.55 eV		3.1-1.9 eV
		(12) (1s2p3p) ⁴ P - (1s2p3d) ⁴ D	0.41 eV			1.0-0 eV
		(13) (1s2s3p) ⁴ P - (1s2s3d) ⁴ D	0.51 eV	0.05 eV		0.6-0 eV

^a Taken from Ref. 11.

Hydrogenic functions with $Z=1$ are to be used to evaluate the Slater integrals. We find $F^0(1s2s) = 17/3^4$, $F^0(1s2p) = 59/3^5$, $F^0(2s2p) = 83/2^9$, $G^0(1s2s) = 16/3^6$.

$$G^1(1s2p) = 112/3^7, \quad G^1(2s2p) = 45/2^9.$$

We also need

$$W_1[1s2s^3S] = F^0(1s2s) - G^0(1s2s)$$

$$\sigma_{2p} = 4\{W_1[1s2s2p^4P] - W_1[1s2s^3P]\} = 1.4342$$

$$\sigma_{2s} = 4\{W_1[1s2s^3S] - 0\} = 0.75176 \quad (\sigma_{1s} = 0)$$

$$\sum \langle 4P \rangle = \sum_{i=1}^3 -\frac{1}{2} \left(\frac{Z - \sigma_i}{n_i} \right)^2 = -\frac{9}{2} \left(\frac{1.5658}{8} \right)^2 - \left(\frac{2.24828}{8} \right)^2 = -5.4383 \text{ a.u.}$$

$$\begin{aligned} \sum \langle 4P \rangle - E_0 &= -7.4780 + 5.4383 \\ &= 2.0397 \text{ a.u.} = 55.47 \text{ eV.} \end{aligned}$$

Holøien¹ has shown that for states which are not electrostatically coupled to the continuum states, which he calls quasisdiscrete, a single configuration gives good values of the energy. The screening theory has been used to evaluate the energies of the pertinent states from Table I. These are shown in Table II. Also shown are the resultant screening parameters. Only those levels have been shown which cannot undergo electrostatic autoionization. Thus, for example, $1s2p3p^4D$, 4S both have energies greater than the $1s2s^3S$ limit and are not shown. This was already reflected in the last column of Table I, where for this configuration only 4P was shown. As indicated in Ref. 1, those states which are strongly coupled to the continuum have mean energies which are substantially different from those predicted by a single configuration calculation. This is expected

and makes the present calculation completely inapplicable for such states.

As indicated in Ref. 7, the theory requires configuration interaction for those states having the same principal quantum numbers, L , S , and parity. In this case the levels $1s2s3d^4D - 1s2p3p^4D$ must be coupled; also $1s2p3p^4S - 1s2s3s^4S$ and finally $1s2p3d^4P$, $1s2p3d^4P$, and $1s2s3p^4P$. This is a complete list of the configuration interaction used.

3. RESULTS AND DISCUSSION

A direct check on these values is given by recent electron-impact experiments.^{9,10} In addition, previous calculations of some of these levels have been made; Table III presents those levels for which there are comparisons. The $1s2s2p^4P_{5/2}$ energy is quoted in Ref. 9 as 58 eV, but has been modified to 56 eV in the more recent work.¹⁰

On the basis of the energies given in Table II, a list of the possible lines from electric-dipole radiative transitions among these states is given in Table IV. (Combinations such as $1s2p^2^4P - 1s2s3p^4P$ are forbidden in the ordinary dipole approximation because two electrons change at once.) The transition probabilities were calculated neglecting spin and using screened hydrogenic wave functions with the σ_i from Table II. Those for (7), (8), (11), (12), and (13) were not calculated but should be large ($\sim 10^9$ /sec). Table IV also shows the wavelengths of the four lines in and near the visible whose explanation is sought.

Several comments are in order. Although the calculated values (1) through (4) correspond reasonably well to the observed lines, (9) through (11) are also in the region and have not been reported. Herzberg and Moore¹¹ discuss a work by Werner in which a line at

⁹ P. Feldman and R. Novick, Phys. Rev. Letters **11**, 278 (1963).

¹⁰ P. Feldman, thesis, Columbia University, 1964 (unpublished).

¹¹ G. Herzberg and H. R. Moore, Can. J. Phys. **37**, 1239 (1959).

9572 Å was observed. This work, unavailable to the present authors, also reportedly shows a line at 1420 Å, although Herzberg and Moore did not observe such a line. If we identify this with line (5), it might be possible to explain the fact that Herzberg and Moore did not see it on the basis of its very low transition probability. Chabbal and Daehler¹² find the main peak of the line at 4607 Å to be less than half as wide as the normal lithium lines and suggest that the line is the strontium singlet resonance line. On their photomultiplier traces the peak appears to be superimposed upon a background somewhat wider than the ordinary lithium lines and covering an area on the order of that under the main peak itself, a circumstance that points to the classification of the line as (4), with a strontium impurity perhaps superimposed. It is not surprising that (7), (8), (12), and (13) have not been observed.

Only the quartet lines have been listed; the doublet lines are expected to be in the red or infrared. From Table III it can be seen that the calculated level positions which can be compared with experiment are within 0.6 eV of the true values and consistently below, so that the differences should be better than this. The last column in Table IV lists the probable ranges, assuming 0.6 eV to be the uncertainty in the difference.

It should be kept in mind that all the higher levels, including those which have been omitted here, can also make radiative transitions to levels which strongly couple to the continuum; such radiation will not be observable as sharp lines, but will deplete these states and make the observable narrow-line transitions weaker. It can be observed that each of the lines (9) through (13) involves at least one ⁴D state, whereas (1) through (8) involve only ⁴S and ⁴P states. It is quite probable that the population mechanisms have much smaller probabilities for states of higher total orbital-angular momentum. For example, for electron-impact excitation in the Born approximation, optically forbidden transitions have a much smaller cross section than do optically allowed ones; D-state transitions would be optically forbidden from the ground state in the limit of electric-dipole interaction. (Of course, electron impact excitations of any quartet state from a doublet requires electron exchange.) Assuming that the ⁴D population is

small compared with that of ⁴S and ⁴P, lines (1) through (8) plus the two doublet lines will be the principal lines in the doubly excited Li I optical spectrum.

A more exact calculation, yielding true bounds and including configuration interaction, is in order. It is possible that such a calculation will show, for example, that levels not included here, such as the $1s2p2p$ ⁴D or $1s3s4p$ ⁴P levels, should be considered and do yield observable lines. However, the present results are probably sufficient to point to the origin of these lines.

4. DOUBLY EXCITED IONIC STATES

A complete survey of the lithium spectrum should include the doubly excited states associated with the Li⁺ ion. The normal one-electron spectrum of the ion is due to levels of the configurations $1sml$, and the doubly excited states correspond to $nl'n'l'$ configurations, with $n, n' \geq 2$. Using the lower bounds as in Sec. 1, it is easily shown that only the $2pnl$ ^{1,3}l levels, with $n \geq 2$ and $l \neq 0$, will be metastable with respect to autoionization via the electrostatic interaction; hence, only these levels can participate in narrow line radiation. The lowest of these levels, $2p^2$ ³P, lies 154.8 eV above the neutral lithium ground state. The lowest levels associated with lines in or near the visible are $2p3p$ ^{3,1}P at 165.7 eV and 166.5 eV, respectively, (transitions from $2pnd$ ^{1,3}D, $n > 3$) and $2p3d$ ^{3,1}D at 165.7 eV and 166.3 eV, respectively (transitions from $2pnl$ ^{3,1}l, $n > 3$ and $l = 1$ or 3). It is expected, however, that all such lines will be extremely weak compared with the normal spectrum and the neutral doubly excited state spectrum, since all the levels which can participate in optical narrow-line radiation result from configurations in which both electrons must be highly excited. If these levels are populated by excitation of either the neutral or the ionic ground state, the excitation probabilities will be small compared with those of other possible transitions. However, more complete calculations of excitation mechanisms and state populations are required to establish this point.

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¹² R. Chabbal and M. Daehler (private communication).