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Absolute term values for the quartet states of neutral lithium

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An extensive configuration-interaction calculation for the $(1s2s3s)\ ^4S$ state of neutral lithium has been carried out in an effort to establish absolute term values for the low-lying quartet states with a few cm^{-1} of accuracy. The lowest quartet state, $(1s2s2p)\ ^4P^o$ is found to be 57.4128 (10) eV above the ground state $1s^22s$, in apparent disagreement with a recent experimental value of 57.4420 (40) eV obtained from Ritz formulas applied to the ^4D states of even and odd parity. The positions of all identified quartets have been recalculated from raw experimental data and new theoretical results.

I. INTRODUCTION

The quartet states of neutral Li, which are metastable against both autoionization and radiative decay to the doublet system, can be selectively produced[1] by electron bombardment of ground-state atoms. They are located in an energy interval ranging from 57.4 eV above the ground state, for the lowest $(1s2s2p)\,^4P^o_{3/2}$ state, up to the $(1s2p)\,^3P$ series limit at 66.672 95 eV.

Transitions between quartet states give rise to narrow-line radiation observed in hollow cathode tube[2,3] and beam-foil[4-8] experiments. Herzberg and Moore[3] earlier suggested that these lines might be ascribed to transitions between doubly excited states of Li$^+$. Garcia and Mack,[9] however, showed that only the $(2pnl)\ ^{1,3}l$ levels with $n\geq 2$ and $l>0$ would be metastable with respect to autoionization via the electrostatic interaction, and they further contended that the transitions between all these Li$^+$ states should be extremely weak compared with the rest of the spectrum since they would be taking place between configurations in which both electrons were highly excited. Garcia and Mack[9] also predicted the existence of quartet states of neutral Li in the same energy region as the Li$^+$ bound states and with half-lives sufficiently long to produce narrow-line radiation.

The first correct assignment of quartet lines came from theoretical calculations.[10,11] The first definitive assignments of the principal quartet lines, however, were obtained by Feldman *et al.*[12] from the results of an atomic-beam Zeeman quenching experiment. In particular, they provided a detailed account of the fine and hyperfine splittings for the $(1s2s3s)\,^4S \longleftarrow (1s2s2p)\,^4P^o$ and $(1s2p^2)\,^4P \longleftarrow (1s2s2p)\,^4P^o$ transitions.

The term diagram for the quartet states of neutral Li was completed, in its present form, with the results of beam-foil experiments[4-8] aided by the theoretical assignments of Holøien and Geltman,[10] and of Weiss.[11] Berry *et al.*[8] also determined the absolute energy of the $(1s2s2p)\,^4P^o$ state as being $T(1s2s2p)\,^4P^o = 57.442(4)$ eV above the ground state $1s^22s$, using Ritz formulas for the ^4D states of even and odd parity.

Soon afterwards, Larsson[13] computed an accurate Hylleraas-type wave function for the $(1s2s3s)\,^4S$ state obtaining an upper bound to the nonrelativistic energy, $E_u = -5.212\,396$ a.u. (Li). Using the arguments given in Sec. II, the experimental term value[3,14,15] for the $(1s2s)\,^3S$ state of Li$^+$ and the experimental energy[3,12] for the $(1s2s3s)\,^4S \longleftarrow (1s2s2p)\,^4P^o$ transition, one can infer from Larsson's result that $T(1s2s2p)\,^4P^o = [57.442(1) + x]$ eV where x is the difference between the exact and upper bound nonrelativistic energy in Larsson's calculation (x is a negative quantity). This result is well outside the error bounds for the experimental value.[8]

The purpose of this paper is to determine precisely the absolute position of the principal quartet states of Li by means of nonrelativistic configuration (CI) calculations, which are now capable of near spectroscopic accuracy.[16] Since energy differences between these quartet states are accurately known,[3] it is sufficient to establish the absolute position of any one of these states. To that end we have performed an extensive CI calculation for the $(1s2s3s)\,^4S$ state, which is a particularly convenient choice because for a given size of the orbital basis, the full CI expansion for the ^4S state is much shorter than for the other quartet states. In Sec. II we discuss the appropriateness of a nonrelativistic calculation for the present study. An outline of the calculation is given in Sec. III. The results are reported and discussed in Sec. IV. In particular, we present a table of absolute term values for ^{7}Li quartets which supersedes a previous compilation.[8]

II. SUITABILITY OF A NONRELATIVISTIC CALCULATION

The differences between experimental E_{exp} and nonrelativistic E_{nr} energies for the Li ground state, and for the $1s^2$, $(1s2s)\,^3S$, and $(1s2p)\,^3P$ states of Li$^+$ are just about equal and close to 112 cm^{-1} with a dispersion of 5 cm^{-1}, see Table I. SCF calculations[17] of relativistic expectation values for singly excited $1s^2nl$ states show that relativistic energy corrections vary smoothly with n for given l. One may expect that the same must be true for the mass-polarization and radiative-energy corrections. In view of the above, it seems reasonable to assume[18] that $E_{\text{exp}} - E_{\text{nr}}$ for $(1s2s3s)\,^4S$ must not differ from $E_{\text{exp}} - E_{\text{nr}}$ for $(1s2s)\,^3S$ of Li$^+$ by more than 8 cm^{-1} $\simeq 0.001$ eV $\simeq 37$ μ hartree; this error bound is on the conservative side. With this assumption, the experimental energy for the $(1s2s3s)\,^4S$ state is given by

$$E_{\text{exp}}(1s2s3s)\,^4S = E_{\text{nr}}(1s2s3s)\,^4S + [E_{\text{exp}}(1s2s)\,^3S - E_{\text{nr}}(1s2s)^3S] \pm 0.000\,037 \text{ a.u. (Li)} . \quad (1)$$

The absolute term value $T(1s2s3s)\,^4S$ is then given by

$$\begin{aligned} T(1s2s3s)\,^4S &= E_{\text{exp}}(1s2s3s)\,^4S - E_{\text{exp}}\,1s^22s \\ &= [E_{\text{exp}}(1s2s)\,^3S - E_{\text{exp}}1s^22s] + [-E_{\text{nr}}(1s2s)\,^3S + E_{\text{nr}}(1s2s3s)\,^4S] \pm 0.000\,037 \text{ a.u. (Li)} \\ &= 519\,520.9 + [5.110\,727 + E_{\text{nr}}(1s2s3s)\,^4S] \times 219\,457.48 \pm 8 \text{ cm}^{-1} , \end{aligned} \quad (2)$$

where use has been made of the data given in Table I.

III. OUTLINE OF THE CALCULATION

We have carried out a standard[16,19] CI calculation,[20] i.e., one based on (i) a Slater-type (STO) basis, (ii) orthogonal symmetry adapted orbitals, and (iii) an N-electron basis with L-S symmetry.

The primitive basis consists of $10s8p6d4f3g2h$ energy optimized STO's, given in Table II. The optimization of the s and p functions is complicated by the fact that the region of localization of the optimal functions extends from 0.5 to 8.0 bohr. Optimization of d-type STO's is further complicated by the relatively large energy contributions that come out of triple excitations of the type p_ip_jd. The optimization of the f-, g-, and h-type STO's is straightforward. Some STO's have been optimized with respect to the $(1s2s2p)\,^4P^o$ and $(1s2p^2)\,^4P$ states, in an attempt to build up a basis suitable for several quartet states.

For the orbital basis we proceed as follows: (i) $10s8p$ natural orbitals (NO's) are obtained from a full CI expansion in the $10s8p$ basis; (ii) six d-type NO's are generated from a limited CI expansion; (iii) the $10s8p6d$ orbitals found in (i) and (ii) are supplemented by $4f3g2h$ Schmidt orthogonalized orbitals and used to construct a good approximation to the full CI; and (iv) from this good wave function NO's are obtained and used to con-

TABLE I. Experimental and nonrelativistic energies for the Li ground state, and for the $1s^2$, $(1s2s)\,^3S$, and $(1s2p)\,^3P$ states of Li$^+$, in a.u. (Li) and in (cm^{-1}). The dispersion of energy differences in the fourth column is equal to 24 μhartree $\simeq$ 5 cm^{-1}. $R(^7\text{Li}) = 109\,728.74$ cm^{-1}. The error bounds are enclosed in parentheses and refer to the last decimal(s).

State	E_{exp}	E_{nr}	Difference
$1s^22s$	−7.478 562(1) [1 641 226.3(2)] [a]	−7.478 055(30) [c]	0.000 507(30)
$1s^2$ Li$^+$	−7.280 403 9(1) [1 597 739.1(2)] [a]	−7.279 913 41(1) [d]	0.000 490 5
$(1s2s)\,^3S$ Li$^+$	−5.111 265 3(2) [1 121 705.4(4)] [b]	−5.110 727 37(1) [b]	0.000 537 9
$(1s2p)\,^3P$ Li$^+$	−5.028 208 7(2) [1 103 478.0(4)] [b]	−5.027 715 70(1) [b]	0.000 493 0

[a] Reference 14.

[b] References 3 and 15.

[c] S. Larsson, Phys. Rev. 169, 49 (1968), value estimated from Larsson's results.

[d] C. L. Pekeris, Phys. Rev. 115, 1216 (1959).

struct the final approximation to the full CI with the given basis.

TABLE II. STO parameters. The building up of this set was particularly tedious and time consuming because the region of localization of the optimal functions is so widespread. Alternative even tempered sets of comparable accuracy are too large in size to be of any practical use.

STO	Orbital exponent	$\langle r\rangle$ (bohr)	Shell
$1s$	2.98	0.50	K
$3s$	3.75	0.93	K
$4s$	3.60	1.01	K
$3s$	1.51	2.32	L
$4s$	1.94	2.32	L
$2s$	0.90	2.78	L
$5s$	1.70	3.24	L
$4s$	1.12	4.02	L,M
$3s$	0.475	7.37	M
$4s$	0.54	8.33	M
$4p$	6.50	0.69	K
$3p$	3.60	0.97	K
$2p$	1.50	1.67	K,L
$2p$	0.91	2.75	L
$3p$	1.27	2.76	L
$4p$	1.57	2.87	L
$3p$	0.80	4.39	L,M
$3p$	0.60	5.83	M
$4d$	5.00	0.90	K
$3d$	2.10	1.67	K,L
$4d$	1.45	3.10	L
$3d$	1.10	3.18	L
$4d$	1.10	4.09	L,M
$5d$	0.80	6.88	M
$5f$	6.0	0.92	K
$4f$	3.25	1.38	K,L
$4f$	1.50	3.0	L
$5f$	1.73	3.18	L
$5g$	3.50	1.57	K,L
$5g$	1.80	3.06	L
$6g$	2.05	3.17	L
$6h$	4.00	1.63	K
$6h$	2.20	2.95	L

IV. RESULTS

A. Nonrelativistic energy of the $(1s2s3s)\,^4S$ state

A 200-term CI expansion gives a rigorous upper bound to the nonrelativistic energy (without mass polarization) $E_u = -5.212\,720$ a.u. (Li). This is 0.0003 a.u. (=0.01 eV) lower than Larsson's[13] result, which was the lowest upper bound previous to the present one. The truncation energy error $\Delta E_{\rm tr}$ due to truncations in the full CI expansion is very small, $\Delta E_{\rm tr} < 1$ μhartree $= 0.2$ cm^{-1} and it was calculated as in previous work,[16] as the sum of a few energy differences between extended and truncated variational wave functions.

We have also estimated the energy errors introduced by the truncation of the STO set[16] by computing energy differences between wave functions obtained with very large basis and the currently used one, for each harmonic. We get a total STO truncation error of $-0.000\,017(3)$ a.u. distributed as follows: 4.0(5) μhartree for s-type STO's, 3.0(5) for p-type, 8(1) for d-type, and 2(1) for f and higher STO's.

The nonrelativistic energy (without mass polarization) is computed in Table III by adding to E_u the truncation errors mentioned above. Estimates for the experimental energy and absolute term value of the ^4S state are also given in Table III.

B. Absolute term values for the quartet states

On the basis of: (i) the experimental wave numbers of Herzberg and Moore[3]; (ii) the positive identification of several transitions by Feldman *et al.*[12] and by Berry *et al.*[7,8]; (iii) the fine and hyperfine structure studies of Feldman *et al.*[12]

TABLE III. Nonrelativistic energy for the $(1s2s3s)^4S$ state, and estimates for the experimental energy and absolute term value. 1 a.u. (^{7}Li) = 219 457.48 cm^{-1}.

	Energy correction	Total energy
E_u, 200-term CI		$-5.212\,720$
Truncation error, full CI	Negligible	
Truncation error, STO basis	$-0.000\,017(3)$	
$E_{\rm nr}$		$-5.212\,737(3)$ a.u. (Li)
$E_{\rm exp}$, Eq. (1)		$-5.213\,275(37)$
$T_{\rm exp}$, Eq. (2)		$497\,134.0 \pm 8$ cm^{-1}

TABLE IV. Absolute term values for ^{7}Li quartets. The first five terms are accurately known from hollow cathode discharge high-resolution spectra. Hyperfine splittings are comparable to the fine structure, so that J-absolute terms refer to the center of the (hyperfine) multiplet. The two $^4P^o$ states above the $(1s2s)^3S$ Li$^+$ threshold at 519 520.9 cm^{-1} should autoionize quite rapidly so that their classification among narrow line emitting states may be wrong. The uncertainty in the values of the fourth column is equal to the one in the third column plus 8 cm^{-1}. 1 eV = 8065.465(27) cm^{-1}.

Term	J	Level (cm^{-1})	Level relative to ground state (cm^{-1})	Level relative to ground state (eV)
$1s2s2p\,^4P^o$	$\frac{3}{2}$	0.0 [a,b]	463 061.1	57.412 8
	$\frac{5}{2}$	1.0	463 062.1	
	$\frac{1}{2}$	2.7	463 063.8	
$1s(2p)^2\,^4P$	$\frac{1}{2}$	26 915.5 [a-c]	489 976.6	60.750 0
	$\frac{5}{2}$	26 915.5	489 976.6	
	$\frac{3}{2}$	26 917.4	489 978.5	
$1s2s3p\,^4P^o$		31 041.6 [a,d]	494 102.7	61.261 5
$1s2s3s\,^4S$	$\frac{3}{2}$	34 072.9 [a,b]	497 134.0 [e]	61.637 4
$1s2s3d\,^4D$		42 779.4 [a,b]	505 840.5	62.716 8
$1s2s4p\,^4P^o$		45 725(7) [f]	508 786	63.082 0
$1s2s4s\,^4S$		45 977(21) [g]	509 039	63.113 4
$1s2s4d\,^4D$		49 026(24) [h]	512 087	63.491 3
$1s2s4f\,^4F^o$		49 439(20) [i]	512 500	63.542 5
$1s2s5p\,^4P^o$		49 689(10) [j]	512 750	63.573 5
$1s2s6p\,^4P^o$		50 741(11) [k]	513 802	63.704 0
$1s2s5d\,^4D$		51 720(26) [l]	514 781	63.825 3
$1s2p3s\,^4P^o$		54 547(8) [m]	517 608	64.175 8
$1s2s\,^3S$ Li$^+$		56 458.3 [n]	519 520.9 [n]	64.413 01
$1s2p3p\,^4P$		59 703(8) [o]	522 764	64.815 1
$1s2p3d\,^4D^o$		61 761(7) [p]	524 822	65.070 3
		61 773(12) [q]		
		61 750(20) [i]		
$1s2p4s\,^4P^o$		66 617(16) [r]	529 678	65.672 3
$1s2p4p\,^4P$		66 733(13) [s]	529 794	65.686 7
$1s2p4d\,^4D^o$		67 552(15) [t]	530 613	65.788 3
		67 556(32) [u]		
$1s2p4f\,^4F$		67 659(20) [i]	530 720	65.801 5
$1s2p5s\,^4P^o$		69 328(18) [v]	532 389	66.008 5
$1s2p5d\,^4D^o$		70 097(19) [w]	533 158	66.103 8
$1s2p\,^3P$ Li$^+$		74 687.2 [n]	537 748.3 [n]	66.672 95

[a] Reference 3.

[b] Reference 12.

[c] Reference 21.

[d] Reference 8.

[e] This work, Table III.

[f] Based on the 5315 ± 2 Å transition (Ref. 8) to the $(1s2p^2)\,^4P$ state, classification supported by the presence of a closed loop.

[g] Based on the 2174 ± 1 Å transition (Ref. 7) to the $(1s2s2p)\,^4P^o$ state, classification supported in Sec. IV C.

[h] Based on the 2039 ± 1 Å transition (Ref. 8) to the $(1s2s2p)\,^4P^o$ state, classification supported as in footnote f.

[i] Theoretical calculation, Ref. 22.

[j] Based on the 4390 ± 2 Å transition (Ref. 8) to the $(1s2p^2)\,^4P$ state.

[k] Based on the 4196 ± 2 Å transition (Ref. 8) to the $(1s2p^2)\,^4P$ state.

[l] Based on the 5440 ± 2 Å transition (Ref. 8) to the $(1s2p5d)\,^4D^o$ state, see also footnote w.

[m] Based on the 3618 ± 1 Å transition (Ref. 7) to the $(1s2p^2)\,^4P$ state.

[n] Obtained from the data in Table I.

[o] Based on the 3488 ± 1 Å transition (Ref. 7) to the $(1s2s3p)\,^4P^o$ state.

[p] Based on the 5267 ± 2 Å transition (Ref. 8) to the $(1s2s3d)\,^4D$ state.

[q] Based on the 2868 ± 1 Å transition (Ref. 7) to the $(1s2p^2)\,^4P$ state.

[r] Based on the 2518 ± 1 Å transition (Ref. 8) to the $(1s2p^2)\,^4P$ state.

[s] Based on the 2801 ± 1 Å transition (Ref. 8) to the $(1s2s3p)\,^4P^o$ state, classification supported as in footnote f.

[t] Based on the 2460 ± 1 Å transition (Ref. 8) to the $(1s2p^2)\,^4P$ state.

[u] Based on the 5395 ± 2 Å transition (Ref. 8) to the $(1s2s3d)\,^4D$ state.

[v] Based on the 2358 ± 1 Å transition (Ref. 8) to the $(1s2p^2)\,^4P$ state.

[w] Based on the 2315 ± 1 Å transition (Ref. 8) to the $(1s2p^2)\,^4P$ state.

and of Gaupp *et al.*[21]; (iv) the absolute term value for the $(1s2s3s)\,^4S$ computed in Table III; and (v) absolute term values[22] for the $(1s2p3d)\,^4D^o$, $(1s2s4f)\,^4F^o$, and $(1s2p4f)\,^4F$ states, we give in Table IV absolute term values for the ^{7}Li quartet states. This table is particularly needed in view that the previous compilations by Berry *et al.*[8] are reproducible from their own raw experimental data with uncertainties which range between 20 and 120 cm^{-1} (larger than the experimental uncertainties, see Table IV). The present revision also helps to bring the experimental data more into line with a previous theoretical calculation,[10] as shown in Sec. IV C.

C. Discussion

In the last column of Table IV we show the positions of the quartet states relative to the ground state, in eV. We find the $(1s2s2p)\,^4P^o$ state at 57.4128(10) eV, in agreement with the earlier electron-impact data[1] of 57.3(3) eV. As in the previous tables, we give more figures than are needed to match the quoted error, in the hope that the latter might turn out to be much smaller.[23]

The absolute positions of the principal quartet states are useful as standards to define the electron energy scale in the 55–65 eV energy range, thus enabling a more precise localization[1] of possible resonance states of Li.

The previous placing of the $(1s2s2p)\,^4P^o$ state at 57.4420(40) eV by Berry *et al.*[8] is apparently too high. Their result, however, is insufficiently documented to allow us to discuss the possible reasons for the discrepancy with the present value.

Berry[8] points out that the energy of the $(1s2s3p)\,^4P^o$ term must remain in doubt because: (i) the transition at 8517 Å observed by Herzberg and Moore[3] and assigned[8] to the $(1s2s3d)\,^4D \longleftarrow (1s2s3p)\,^4P^o$ transition has never been observed in beam foil spectra; and (ii) earlier theoretical calculations[10] for the energy do not agree with the experimentally suggested value. Holøien and Geltman (HG),[10] however, placed the first two $^4P^o$ states at 57.47 and 61.33 eV, respectively, compared with our more accurate values of 57.41 and 61.26 eV, see Table IV. Thus HG's calculations are 0.06 eV too high for the lowest $^4P^o$ state and 0.07 eV too high for the next $(1s2s3p)\,^4P^o$ state, which seems quite reasonable from the viewpoint of accumulation of energy errors for higher excited states of the same symmetry. The HG's calculations, therefore, support the current assignment of the $(1s2s3p)\,^4P^o$ term although the $(1s,23sp+)$ character of this term, postulated by these authors, has not been confirmed.[11]

The earlier theoretical calculations[10] also support the assignment of the $(1s2s4s)\,^4S$ state as the one responsible for the transition at 2174 Å. HG get[10] 61.69 and 63.18 eV for the $(1s2s3s)$ and $(1s2s4s)\,^4S$ states, respectively. These values should be compared with the present ones (see Table IV) of 61.637 and 63.113 eV, respectively. We see that the first two ^4S states of HG are too high by an amount similar to the one previously found for the first two $^4P^o$ states.

The third $(1s2s4p)\,^4P^o$ state is given by HG at 62.77 eV while experiment (see Table IV) suggests that it must be at 63.082. Either the closed loop which provided the experimental identification is accidental or HG's result is wrong, since the variational wave functions can only give energy upper bounds to the exact ones (the uncertainty due to possible relativistic effects is only 8 cm^{-1} $=0.001$ eV). The energy for the $(1s2p^2)\,^4P$ state found by HG is again too low; this is discussed in the following paper.

Should the need for more precision be justified, then the calculation of the energy would have to include relativistic, radiative, and mass polarization E_{rrmp} energy corrections; the uncertainty in our reported E_{nr} (see Table III) is only 3 μhartree $=0.5$ cm^{-1}, while the admitted reliability in $E_{\mathrm{rrmp}} = E_{\mathrm{exp}} - E_{\mathrm{nr}}$ amounts to 8 cm^{-1}.

Oscillator strengths for transitions involving ^4S, $^4P^o$, ^4P, $^4D^o$, ^4D, $^4F^o$, and ^4F states are reported in the following paper.[22] An analysis of the electron correlation for these states shall be given elsewhere.[24]

Note added in proof. T. Ahlenius, R. Crossley, and S. Larsson [Phys. Lett. 63A, 270 (1977)] have given strong evidence to support a new classification for the transitions between $(1s2smp)\,^4P^0$ and $(1s2pnp)\,^4P$ states. The new (old) term values for $1s2s3p$, $1s2s4p$, $1s2p3p$, and $1s2p4p$ states are 62.350 (61.2615), 63.356 (63.0820), 64.811 (64.8151), and 65.688 (65.6867) eV, respectively, thus updating the corresponding data in Table IV. The authors are grateful to Dr. Crossley for correspondence and for a preprint of his work.

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[23] This hope is based on the fact that the relativistic energies, Ref. 17, for $1s^2 3s$ and $1s^2$ Li$^+$ differ in less than 1 cm^{-1} while we have assumed (Sec. II) that the corresponding energy difference between $(1s2s3s)^4S$ and $(1s2s)^3S$ of Li$^+$ is ± 8 cm^{-1}.

[24] A. V. Bunge and C. F. Bunge (unpublished).