

# Hartree–Fock and Configuration Interaction Calculations of Hyperfine Constants in Quartet States of Three-electron Atoms

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## Abstract

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The hyperfine structure constants in the lowest  ${}^4P^{\circ}$  and  ${}^4P^{\circ}$  states of the isoelectronic sequence  $\text{Li}-\text{F}^{6+}$  have been calculated from Hartree–Fock and accurate configuration interaction (CI) wavefunctions, in good agreement with available experimental results for Li. In addition, Hartree–Fock calculations of energies and hfs constants for several higher  ${}^4S$ ,  ${}^4P^{\circ}$ ,  ${}^4D$  and  ${}^4D^{\circ}$  states of Li are reported.

## 1. Introduction

The beam-foil technique has provided a possibility of observing excited atomic species which were previously difficult or impossible to study [1]. One such example is the multiple-excited states of the three-electron atoms, for which many lines have first been observed in beam foil spectra [2]. Although these states lie above the ionization limit for Li, and thus can autoionize, selection rules against autoionization can make photon emission the dominant decay mode, making their observation by optical means possible. In conjunction with the beam-foil method, the so-called quantum-beat technique in addition allows the determination of the fine and hyperfine structure of the decaying state [3].

The development in experimental technique also provides new motivation for theoretical studies of multiple-excited states of light atoms. The energies of several quartet states of the Li isoelectronic sequence have been accurately calculated by Holøien and Geltman [4] and Weiss [5, 6], who, however, do not report any fine or hyperfine structure parameters. In this paper we report hyperfine parameters for the lowest  ${}^4P^{\circ}$  and  ${}^4P^{\circ}$  states of the Li isoelectronic series up to  $Z=9$ , obtained from configuration interaction (CI) wave functions of the same quality as those of Holøien and Geltman. In addition, we report so-called natural orbitals for some typical states, which give increased insight into the type of correlation and configuration interaction effects which are important in these states, plus Hartree–Fock results for several other quartet states of neutral Li.

## 2. Method

The Hartree–Fock calculations were performed by a method described previously [7], which is especially well suited for calculations involving many states of the same symmetry and/or more than one open shell per symmetry. The CI calculations were carried out using a program written by one of us (NHFB), which is described elsewhere [8]. Most of the calculations were done on

the IBM 370/155 at Uppsala University, using a version of the CI program which is restricted to 20 basis functions (all  $m$ -values included). This restriction is caused by the storage demands required by the program in order to maintain a list of all two-electron integrals in core. A new version which is in operation on the CDC 6400 at Aarhus University employs symmetry packing to store only the *unique* two-electron integrals. This results in great savings of storage, allowing in practice up to about 60 basis functions for atoms and diatomic molecules, while avoiding the very considerable complication of constructing matrix elements from two-electron integrals in random order on external mass storage.

The new symmetry-packing scheme is based on the observation that in atomic or linear molecule symmetry with complex spherical harmonics, the integral  $(ij|kl)$  is identical to  $(i^*j^*|k^*l^*)$ , where the asterisk denotes complex conjugation, and Mulliken notation is used, so that the indices to the left of the bar refer to electron 1, and those to the right, to electron 2. In addition,  $(ij|kl)$  is identical in absolute value to  $(ij|l^*k^*)$  and  $(j^*i^*|kl)$ . With the usual definition of spherical harmonics, an integral such as  $(sp_+|sp_-)$  would be numerically the same as  $(sp_+|p_+s)$ , but of opposite sign. To eliminate time-consuming and laborious sign checking, the sign difference is removed by redefining the spherical harmonics so that the usual factor  $(-1)^m$  for  $m < 0$  is omitted. This makes  $(ij|kl) = (i^*j^*|k^*l^*) = (j^*i^*|kl) = (ij|l^*k^*)$ , and since the integrals are zero unless  $m_i - m_j = m_l - m_k$ , they can be grouped into symmetry blocks classified by  $|m_i - m_j|$ . For atomic cases, further classification by inversion symmetry of  $(ij)$  or  $(kl)$  is possible.

As an illustration of the savings afforded by this scheme, the largest basis used in these calculations was an  $8s, 5p, 2d, 1f$ , with 40 functions in all. Without taking advantage of symmetry, the two-electron integrals would require

$$N(N+1)/2 \cdot (N(N+1)/2 + 1)/2 = 336\,610$$

storage locations. Using  $m$ -symmetry alone reduces this to 33 410, and including inversion symmetry reduces it further to 18 559. The decrease in the integral transformation time is needless to say substantial, which is important since this is the most time-consuming step in large basis CI calculations.

As mentioned above, the bulk of the CI calculations was done with the older version of the program, restricting the number of basis functions to 20. After some experimentation, a set of six  $s$ -orbitals, three  $p$ -orbitals and one  $d$ -orbital was chosen. The inclusion of a  $d$ -orbital was considered to be important to obtain a reliable result for the spin–dipolar term, which is known to be sensitive to  $d$ -type polarization distortions of the  $s$ -orbitals [9], and was also found to give a significant contribution to the energy

Table I. Calculated and experimental results for the two lowest  ${}^4P^o$  and  ${}^4P$  states of Li (a.u.)

State	Method	Energy	$a_c$	$a_l$	$a_d$
$1s2s2p\ {}^4P^o$	RHF	-5.35831	37.498	0.3050	-0.06100
	UHF	-5.35886	37.494	0.3049	-0.06177
	Full CI <sup>a</sup>	-5.36677	37.454	0.3079	-0.06330
	Ref. 4	-5.36589			
	Ref. 5	-5.3672			
	Exp.	$-5.37 \pm 0.01^d$	$37.36 \pm 0.11^e$	—	—
$1s2s3p\ {}^4P^o$	RHF	-5.18164	38.220	0.03772	-0.007543
	UHF	-5.18165	38.220	0.03772	-0.007529
	Full CI <sup>b</sup>	-5.18497	38.137	0.03975	-0.008570
	Single and double excitation CI <sup>b</sup>	-5.18669			
	Ref. 4	-5.22396			
	Ref. 5	-5.1864			
	Exp.	—			
$1s(2p)^2\ {}^4P^o$	RHF	-5.23184	35.400	0.2997	0.05994
	Full CI <sup>a</sup>	-5.24326	35.356	0.3105	0.06261
	Ref. 4	-5.24592			
	Ref. 5	-5.245			
	Exp.	$-5.25 \pm 0.01^f$	$34.0 \pm 0.5^g$	$0.59 \pm 0.38^g$	
$1s2p3p\ {}^4P^o$	Full CI <sup>b</sup>	-5.09230	35.494	0.2373	0.04774
	Full CI <sup>c</sup>	-5.09408	35.444	0.2481	0.04962
	Ref. 4	-5.09387			
	Ref. 5	-5.096			
	Exp.	—			

<sup>a</sup> Basis:  $1s$  (3.),  $3s$  (12.98, 4.569, 3.406, 1.676, 1.032),  $2p$  (2.558, 0.7613),  $3p$  (0.8799),  $3d$  (1.087).

<sup>b</sup>  $1s$  (3., 1.),  $2s$  (1.02, 0.6),  $3s$  (1.7, 0.5),  $2p$  (1.23),  $3p$  (0.88, 0.38)  $3d$  (0.38)

<sup>c</sup>  $1s$  (3.),  $3s$  (9., 5., 3., 1.),  $2p$  (2., 1.23, 0.88),  $3p$  (0.88, 0.38).

<sup>d</sup> Ref. 11. <sup>e</sup> Ref. 12. <sup>f</sup> Ref. 2. <sup>g</sup> Ref. 13.

<sup>h</sup>  $1s$  (3., 1.),  $2s$  (1.02, 0.6),  $3s$  (1.7, 0.5, 0.38),  $4s$  (0.25),  $2p$  (1.23, 0.7613),  $3p$  (0.88, 0.38)  $4p$  (0.25),  $3d$  (1.037, 0.38),  $4f$  (0.50).

for the lowest  ${}^4P^o$  states. By careful exponent optimization it was possible to reproduce, and somewhat improve upon, Holøien and Geltman's energies for the  $1s2s2p\ {}^4P^o$  states. The same basis sets were then used also for the  $1s2p^2\ {}^4P^o$  states, which gave slightly higher energies than Holøien and Geltman's for Li and  $\text{Be}^+$ , but lower energies for the other  $Z$ -values. For the  $1s2p3p\ {}^4P^o$  state we did not quite manage to reproduce the energies of ref. [4], despite extensive exponent variation. Since it was found from the natural orbital analysis (see next section) that the importance of the  $d$ -orbital decreases sharply in this state, compared to the two previous states, this state was calculated also with a five  $s$ , five  $p$  basis. This led to a significant improvement in the energy, so that the final energy was lower than that of Holøien and Geltman [4]. The second lowest  ${}^4P^o$  state poses special problems and is discussed in some detail further below.

The abovementioned calculations were in all cases full CI calculations, i.e. all possible configurations of correct spin and angular momentum that could be constructed from the original basis were included in the configuration interaction. The  $6s$ ,  $3p$ ,  $1d$  set of orbitals gives rise to a total of 75 configurations containing 411 determinants in the case of  ${}^4P^o$  symmetry, and 52 configurations containing 357 determinants in the case of  ${}^4P$  symmetry. The construction of the appropriate determinant lists, which needed to be done only once for each symmetry, required about 1 minute of CPU time on an IBM 370/155 computer. The remainder of the CI calculation, including the construction of the first order density matrix and natural orbitals for the two lowest states, took around 45 seconds, and was repeated for each set of orbital exponents. The timings for the  $5s$ - $5p$  basis were similar.

### 3. Results

#### 3.1. Energies and hyperfine structure constants

Energies and hfs constants for the two lowest states of  ${}^4P^o$  and  ${}^4P$  symmetry of the Li atom are reported in Table I. For comparison the energies obtained by Holøien and Geltman [4] are also included, as well as experimental energies and hyperfine parameters, where available. For the  ${}^4P^o$  states, Table I also includes single determinant, restricted (RHF) and unrestricted Hartree-Fock (UHF) calculations with large basis sets (eight  $s$ , seven  $p$  and three  $d$ -functions), using the computational technique mentioned above [7].

There are several points to be noticed in Table I. The present FCI energy for the  $1s2s2p\ {}^4P^o$  state is somewhat lower than Holøien and Geltman's [4]. Also for the  $1s(2p)^2\ {}^4P^o$  and  $1s2p3p\ {}^4P^o$  states there is good agreement between the different calculations, the differences being a few thousands of an atomic unit in all cases. For the  $1s2s3p\ {}^4P^o$  state, however, we did not manage to get closer to Holøien and Geltman's result than 0.04 a.u. Even though it is to be expected that the limitation in the number of basis functions should be more serious for a state involving three shells rather than two, this big discrepancy was somewhat unexpected, especially since it did not arise in the  $1s2p3p\ {}^4P^o$  state.

In order to test the basis set for any serious omissions we augmented it by two  $s$ -, two  $p$ -, one  $d$ - and one  $f$ -function, giving a total of 40 functions. With these, a full CI would require a few thousand configurations, which would be almost unmanageable, so that only all single and double excitations from the  $1s2s2p$  configuration were included. Similar calculations were carried out for the  $5s$ ,  $5p$  basis set, for which the full CI results are available, in order to examine the effect of this limitation in the selection of configurations. In each of the single and double excitation calculations, the natural orbitals of the lowest state were used as input orbitals for a new CI calculation, and the process was repeated until the total energy decrease was less than  $10^{-5}$  a.u., or the energy increased, which meant one or two iterations, depending on which state was calculated. One natural orbital iteration for the  $8s$ ,  $5p$ ,  $2d$ ,  $1f$  basis took about 1 050 s on the CDC 6 400, of which 770 s was required for the integral transformation.

The results for the single and double excitation CI calculations with the larger basis are included in Table I. As can be seen, the energy improvement over the  $6s$ ,  $3p$ ,  $1d$  basis is only 0.0015 a.u. In the control calculation with the  $5s$ ,  $5p$  basis, the single and double excitation CI and the full CI only differed in the fourth decimal. This indicates that any sizable basis set effects should be clearly seen also in the limited CI. Since this was not the case, we see no simple explanation for the large discrepancy with ref. [4] for this state. It can, however, be noted that Junker and Bardsley [10] have performed CI calculations on the iso-electronic ions  $\text{O}^{5+}$  and  $\text{F}^{6+}$ , where the agreement with ref. [4] also is much better for the lowest  ${}^4P^o$  states than for the next lowest ones.

Unfortunately, there do not exist any direct experimental determinations of the absolute energies of the quartet states of sufficient accuracy to compare with. The most accurate direct determination of the energy of the  $1s2s2p\ {}^4P^o$  state [11] of Li carries an uncertainty of  $\pm 0.3$  eV. Even though accurate values for the wavelengths for transitions between quartet states exist [2], this uncertainty carries over to the other quartet states as well. Moreover, the assignments of the quartet spectrum must still be regarded as tentative, which introduces additional uncertainty about the experimental energies.

The study of the hyperfine structure of decaying levels in the beam-foil technique utilizing the quantum-beat method [3] can be of help in the identification of observed transitions where assignments based solely on energy values are difficult. For this reason we have calculated the hyperfine parameters for all the states considered. As far as we know, there exist only two experimental hfs determinations for three-electron quartet states, namely for the  $1s2s2p\ ^4P^o$  [12] and  $1s(2p)^2\ ^4P^o$  states [13] of Li I. From Table I we see that the hyperfine structure is strongly dominated by the Fermi contact interaction, which in turn has its largest contribution from the  $1s$  orbital. The  $1s$  contribution varies relatively little, from 35.2–35.5 a.u., between the different states. For the  $1s2snp\ ^4P^o$  states the  $2s$  orbital contributes an additional 2.3–3.0 a.u. to the Fermi contact term, depending on the state considered. The difference between theory and experiment is about 1% for the  $1s2s2p\ ^4P^o$  state and somewhat less than 3% for the  $1s2p^2\ ^4P^o$  state, while the difference between the  $^4P^o$  and  $^4P^e$  states is 5–8%. This suggests that a hfs measurement of the upper state in a beam-foil experiment could distinguish between configurations of the types  $1s2snl$  and  $1s2pnl$ , which would be a check on the assignments of the observed transitions.

### 3.2. Natural orbital analysis

The extent of configuration mixing in the  $^4P^o$  states have been discussed by several authors [2, 4–6]. Holøien and Geltman [4] suggested that there is strong mixing between the  $1s2s3p\ ^4P^o$  and  $1s3s2p\ ^4P^o$  states and suggested a  $\pm$  classification similar to that in the two-electron ions. Berry et al. [14], however, claim that they can achieve a more consistent classification of the experimental spectrum if they assume little or no configuration interaction. A transparent way of analyzing problems of this type is provided by the so-called natural orbital analysis [15], which is applied to the two lowest states of each symmetry in Table II.

In a state exhibiting neither correlation nor configuration interaction effects the occupation numbers of the natural orbitals are either 1 or 0 (except for e.g. the  $1s2pnp\ ^4P^e$  states, where one would have 1, 0.5, 0.5, 0.5, 0.5, on account of symmetry) [15]. Considering first the  $1s2s2p\ ^4P^o$  state, one can see from Table II that three natural orbitals have occupation numbers close to one, while the remaining ones have very small occupation numbers. This shows that correlation and configuration interaction effects are small in this state, which also can be seen from the close agreement between Hartree-Fock and CI hfs parameters and energies. This is, of course, to be expected, since all spins are parallel, so that the electrons are kept apart by the anti-symmetry, and there are no other close-lying states of the same symmetry with which to interact.

Turning to the next  $^4P^o$  state, we see that also this state has three natural orbitals with occupation numbers close to unity. The  $\langle r \rangle$ -values for these first three natural orbitals, 0.5015, 9.6007 and 2.5129, respectively, are very close to the values 0.5153, 9.6000 and 2.5013 obtained for the  $1s$ ,  $3p$  and  $2s$  Hartree-Fock orbitals. Holøien and Geltman [4] suggest the designation  $1s23sp+$  for this state, implying strong configuration interaction between the  $1s2s3p$  and  $1s3p2s$  configurations, which are degenerate in the absence of inter-electronic repulsion. The natural orbital analysis, however, does not show any such strong CI effects and indicates an unambiguous  $1s2s3p$  classification, thus giving a theoretical confirmation of the experimental conclusion drawn in ref. [14].

In addition to the first three, strongly occupied, natural orbitals there exist six more natural orbitals of non-negligible occupation

Table II. Natural orbitals with occupation number  $>10^{-4}$  for the two lowest  $^4P^o$  and  $^4P$  states of Li

$M_L = 1$  component

Occupation number	Symmetry <sup>a</sup>	$\langle r \rangle$	Occupation number	Symmetry	$\langle r \rangle$
$1s2s2p\ ^4P^o$			$1s2s3p\ ^4P^o$		
0.99694	$s$	0.50065	0.999948	$s$	0.50148
0.989085	$s$	2.79204	0.975863	$p_{+1}$	9.60071
0.989027	$p_{+1}$	2.82869	0.975836	$s$	2.51293
0.005953	$p_{-1}$	2.56765	0.009872	$p_{+1}$	2.90247
0.005944	$d_{+2}$	3.21987	0.009857	$s+d_0$	9.03142
0.002998	$p_0$	2.56162	0.009174	$p_{-1}$	2.58940
0.002972	$d_{+1}$	3.21987	0.009162	$d_{+2}$	9.21053
0.002004	$p_{+1}$	3.36732	0.004593	$p_0$	2.58942
0.002003	$s$	3.37634	0.004581	$d_{+1}$	9.21053
0.000123	$p_{+1}$	2.04843	0.000546	$p_{+1}$	4.23917
			0.000096	$s$	4.12150
$1s(2p)^2\ ^4P^e$			$1s2p3p\ ^4P^e$		
0.999413	$s$	0.50811	0.999778	$s$	0.50633
0.987554	$p_0$	2.88246	0.630871	$p_0$	5.46016
0.987548	$p_{+1}$	2.88247	0.630868	$p_{+1}$	5.46025
0.005515	$p_0$	3.56934	0.367869	$p_0$	7.09731
0.005505	$p_{+1}$	3.57428	0.367867	$p_{+1}$	7.09723
0.004093	$d_{+1}$	3.21987	0.000843	$p_0$	4.18488
0.004080	$d_0$	3.21964	0.000838	$p_{+1}$	4.18486
0.002751	$d_{+2}$	3.21987	0.000263	$d_{+1}$	9.21053
0.002717	$d_{-1}$	3.21987	0.000260	$d_0$	9.18414
0.000436	$s$	1.40187	0.000183	$d_{+2}$	9.21053
0.000158	$p_0$	1.78264	0.000172	$d_{-1}$	9.21053
0.000147	$p_{+1}$	1.77767	0.000159	$s$	1.48222

<sup>a</sup> To be exact, only  $m_l$  and parity are defined for the natural orbitals of a  $P$  state. The natural orbitals with  $m_l=0$  can thus have both  $s$ - and  $d_0$ -components. In most cases encountered here, however, there is very little mixing, so that these orbitals can be characterized as  $s$ - or  $d_0$  to a good approximation. The only exception is the fifth natural orbital of the  $1s2s3p\ ^4P^o$  state, which has 84%  $s$  and 16%  $d$  character.

numbers. The first of these is a  $p_{+1}$  orbital with  $\langle r \rangle = 2.9025$ , which is close to the value 2.8187 for the  $2p$  orbital in the  $1s2s2p\ ^4P^o$  state. The next one is a distorted  $3s$ -orbital (see footnote to Table II). The appearance of these two natural orbitals does indicate a mixing with a  $1s3s2p\ ^4P^o$  configuration, as suggested in ref. [4], but with a small coefficient. The  $d_0$ -admixture in the  $3s$  orbital reflects the polarization caused by the  $p$ -orbital (cf, e.g., refs. [7] and [9]). The next four natural orbitals are just different  $m_l$ -components of these  $2p$  and  $3d$  orbitals.

Also the  $1s(2p)^2\ ^4P^e$  state is well described by a single configuration, as can be seen both from the occupation numbers, which are very close to unity, and the  $\langle r \rangle$ -values, which are close to the expected values for a single determinant (Slater's rules give  $\langle r \rangle = 2.8$  for the  $2p$ -orbitals). The only state of those examined in Table II which exhibits strong configuration mixing is the  $1s2p3p\ ^4P^e$  state. This is seen both from the occupation numbers and from the  $\langle r \rangle$ -values. Clearly, the second and third natural orbitals are more expanded than what one would expect for a single configuration, indicating a rather strong configuration mixing with the  $1s(3p)^2\ ^4P^e$  state, and possibly also other states.

### 3.3. Higher states

A comparison of Hartree-Fock and CI hfs parameters in Table I shows that they agree very closely, where both are calculated. While a good CI calculation becomes increasingly difficult to do with increasing degree of excitation, this is not true to the same extent for a Hartree-Fock calculation. For this reason we carried out Hartree-Fock calculations for a number of states, which in view of the previous discussion can be expected to be

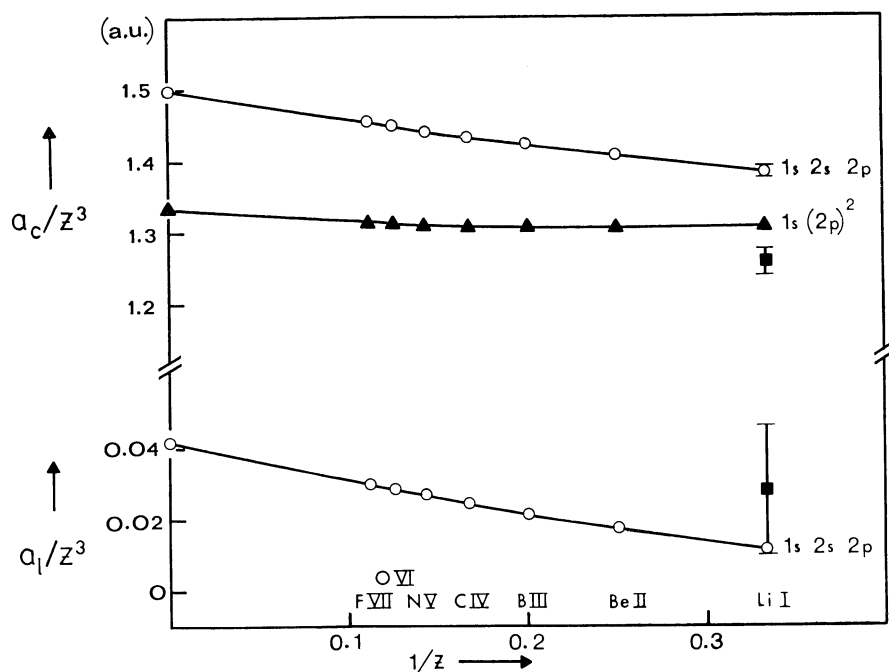


Fig. 1. Hfs parameters for the lowest  $4P^o$  and  $4P^e$  states of the Li isoelectronic series as functions of the nuclear charge. The  $1s2s2p$   $4P^o$  state is denoted by circles and the  $1s(2p)^2$   $4P^e$  state by triangles. The orbital hfs term is shown only for one of the states since the two states are indistinguishable on this scale. Experimental values for Li are shown with the reported error limits (cf. Table I).

well described by single-determinant wavefunctions. These are reported in Table III.

A few features of Table III deserves comments. Firstly, the energy difference between the  $1s2s3p$  and  $1s3s2p$  states is large, so that one should not expect any significant configuration mixing between these states, in agreement with the results of Table II (the matrix element between these states is also very small,  $-0.001$  a.u.). Secondly, all of the calculated  $1s2snp$  levels fall below the  $1s3s2p$  level. Moreover, by extrapolation one predicts a theoretical ionization limit for the  $1s2snp$  series which falls below the  $1s3s2p$  level. These results are, of course, only true at the Hartree-Fock level of approximation, but nevertheless leaves the question open whether the  $1s3s2p$   $4P^o$  state is observable at all in beam-foil spectra or auto-ionizes too fast through interaction with the  $1s2s\epsilon p$   $4P^o$  continuum.

It is interesting to note that, since the  $1s3s2p$   $4P^o$  and  $1s2s3p$   $4P^o$  states become degenerate for large  $Z$ , there will arise complicated configuration interaction effects as the  $1s3s2p$  level moves down

Table III. Calculated (Hartree-Fock) energies and hfs constants for some quartet states of Li

State	Energy (a.u.)		$a_c$ (a.u.)	$a_l$ (a.u.)	$a_d$ (a.u.)
	This work	Ref. [4]			
$1s2s3s$ $4S$	$-5.20445^a$	$-5.21240^a$	38.45	—	—
$4s$ $4S$	$-5.15490$	$-5.15624$	38.31	—	—
$5s$ $4S$	$-5.13614$	$-5.13653$	38.27	—	—
$6s$ $4S$	$-5.12698$	$-5.12649$	38.27	—	—
$7s$ $4S$	$-5.12096$	$-5.11767$	38.27	—	—
$1s2s4p$ $4P^o$	$-5.14678^b$	$-5.17127^c$	38.26	0.0142	$-0.0028$
$5p$ $4P^o$	$-5.13226$	$-5.12847^c$	38.27	0.0068	$-0.0014$
$6p$ $4P^o$	$-5.12479$	$-5.11862^c$	38.28	0.0038	$-0.0008$
$1s3s2p$ $4P^o$	$-5.11365$	—	35.78	0.4555	$-0.0911$
$1s2s3d$ $4D$	$-5.16640$	—	38.26	0.0068	$-0.00098$
$4d$ $4D$	$-5.14129$	—	38.27	0.0030	$-0.00043$
$5d$ $4D$	$-5.12959$	—	38.28	0.0017	$-0.00024$
$1s2p3d$ $4D^o$	$-5.08262$	—	35.53	0.1583	0.0916

<sup>a</sup> S. Larsson, Phys. Rev. A **6**, 1786 (1972).

<sup>b</sup> A single + double excitation CI with basis h) gave the energy  $-5.14858$  a.u.

<sup>c</sup> Denoted in [4] as  $1s23sp-$ ,  $1s24sp+$  and  $1s24sp-$ , respectively.

among the  $1s2snp$  levels when  $Z$  increases. This must happen in the region  $Z=4-7$ , since already at  $Z=8$  is  $1s3s2p$  reported to be the dominant configuration in the third state of  $4P^o$  symmetry [10].

### 3.4. The isoelectronic sequence

In Table IV we report full CI results for energies and hfs parameters for some quartet states of the isoelectronic ions  $Be^+$  through  $F^{6+}$ . Again, the quality of the wavefunctions is comparable to that of Holøien and Geltman, as seen from the energies, which are slightly below or slightly above those of ref. [4]. For most of the ions only the lowest state of each symmetry was calculated, since the Fermi contact term, which is the dominant hfs parameter, is virtually the same for the higher states (cf. Tables I and III).

The dependence of the Fermi contact and orbital hfs terms on the nuclear charge  $Z$  is shown graphically in Fig. 1. In the

Table IV. Calculated energies and hfs parameters for the lowest  $4P$  and  $4P^o$  states of the ions  $Be^+-F^{6+}$  (atomic units)

The results of ref. [4] are given within parentheses

Z	$4P$			$4P^o$				
	Energy ...	$a_c$	$a_l$	$a_d$	$a_c$	$a_l$	$a_d$	
4	$-9.86836$ ( $-9.86880$ )	83.64	1.117	0.23	$-10.06492$ ( $-10.06280$ )	90.10	1.122	$-0.23$
	$-9.42397$ ( $-9.42320$ )	83.99	0.81	0.16				
5	$-15.99758$ ( $-15.99675$ )	163.4	2.69	0.54	$-16.25632$ ( $-16.26300$ )	177.8	2.710	$-0.55$
	$-15.11908$ ( $-15.11900$ )	164.4	1.89	0.38				
6	$-23.62843$ ( $-23.62716$ )	282.8	5.29	1.07	$-23.96663$ ( $-23.96430$ )	309.6	5.32	$-1.07$
7	$-32.75994$ ( $-32.75871$ )	449.6	9.14	1.84	$-33.16829$ ( $-33.16639$ )	494.5	9.19	$-1.85$
8	$-43.39177$ ( $-43.39104$ )	672.0	14.51	2.92	$-43.87007$ ( $-43.86880$ )	741.5	14.59	$-2.93$
9	$-55.52383$ ( $-55.52388$ )	957.9	21.65	4.36	$-56.07182$ ( $-56.07144$ )	1060.	21.74	$-4.37$

hydrogenic limit ( $Z \rightarrow \infty$ ) we get the contributions  $4Z^3/3$  and  $Z^3/6$  a.u., respectively, to  $a_c$  from the  $1s$  and  $2s$  orbitals, and  $Z^3/24$  to  $a_l$  from the  $2p$  orbital. For finite  $Z$  one can observe an approximately linear relation between the hfs constants (in units  $Z^3$  a.u.) and  $Z^{-1}$ . This can be understood from simple screening arguments. If we, for example, consider the orbital hfs term in the  $1s2s2p\ ^4P^o$  state, and approximate the  $2p$  orbital by a screened hydrogenic  $2p$  orbital with effective nuclear charge  $Z-s$ , we get

$$a_l/Z^3 = (Z-s)^3/24Z^3 = \frac{1}{24}(1-3sZ^{-1}) + O(Z^{-2})$$

i.e. to first order a straight line with slope  $-0.125 \cdot s$ . This simple picture is of course rather crude, especially for low  $Z$ , but does explain the gross features of Fig. 1.

The experimental values given in [12] and [13] are also included in Fig. 1. The agreement is excellent for the  $1s2s2p$  state but somewhat less so for the  $1s(2p)^2$  state. It is difficult to say presently whether the error lies mostly in the experimental or the theoretical values, although the close agreement between the Hartree-Fock and CI results puts some confidence into the latter. The two experiments are, however, not directly comparable, since Feldman et al. [12] measure only the total hyperfine interaction and deduce a value for the Fermi contact term by inserting a theoretically calculated value of  $a_l$ . Gaupp et al. [13] make no a priori assumptions about the relative contributions of  $a_c$ ,  $a_l$  and  $a_d$  and derive all three directly from experiment. The fact that their Fermi contact term is smaller than the theoretical one, while the orbital term is larger, suggests that the subdivision of the total hyperfine interaction into its different components is responsible for most of the uncertainty in the final values.

Lastly, a comment on the assignment of the observed quartet transitions in Li I. According to the assignments of e.g. ref. [2], the  $1s2s3s\ ^4S^o$  and  $1s2s3p\ ^4P^o$  states are 4.22 and 3.85 eV, respectively, above the  $1s2s2p\ ^4P^o$  state. The present Hartree-Fock calculations give 4.19 and 4.81 eV, respectively. Even with reservation for the inherent limitations of the Hartree-Fock approximation, we find it surprising that the second energy difference is almost 1 eV in error, when the first one is off by only 0.03 eV. The latter assignment relies heavily on Holøien and Geltman's theoretical result for the  $1s2s3p\ ^4P^o$  state, which in the light of the present calculations must be questioned. We therefore think that additional evidence, such as closed loops or hfs measurements, should be searched for, before the term diagram of Li can be considered as definitive.

#### 4. Conclusion

We have calculated energies and hfs parameters for the Li iso-electronic series, using both Hartree-Fock and configuration interaction methods. The agreement with available hfs measurements on the  $1s2s2p\ ^4P^o$  and  $1s(2p)^2\ ^4P^o$  states of Li is very good. The amount of configuration interaction in the  $1s2s3p\ ^4P^o$  state of Li was studied, using a natural orbital analysis, and was found to be small, in support of recent experimental suggestions. It is suggested that further work is needed before the quartet term structure of Li can be considered as completely resolved.

#### Note added in proof

The energy of the  $1s2s3p\ ^4P^o$  state attributed to Weiss in ref. [6] is incorrectly quoted. The correct value is given in Table I and can be seen to be in excellent agreement with your own. We are grateful to Dr. R. Crossley for pointing this out.

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