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Configuration-interaction studies of transition energies and oscillator strengths for the lowest quartet states of neutral lithium

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Configuration-interaction calculations for the lowest ^4S, $^4P^o$, ^4P, $^4D^o$, ^4D, $^4F^o$, and ^4F states of neutral lithium have been carried out with a basis of $10s8p8d6f3g2h1i$ Slater-type orbitals. The nonrelativistic-energy upper bounds converge to within 4–45 cm^{-1} of the expected nonrelativistic energies. An explanation is given for the fact that transitions from ^4F states have not been observed in beam-foil experiments. Some aspects involved in the assessment of the reliability of calculated oscillator strengths are discussed, and the calculated mean lifetimes for electric dipole decay are compared with experiment.

I. INTRODUCTION

The term system and the mean lifetimes of the quartet states[1] of neutral lithium have been studied mainly by beam-foil spectroscopy.[2-6] The quartet states below the $(1s2p)\,^3P$ series limit (which is located 66.672 95 eV above the $1s^22s$ ground state) are believed to be metastable againt autoionization. They decay by narrow-line radiation to the lowest $(1s2s2p)\,^4P^0$ state which is metastable againt radiative decay and autoinonizes slowly[7] in about 5 μsec.

In a previous paper,[8] the results of an extensive configuration interaction (CI) calculation for the $(1s2s3s)\,^4S$ state of neutral lithium were used to establish absolute term values for the low-lying quartet states. In the present work, we extend our calculations to the lowest $(1s2s2p)\,^4P^0$, $(1s2s3d)\,^4D$, $(1s2s4f)\,^4F^0$, $(1s2p^2)\,^4P$, $(1s2p3d)\,^4D^0$, and $(1s2p4f)\,^4F$ states. The $^4F^0$ and ^4F states are considered here for the first time.

In Sec. II we describe the wave functions and discuss our results for the transition energies including previous theoretical work.[9,10] The numerical formulas for the oscillator strengths are written down in Sec. III together with numerical results and some considerations which are useful to assess the reliability of the calculated f values. Mean lifetimes for electric dipole decay and comparisons with experiment are given in Sec. IV. Conclusions are presented in Sec. V.

II. WAVE FUNCTIONS AND TRANSITION ENERGIES

The nonrelativistic wave functions Ψ have been approximated by finite CI expansions[11,12]:

$$\Psi = \sum_{K,p} \Phi_K^{(p)} a_{Kp}\,, \tag{1}$$

based on (i) a Slater-type (STO) basis, (ii) orthogonal symmetry adapted orbitals common to all excited states, and (iii) L-S eigenfunctions $\Phi_K^{(p)}$, also called configuration state functions (CSF's). In Eq. (1) the superscript p is used to distinguish the elements of a possible degenerate configuration K, and it may be associated with a particular internal coupling of electron groups.[12]

The eigenvector coefficients a_{Kp} are computed by means of Shavitt's algorithm[13] to five decimals of precision. A Burroughs 6700 computer and double-precision arithmetic (22 ciphers) are used throughout.

A. STO Basis

The STO basis for the $(1s2s3s)\,^4S$ state is the one used in the previous paper.[8] For the other states the basis has been extended to include the $3d$ and $4f$ spectroscopic orbitals and partial correlation in the outer shells. The new STO's are $3d = 0.333$, $4d = 0.34$, $4f = 0.25$, $4f = 0.50$, and $7i = 2.50$.

Studies of STO truncation energy errors ΔE_t have not been made, except for the $(1s2s3s)\,^4S$ state for which $\Delta E_t = 17 \pm 3$ μhartree.[8] The nonrelativistic energy limits (see Sec. II C) given in Table I suggest that, for both the $(1s2s2p)\,^4P^0$ and $(1s2p^2)\,^4P$ states, $\Delta E_t \sim 50$ μhartree. For the D and F states there is a definite need for additional p- and f-type STO's localized in the M shell, but a large part of the difference between the calculated and the suggested energies given in Table I is due to truncations in the full CI expansion, see Sec. II C.

B. Orbital Basis

The orthogonal orbital basis is common to all states other than the ^4S, so that f values can be

TABLE I. Calculated and estimated nonrelativistic energies E_{nr} for the lowest quartets of neutral Li within a given symmetry, in a.u. (Li).

State	Previous work		This work	Suggested values
$(1s2s2p)\,{}^4P^o$	-5.3659 [a]	$-5.367\,24$ [b]	$-5.367\,948$	$-5.367\,992(37)$ [c]
$(1s2p^2)\,{}^4P$	-5.2459 [a]	$-5.244\,93$ [b]	$-5.245\,308$	$-5.245\,351(37)$ [c]
$(1s2s3s)\,{}^4S$	-5.2110 [a]	$-5.212\,39$ [b]	$-5.212\,720$	$-5.212\,737(3)$ [d]
$(1s2s3d)\,{}^4D$		$-5.172\,50$ [b]	$-5.172\,852$	$-5.173\,064(37)$ [c]
$(1s2s4f)\,{}^4F^o$			$-5.142\,503$	$-5.142\,71$ [e]
$(1s2p3d)\,{}^4D^o$		$-5.086\,21$ [b]	$-5.086\,408$	$-5.086\,570(68)$ [f]
$(1s2p4f)\,{}^4F$			$-5.059\,481$	$-5.059\,69$ [e]

[a] Reference 9.

[b] Reference 10.

[c] Obtained by combining the estimated E_{nr} for $(1s2s3s)\,{}^4S$, see Table III of Ref. 8, with the experimental transition energies, see Table IV of Ref. 8. The uncertainty of 37 μhartree is due to possible relativistic effects, see Sec. II of Ref. 8.

[d] Reference 8.

[e] Obtained from E_{nr} calculated in this work by adding a correction of -210 μhartree, which is the one experimentally found for our calculated E_{nr} of $(1s2s3d)\,{}^4D$.

[f] Same as footnote c but the larger uncertainty of 68 μhartree arises from experimental uncertainties.

readily calculated. The s- and p-type orbitals are (i) natural orbitals[14] (NO's) of the $(1s2s2p)\,{}^4P^0$ $10s7p$ full CI wave function plus and STO $3p = 0.60$ orthogonalized to the previous ones and thus very much localized in the M shell. This last orbital p_8 is chosen in this particular way in order to assess the importance of M-shell localized p orbitals, which are poorly represented in the present work. The first d orbital is such that it maximizes the contribution of the $1s2s3d$ configuration to the lowest ${}^4D$ state. The first f orbital is chosen analogously with respect to the $(1s2s4f)\,{}^4F^0$ state. Orbitals d_2 and d_3 maximize the eigenvector components of configurations $1s2pd_2$ and $2s2pd_3$ for the ${}^4P^0$ state, respectively. The other orbitals are Schmidt orthogonalized in an order which emphasizes their localization in either the K, L, M, or the N shell. Natural orbitals of d-type and higher l values have not been considered.[15] For the ${}^4S$-${}^4P^0$ transition the s-type orbitals are NO's corresponding to the ${}^4S$ state and the new STO's (Sec. II A) are not included. The orbital basis appears to be adequate for all regions of space except for the M shell, where p- and f-type symmetries are represented only by orbitals p_8 and f_6, respectively.

C. Truncations of Full CI

For the $(1s2s2p)\,{}^4P^0$ and $(1s2p^2)\,{}^4P$ states, accurate approximations to the full CI expansions have been obtained. The energy contributions of triple-excited configurations are only 0.5 cm^{-1} for the $(1s2s2p)\,{}^4P^0$ state, but they rise to 190 cm^{-1} for the $(1s2p^2)\,{}^4P$ state, due to changes in the $1s$ natural orbital in going from the odd to the even-parity states (appreciable energy contributions come from configurations such as $2sd_2^2$, $2sp_2^2$, etc.).

The CI expansions for the D and F states have been approximated within the minimum-Hartree-Fock interacting space[11] (minHFI), which is the space of all singly and doubly excited determinants projected into L-S symmetry.[12]

The energy of the $(1s2s3d)\,{}^4D$ state is about 210 μhartree (~46 cm^{-1}) above the value suggested by experiment, see Table I. We assume that the same energy error is present for the ${}^4D^0$, ${}^4F$, and ${}^4F^0$ states. A large part of this error is due to the truncation of the full determinantal space into the minHFI space for the orbital basis common to all these states. Additional truncations based on an eigenvector component criterion have been made to evaluate oscillator strengths.

D. Transition Energies

In Table I we present calculated and estimated nonrelativistic energies E_{nr} for the lowest quartet of each symmetry for neutral Li. These energies may be used as a reference for calculations on higher-excited states, especially for those whose classification is uncertain.[1] The present improvement over Weiss' results[10] is due essentially to our use of a more extended basis set. For the lowest ${}^4P$ state, the variational energy -5.3659 reported by Holøien and Geltman[9] is definitely below any reasonable estimate of it.

In Table II we compare experimental and calculated transition energies. We see that all the

TABLE II. Comparison of experimental and calculated transition energies, in cm^{-1}.

Transition	Experimental[a]	Calculated[b]
$(1s2s2p)\,^4P^o \rightarrow (1s2p^2)\,^4P$	26 915	26 914
$\rightarrow (1s2s3s)\,^4S$	34 072	34 065
$\rightarrow (1s2s3d)\,^4D$	42 779	42 815
$(1s2p^2)\,^4P \rightarrow (1s2p3d)\,^4D^o$	34 846	34 872
$(1s2s3d)\,^4D \rightarrow (1s2s4f)\,^4F^o$		6 660
$\rightarrow (1s2p3d)\,^4D^o$	18 982	18 971
$(1s2s4f)\,^4F^o \rightarrow (1s2p4f)\,^4F$		18 220
$(1s2p3d)\,^4D^o \rightarrow (1s2p4f)\,^4F$		5 898

[a] Energy difference between the centers of the multiplets, Ref. 8.

[b] This work.

transitions involving F states are in the infrared, except for (i) the $(1s2p4f)\,^4F \rightarrow (1s2s4f)\,^4F^0$ transition at 18220 cm^{-1}, which corresponds to $\lambda_{\mathrm{vac}} = 5488$ Å or $\lambda_{\mathrm{air}} = 5486$ Å, and (ii) the weaker transitions $(1s2pnf)\,^4F \rightarrow (1s2s4f)\,^4F^0$ further towards the uv region. Transitions between quartet F states, however, have not been identified in the beam-foil spectra of Li, although similar transitions are well known[1] for the higher members of the Li isoelectronic sequence.

An explanation for the failure to identify the 5486-Å transition in beam-foil spectroscopy can be inferred at once by looking at Fig. 8 of Ref. 1, which shows a very intense and broad feature at 5485 ± 10 Å, corresponding to the resonant transition $(1s2p)\,^3P \rightarrow (1s2s)\,^3S$ in Li^+. Thus the relatively weak (see Table III) transition between quartet states at 5486 Å is masked by a very intense and broad transition in the Li^+ system.

Herzberg and Moore[16] have made a detailed study of the fine and hyperfine structure of the 5485-Å line, but they do not report unaccounted lines nearby. This should be attributed to the excitation conditions in the hollow cathode discharge which cannot even produce the lower-lying $(1s2p3d)\,^4D^0$ state in any appreciable amount.

III. OSCILLATOR STRENGTHS

A. Basic formulas

In the LS coupling approximation one may introduce a line strength $S(i,k)$ defined by[17]

$$S(i,k) = \sum_{M_S, M_S'} \sum_{M_L, M_L'} \left| \left\langle \Psi_{iM_LM_S} \left| \sum_{p=1}^{N} \vec{\mathrm{T}}_p \right| \Psi_{kM_L'M_S'} \right\rangle \right|^2 \tag{2a}$$

$$= g_i \sum_{M_L'} \left| \left\langle \Psi_{iM_LM_S} \left| \sum_{p=1}^{N} \vec{\mathrm{T}}_p \right| \Psi_{kM_L'M_S'} \right\rangle \right|^2 . \tag{2b}$$

In Eqs. (2), $S(i,k)$ is given in a.u. (1 a.u. $= a_0^2 e^2 = 6.4606 \times 10^{-36}\ \mathrm{cm}^2\,\mathrm{esu}^2$); g_i denotes the statistical weight of the lower multiplet i and $\vec{\mathrm{T}}$ (in a.u.) may be expressed either in dipole length form $\vec{\mathrm{T}}^l$, in dipole velocity form $\vec{\mathrm{T}}^v$, or in dipole acceleration form $\vec{\mathrm{T}}^a$ [18,19]:

$$\vec{\mathrm{T}}^l = \vec{\mathrm{r}} , \tag{3}$$

$$\vec{\mathrm{T}}^v = (E_k - E_i)^{-1} \vec{\nabla} , \tag{4}$$

$$\vec{\mathrm{T}}^a = Z (E_k - E_i)^{-2} \vec{\mathrm{r}} / r^3 , \tag{5}$$

or in other less familiar forms.[20] The absorption oscillator strength f_{ik} (dimensionless) from a lower multiplet i to an upper multiplet k is then given by

$$f_{ik} = \tfrac{2}{3} g_i^{-1} (E_k - E_i) S(i,k) , \tag{6a}$$

where the transition energy $E_k - E_i$ is in a.u. The emission oscillator strength f_{ki}, which is related to the absorption oscillator strength by

$$f_{ki} = -(g_i/g_k) f_{ik} , \tag{6b}$$

is not used in this work. The transition probability A_{ki} (in sec^{-1}) for spontaneous emission is given (in the electric dipole approximation) by

$$A_{ki} = C \lambda^{-2} (g_i/g_k) f_{ik} , \tag{7a}$$

$$C = 64\pi^4 R_\infty e^2 a_0^2 10^{16} / h^2 c$$

$$= 6.67025 \times 10^{15}\ \mathrm{sec}^{-1} , \tag{7b}$$

when $\lambda \equiv \lambda_{\mathrm{vac}} > \lambda_{\mathrm{air}}$ is expressed in angstroms. If one sums A_{ki} over all multiplets i with energy E_i lower than E_k, one arrives at the total probability per unit time P_k that the multiplet k decays through spontaneous emission

$$P_k = \sum_{i<k} A_{ki} . \tag{8}$$

The reciprocal of P_k is called the mean lifetime of the multiplet k,

$$\tau_k = 1/P_k . \tag{9}$$

The evaluation of the summation in Eq. (2b) is described by Slater[21] for $\vec{\mathrm{T}}^l$; the same formulas also apply to $\vec{\mathrm{T}}^v$ and to $\vec{\mathrm{T}}^a$, after making the necessary substitutions in the corresponding one-electron integrals,[19] since the Cartesian components of $\vec{\mathrm{T}}^v$ and $\vec{\mathrm{T}}^a$ have the same commutation properties as those of $\vec{\mathrm{T}}^l$ with respect to the total angular momentum.

We now concentrate on the expression for the line strength $S(i,k)$. From Eq. (2) and the expansion of Ψ in terms of Slater determinants it follows that

$$S(i,k) = \left(\sum_{l=0} \sum_{n,n'} t^{(q)}_{nl;n',l+1} \right)^2 , \tag{10}$$

$$t^{(q)}_{nl;n',l+1} = B(S,L,M_L) \sum_{K,L} a_K a_L c^{(q)}_{lm} D^{(q)}_{nl;n',l+1} , \tag{11}$$

where $q=l$, v, or a according to which one of Eqs. (3)–(5) is utilized. In Eq. (11) we have a factor $B(L,S,M_L)$ depending on the L-S symmetry of initial and final states multiplying a sum of products of CI coefficients times a factor $c_{lm}^{(q)}$ times the integral $D_{nl;n',l+1}^{(q)}$:

$$D_{nl;n',l+1}^{(q)}=A_{nl;n',l+1}^{(q)} \text{ or } A_{n',l+1;nl}^{(q)}, \tag{12}$$

$$A_{n',l+1;nl}^{(l)}=A_{nl;n',l+1}^{(l)}=\int_0^\infty r^3 R_{nl} R_{n',l+1}\,dr, \tag{13}$$

$$A_{nl;n',l+1}^{(v)}=\int_0^\infty r^2 R_{nl}[-(l+1)R_{n',l+1}+R'_{n',l+1}]dr, \tag{14a}$$

$$A_{n',l+1;nl}^{(v)}=\int_0^\infty r^2 R_{n',l+1}(-lR_{nl}+R'_{nl})dr, \tag{14b}$$

$$A_{n',l+1;nl}^{(a)}=A_{nl;n',l+1}^{(a)}=\int_0^\infty R_{nl}R_{n',l+1}\,dr. \tag{15}$$

Since the set of radial orbitals $\{R_{nl}\}$ always includes the major orbitals which are those participating in the leading configurations of Ψ_i and Ψ_k, the quantities $t_{nl;n',l+1}^{(q)}$ are useful to interpret the nature of correlation effects in $S(i,k)$: if at the single-configuration level of approximation the transition can be described as $R_{il}\to R_{k,l+1}$, correlation effects will be small if $t_{il;k,l+1}^{(q)} \gg t_{nl;n',l+1}^{(q)}$ for $n\neq i, n'\neq k$. This is often the case for $q=l$ or v, but it rarely happens for $q=a$.

The quantities $t_{nl;n',l+1}^{(q)}$ can be summed over one of the orbital indices to yield orbital contributions to the square root of $S(i,k)$:

$$or(l,l+1)_{nl}^{(q)}=\sum_{n'} t_{nl;n',l+1}^{(q)}, \tag{16a}$$

$$or(l,l+1)_{n',l+1}^{(q)}=\sum_{n} t_{nl;n',l+1}^{(q)}, \tag{16b}$$

$$S_l^{(q)}=\sum_n or(l,l+1)_{nl}^{(q)}=\sum_{n'} or(l,l+1)_{n',l+1}^{(q)}, \tag{17}$$

$$S(i,k)^{1/2}=\sum_{l=0} S_l^{(q)}. \tag{18}$$

In particular, we shall make use of the percentages of orbital contributions $o(l,l+1)^{(q)}$,

$$o(l,l+1)_{nl}^{(q)}=or(l,l+1)_{nl}^{(q)}\times 100/S^{(q)}(i,k)^{1/2}. \tag{19}$$

In the Sec. III B we will discuss how to obtain an assessment of the reliability of calculated f values from an analysis of the orbital contributions to the line strength in the length, velocity and acceleration forms.

B. f values and their reliability

The length, velocity, and acceleration f values must agree with each other when computed with the exact nonrelativistic wave functions. Agreement between the l, v, and a forms, however, is not sufficient to assess the reliability of the calculated f values. These are given in Table III and their reliability is discussed below.

The difference between the exact f value f_{ex} and an approximate one $f_{ap}^{(q)}$ may be written as a sum of two terms,

$$f_{ex}-f_{ap}^{(q)}=\Delta_{FB}^{(q)}+\Delta_{TCI}^{(q)}. \tag{20}$$

In Eq. (20), Δ_{FB} is the error due to the use of a finite orbital basis (FB effects), and Δ_{TCI} is the error introduced by truncating the full CI expansion corresponding to the given orbital basis (TCI effects). Although Δ_{FB} and Δ_{TCI} escape precise determination in an economic way, an analysis of $t^{(q)}$ and $o(l,l+1)^{(q)}$ quantities usually gives an indication about orders of magnitude of these errors.

Let us first consider FB effects. As was discussed in Sec. II B, orbitals p_8 and f_6 are localized in regions of space which are not sufficiently well represented with the full basis; this is believed to be the only shortcoming of the present basis.[22] The FB errors $\Delta_{FB}^{(q)}$ may be thought to be of the order of magnitude of $o(l,l+1)^{(q)}$ quantities corresponding to orbitals p_8 and f_6. In this work we have assumed that

TABLE III. Calculated absorption oscillator strengths for transitions between quartet states which are lowest for a given symmetry.

Transition	Wave number (cm^{-1})	$f_{ik}^{(l)}$	$f_{ik}^{(v)}$	$f_{ik}^{(a)}$	f (estimated)	A_{ki} (10^8 sec^{-1})	$S(i,k)$
$(1s2s2p)\,^4P^o \to (1s2p^2)\,^4P$	26 915	0.3591	0.3576	0.3948	0.359(3)	1.735(15)	52.7(4)
$\to (1s2s3s)\,^4S$	34 072	0.0640	0.0640	0.0597	0.0640(2)	1.487(4)	7.43(2)
$\to (1s2s3d)\,^4D$	42 779	0.3289	0.3274	0.3180	0.328(3)	2.41(2)	30.3(3)
$(1s2p^2)\,^4P \to (1s2p3d)\,^4D^o$	34 846	0.3904	0.3912	0.3945	0.391(3)	1.900(15)	44.3(3)
$(1s2s3d)\,^4D \to (1s2s4f)\,^4F^o$	6 660	0.784	0.743	0.416	0.78(3)	0.165(6)	771.(30)
$\to (1s2p3d)\,^4D^o$	18 982	0.134	0.140	0.155	0.140(6)	0.336(14)	48.6(2.1)
$(1s2s4f)\,^4F^o \to (1s2p4f)\,^4F$	18 220	0.135	0.112	0.152	0.135(4)	0.299(9)	68.2(2.0)
$(1s2p3d)\,^4D^o \to (1s2p4f)\,^4F$	5 898	0.814	0.822	1,12	0.82(2)	0.136(3)	914.(22)

TABLE IV. Percent of orbital contributions $o(l, l+1)_{nl}^{(q)}$ and $o(l, l+1)_{n', l+1}^{(q)}$, Eq. (19), for the $(1s2s3d)\,{}^4D \rightarrow (1s2s4f)\,{}^4F^o$ transition.

Orbital	Length	Velocity	Acceleration
$l=0$			
s_1	−0.1	−2.3	−405
s_2	−3.8	−1.0	159
s_3	0.1	−0.9	−16
s_4-s_{10}	0	0.1	−6
Subtotal	−3.8	−4.1	−268
p_1	−3.9	−5.5	−721
p_2	0.1	1.7	177
p_3-p_8	0	−0.3	276
Subtotal	−3.8	−4.1	−268
$l=1$			
p_1	0	0.2	0
p_2	0.4	0.7	0
p_3-p_8	1.1	0.5	0
Subtotal	1.5	1.4	0
d_1	1.5	1.5	0
d_2-d_8	0	−0.1	0
Subtotal	1.5	1.4	0
$l=2$			
d_1	108.7	103.2	367
d_2	−1.5	−0.3	1
d_3	−0.7	−0.1	0
d_4	0	0	0
d_5	−0.5	−0.1	0
d_6	−1.6	0	0
d_7	−1.4	0	0
d_8	−0.6	0	0
Subtotal	102.3	102.7	368
f_1	100.5	99.1	335
f_2	0.1	0.5	18
f_3-f_5	0.1	0.1	3
f_6	1.6	3.0	12
Subtotal	102.3	102.7	368

$$\Delta_{\mathrm{FB}}^{(q)}/f_{\mathrm{ex}} = o(0,1)_{81}^{(q)} + o(1,2)_{81}^{(q)} + o(2,3)_{63}^{(q)} + o(3,4)_{63}^{(q)} . \tag{21}$$

The $\Delta_{\mathrm{FB}}^{(q)}$'s estimated by Eq. (21) range between 0.1% and 15% of the corresponding f values, for $q=l$ and $q=v$, the length form usually being least sensitive to FB effects for the present orbital basis. As an example, in Table IV we give the percentages of orbital contributions to $S(i,k)^{1/2}$ for the $(1s2s3d)\,{}^4D \rightarrow (1s2s4f)\,{}^4F^o$ transition. Note that the signs of the $o^{(q)}$ quantities are independent of an arbitrary phase on the orbitals. From the data in Table IV one may expect that additional d-orbitals might lower $f^{(l)}$. Substantial errors, however, appear to be associated with the significant contributions of orbital f_6 to both $f^{(l)}$ and $f^{(v)}$, forecasting large FB effects. Although no rigorous statement can be made about the sign of these FB effects, the data in Table IV suggest $\Delta_{\mathrm{FB}}^{(v)} > \Delta_{\mathrm{FB}}^{(l)} > 0$, which is consistent with the result $f^{(l)} > f^{(v)}$ given in Table III. The large error in $f^{(a)}$ may be interpreted as follows: the orbital contributions for sub-block $l=2$ are probably correct, since most configurations making direct contributions to this sub-block have been included in the wave functions. However, the same is not true of sub-block $l=0$; here the orbital contributions must be 60% too large in order to explain the $f^{(a)}$ value in Table III. Incidentally, for $l=0$, the errors in the orbital contributions to $f^{(l)}$ should be considerably smaller than 60% since they are significant only for s_2 and p_1, and *all*

TABLE V. Percent of orbital contributions $o(l, l+1)_{nl}^{(q)}$ and $o(l, l+1)_{n', l+1}^{(q)}$, Eq. (19), for the $(1s2s2p)\,{}^4P^o \rightarrow (1s2s3s)\,{}^4S$ transition.

Orbital	Length	Velocity	Acceleration
$l=0$			
s_1	0.4	−4.2	346
s_2	−64.1	59.8	−403
s_3	161.5	40.0	163
s_4	−0.3	1.1	−0.1
s_5	−0.2	0.3	5.2
s_6	−0.1	0.2	−0.4
s_7-s_{10}	0	0	−3.0
Subtotal	97.2	97.2	108
p_1	87.1	85.6	−169
p_2	11.3	17.3	190
p_3	−0.5	−12.4	−116
p_4	−0.4	3.1	440
p_5	−0.3	−2.7	−412
p_6	0	1.4	414
p_7	0	−0.8	−341
p_8	0	0.5	102
Subtotal	97.2	97.2	108
$l=1$			
p_1	0.4	−1.0	5.4
p_2	2.2	3.8	−14.2
p_3	0.2	0	4.2
p_4-p_8	0	0	−3.0
Subtotal	2.8	2.8	−7.6
d_1	−2.5	3.8	−4.7
d_2	4.1	−1.0	3.6
d_3	0.2	0	−6.5
d_4	0.3	0	4.9
d_5	0.7	0	−1.2
d_6	0	0	−3.7
Subtotal	2.8	2.8	−7.6
$l=2$			
d_1-d_6; f_1-f_4	Negligible	Negligible	Negligible

TABLE VI. Percent of orbital contributions $o(l,l+1)^{(q)}_{nl}$ and $o(l,l+1)^{(q)}_{n',l+1}$, Eq. (19), for the $(1s2s3d)\,{}^4D \rightarrow (1s2p3d)\,{}^4D^o$ transition.

Orbital	Length	Velocity	Acceleration
$l=0$			
s_1	3.0	52.0	564
s_2	87.4	11.4	−512
s_3	−2.9	20.6	25
s_4–s_{10}	0	−1.9	10
Subtotal	87.5	82.1	87
p_1	92.5	124.3	1159
p_2	−5.4	−49.5	−495
p_3	0.2	8.0	−485
p_4–p_8	0.2	−0.7	−92
Subtotal	87.5	82.1	87
$l=1$			
p_1	1.5	3.0	13
p_2	7.4	5.2	5
p_3	2.1	0.7	2
p_4	3.8	1.2	2
p_5	2.7	0.5	1.5
p_6	1.2	0.3	0
p_7	1.1	0.2	0
p_8	7.8	0.1	1.5
Subtotal	27.6	11.2	25
d_1	27.0	9.7	15
d_2	0.6	1.5	10
d_3–d_8	0	0	0
Subtotal	27.6	11.2	25
$l=2$			
d_1	−15.1	6.7	−12
d_2–d_8	0	0	0
Subtotal	−15.1	6.7	−12
f_1–f_5	−8.6	3.0	−7
f_6	−6.5	3.7	−5
Subtotal	−15.1	6.7	−12

configurations making the corresponding direct contributions have been included.

TCI effects are considered next. Table V shows data similar as those in Table IV, but for the $(1s2s2p)\,{}^4P^o \rightarrow (1s2s3s)\,{}^4S$ transition, for which $\Delta^{(l)}_{\mathrm{FB}}$ is thought to be negligible. While $f^{(l)}$ and $f^{(v)}$ agree to 0.08% (see Table III) the largest $o^{(l)}$ quantities in Table V differ from their $q=v$ counterparts in several percent, so that the degree of agreement between $f^{(l)}$ and $f^{(v)}$ is probably not a fortuitous one, as far as TCI effects are concerned. To estimate the exact f value in the present example, we have averaged $f^{(l)}$ and $f^{(v)}$ and given it a conservative uncertainty of 0.3% (see Table III).

In Table VI we illustrate a case where $f^{(v)}$ appears to be clearly superior to the other forms, regarding both FB and TCI effects. It is seen that $\Delta^{(v)}_{\mathrm{FB}}$ is about 4% of $f^{(v)}$, whereas $\Delta^{(l)}_{\mathrm{FB}}$ might be as large as 14% if we disregard the meaning of the sign of the $o^{(q)}$ quantities. The results for the sub-block $l=0$ show that length, velocity, and acceleration subtotals are just approximately equal with each other and about 85%. Furthermore, the fact that $o(0,1)^{(a)} \sim 10 o(0,1)^{(v)}$ suggests that the velocity subtotal is accurate to about 1% since $f^{(v)}$ and $f^{(a)}$ differ in only 10% (see Table III). Moreover, the sub-blocks $l=1$ and $l=2$ give significantly smaller subtotals for the velocity form than for either the length or the acceleration form, suggesting that the degree of agreement between velocity and length or acceleration form must be a measure of the total error in $f^{(v)}$.

IV. MEAN LIFETIMES

In Table VII we compare the beam-foil spectroscopy experimental mean lifetimes with those calculated by Eqs. (2)–(9), i.e., by assuming decay by electric dipole radiation only, thus neglecting possible autoionization.

Of the six mean lifetimes reported, two of them are in agreement with experiment, two other ones are in significant disagreement, while no experimental data exists for the other two.

The first instance of disagreement between experiment and calculations concerns the $(1s2s3s)\,{}^4S$ state. While both theoretical calculations agree well with each other, τ_{exp} is 40% too high, suggesting a typical case of unaccounted cascade repopulation of the $(1s2s3s)\,{}^4S$ state in the

TABLE VII. Comparison of experimental and calculated mean lifetimes, in nsec. Experimental values lying above calculated ones suggest unaccounted cascades while the opposite suggests autoionization of the upper level.

State	τ_{exp} [a]	τ_{calc} [b] (This work)	τ_{calc} [b,c]
$(1s2p^2)\,{}^4P$	5.8 ± 0.7 [d]	5.76 ± 0.05	5.75
$(1s2s3s)\,{}^4S$	9.7 ± 0.7	6.72 ± 0.02 [e]	6.90
$(1s2s3d)\,{}^4D$	4.5 ± 0.4	4.15 ± 0.04 [e]	4.22
$(1s2s4f)\,{}^4F^o$	⋯	60.6 ± 2.3	⋯
$(1s2p3d)\,{}^4D^o$	2.1 ± 0.4 [f]	4.47 ± 0.06 [e]	4.50
$(1s2p4f)\,{}^4F$	⋯	23.0 ± 0.7 [e]	⋯

[a] Quoted in Ref. 1.

[b] Decay by electric dipole radiation only, Eq. (9). Autoionization is also neglected.

[c] Reference 10.

[d] Other values quoted in Ref. 1 are: 7.0 ± 2.0, 6.4 ± 0.3, and 6.5 ± 0.3.

[e] Neglecting very weak transitions to states not lowest in a given symmetry. These calculated mean lifetimes are thus upper bounds to the exact ones.

[f] Another value quoted in Ref. 1: 2.3 ± 0.4.

analysis of the experimental data.[2] It is intriguing to verify, however, that cascades were indeed considered[2] in the determination of $\tau_{\exp}$. Still more surprising is the fact that none of these cascading levels appears to be identified[1] (they should be ${}^4P^o$ states).

The second case of disagreement between experiment and calculations concerns the $(1s2p3d)\,{}^4D^o$ state. Here $\tau_{\exp}$ is less than one half the calculated τ's which agree well with each other. The only reasonable explanation appears to be autoionization of the $(1s2p3d)\,{}^4D^o$ state, whose effect is included in $\tau_{\exp}$ but not in τ_{calc}.

V. CONCLUSIONS

The energies and wave functions obtained for the $(1s2s2p)\,{}^4P^o$, $(1s2p^2)\,{}^4P$, and $(1s2s3s)\,{}^4S$ states are very accurate by present day standards.[23] For the D and F states the energies and wave functions can still be significantly improved upon, but they are sufficiently accurate to provide (i) f values with uncertainties smaller than the experimental ones, and (ii) an explanation of why transitions from ${}^4F$ states have not been observed in beam-foil experiments on Li, while they are well known[1] for the higher members of the Li sequence.

The STO basis developed in the present study, together with the analysis given about its deficiencies, may be used as a starting point for attacking specific problems in the interpretation of the spectra of Li quartets. Particulary intriguing are (i) the location and classification of the higher ${}^4P^o$ states, and (ii) the interpretation of those states above the $(1s2s)\,{}^3S$ threshold which are presently classified as narrow-line-emitting ${}^4P^o$ states in apparent conflict with their possibility of undergoing rapid autoionization through the electrostatic interaction.

Perhaps the most significant part of this work is the application of the ideas given in Sec. III for the assessment of the reliability of calculated f values. The emphasis is placed on the diagnosis of an f value which purports to approximate as much as possible the full CI result for a given orbital basis. The remaining uncertainties in the f values are due to the incompleteness of the STO set. It is suggested that those STO's localized in regions of space where more primitive functions are needed should be successively orthogonalized to the orbitals which expand over the better represented regions. In this way the specific contribution of those STO's can be readily identified.

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