

## Large multiconfigurational Hartree-Fock calculations on the hyperfine structure of $\text{Li}(^2S)$ and $\text{Li}(^2P)$

Dage Sundholm

*Department of Chemistry, University of Helsinki, Et. Hesperiank. 4, SF-00100 Helsinki, Finland*

Jeppe Olsen

*Theoretical Chemistry, Chemical Centre, University of Lund, P.O. Box 124, S-22100 Lund, Sweden*

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Extensive multiconfigurational Hartree-Fock (MCHF) calculations on the  $^2S$  ground state and the  $^2P$  excited state of lithium are reported. MCHF problems involving full configuration-interaction calculations within up to 85 orbitals are solved numerically using the finite-element method. Systematic studies of the convergence of the hyperfine parameters with respect to the size of the active space are given. The Fermi contact term of  $\text{Li}(^2S)$  has an accuracy of 0.07%. The Fermi contact, the orbital, the spin-dipolar, and the electric quadrupole terms of  $\text{Li}(^2P)$  have an estimated inaccuracy of 0.7%, 0.13%, 0.15%, and 0.35%, respectively.

### I. INTRODUCTION

During the past few years an atomic multiconfigurational Hartree-Fock (MCHF) program based on the finite-element method and the direct configuration-interaction (CI) technique has been developed.<sup>1,2</sup> The direct CI technique<sup>3</sup> and the energy function formalism<sup>4</sup> make it possible to solve large-scale MCHF problems.

The hyperfine parameters are known to be very sensitive to the quality of the wave function. The hyperfine parameters of  $\text{Li}(^2S)$  and  $\text{Li}(^2P)$  have earlier been studied theoretically using both the Hylleraas expansion approach,<sup>5-9</sup> many-body perturbation methods (MBPT),<sup>10-12</sup> and configuration-interaction approaches.<sup>13-15</sup> The experimental value for the Fermi contact term of  $\text{Li}(^2S)$ , which is the only magnetic hyperfine parameter for the ground state of Li, is

$A_{1/2} = 401.752\,043\,3(5)$  MHz.<sup>16,17</sup> The magnetic hyperfine coupling constants of  $\text{Li}(^2P)$  are  $A_{1/2} = 45.914(25)$  MHz and  $A_{3/2} = -3.055(14)$  MHz,<sup>18-20</sup> respectively. The off-diagonal coupling constant [ $A_{3/2,1/2} = 11.85(35)$  MHz] (Ref. 20) and the diagonal ones ( $A_{1/2}$  and  $A_{3/2}$ ) yield experimental estimates of the Fermi contact, orbital, and spin-dipolar terms of  $\text{Li}(^2P)$ .

The MCHF wave function is relatively compact and the results are analyzable in terms of contributions from different shells of a given symmetry and in terms of contributions from different symmetries of shells. By using systematic sequences of active shells in the MCHF calculations, it is possible to extrapolate the results, and to obtain the  $s$ ,  $sp$ , and  $spd$  limits of the hyperfine parameters. The contributions from shells of higher symmetries decrease relatively fast and the extrapolation to the nonrela-

TABLE I. The  $s$ ,  $sp$ ,  $spd$ ,  $spdf$ , and  $spdfg$  limits of the Fermi contact term of  $\text{Li}(^2S)$  (in a.u.).

$n^a$	$s$	$sp$	$spd$	$spdf$	$spdfg$
2	2.0932	2.0938	2.0919		
3	2.8388	2.9444	2.9426	2.9418	
4	2.7341	2.8240	2.8249	2.8242	2.8224
5	2.8055	2.9039	2.9142	2.9139	2.9135
6	2.7847	2.8796	2.8890	2.8898	
7	2.7983	2.8960	2.9054		
8	2.7970	2.8932	2.9024		
9	2.7963	2.8936	2.9031		
10	2.7970	2.8935			
11	2.7965				
12	2.7968				
$\infty^b$	2.7967	2.8936	2.9031	2.9039	

<sup>a</sup>The number of active shells are  $ns$ ,  $nsnp$ ,  $nsnp(n-1)d$ ,  $nsnp(n-1)d(n-2)f$ , and  $nsnp(n-1)d(n-2)f(n-3)g$  for the  $s$ ,  $sp$ ,  $spd$ ,  $spdf$ , and  $spdfg$  limit calculations, respectively.

<sup>b</sup>Estimated limits.

TABLE II. The Fermi contact term of  $\text{Li}(^2S)$  (in a.u.).

	Value	Reference
<i>s</i> limit	2.7967	This work
<i>sp</i> limit	2.8936	This work
<i>spd</i> limit	2.9031	This work
<i>spdf</i> limit	2.9039	This work
NR limit	2.9039(20)	This work
Rel. and finite mass corrected	2.9049(20)	This work <sup>a</sup>
NR limit, Hy	2.906	5
NR limit, Hy	2.9041	8
NR limit, Hy	2.9062	9
Finite mass corrected	2.9057	9
Rel. and finite mass corrected	2.9074	9 <sup>a</sup>
NR limit, CI	2.909 57	15
MBPT	2.9189	11
Experiment	2.9096	16,17 <sup>b</sup>
Experiment	2.906 06	16,17 <sup>c</sup>

<sup>a</sup>The relativistic correction is 0.0017 a.u. (Ref. 11). The relative correction factor for the finite nuclear mass correction is 0.999 765 yielding a correction of  $-0.000 68$  a.u.

<sup>b</sup>Recalculated experimental value in Ref. 11.

<sup>c</sup>Recalculated in Ref. 9 using the new conversion factors of Ref. 25.

tivistic limit is obvious.

In the Hylleraas (Hy) expansion approach the situation is different, the wave function cannot be interpreted in terms of symmetries, and therefore it is not possible to take advantage of the symmetry of the operator in question. To obtain reliable values for the hyperfine parameters from a Hy calculation, the accuracy of the energy must be pushed close to the nonrelativistic limit. By comparing, for example, the two Hy calculations by Ahlenius and Larsson on  $\text{Li}(^2P)$  (Refs. 6 and 7) the obtained energies are  $-7.409 99$  and  $-7.410 078$  a.u. and the corresponding electric quadrupole terms are  $-0.0202$  and  $-0.022 36$  a.u. A less drastic example is the Hy calculation on  $\text{Li}(^2S)$  by King<sup>9</sup> where the change in energy is less than  $1 \mu\text{H}$  when adding further 102 terms to a 500-term Hy expansion, resulting in a  $0.000 333$  a.u. change of the Fermi contact term. However, the change

of the Fermi contact term is in the wrong direction, away from the experimental value.

Though the MCHF energy is not as accurate as the energy obtained from a Hylleraas calculation, the one-body density matrices and the one-particle properties in the MCHF approach converge even more rapidly than the energy with increasing  $l$  quantum number.<sup>21</sup> In the Hylleraas approach, the error of the wave function and the error of the one-particle properties are proportional to the square root of the error in the energy.

The purpose of this work is to calculate the hyperfine structure parameters of the  $\text{Li}(^2S)$  and  $\text{Li}(^2P)$  states by using a large-scale MCHF method, and to study the convergence of the hyperfine parameters towards the nonrelativistic limit by using systematic sequences of active spaces. By using systematic sequences of energy optimized shells in the active spaces, discrepancies between the theoretical and experimental values are better understood.

## II. METHODS

In this numerical multiconfigurational Hartree-Fock method, the radial part of the occupied orbitals, Coulomb potential, and exchange potentials are confined to the interval  $[0, R_{\max}]$  and the domain is divided into a number of subdomains (elements), each containing  $n_p$  element functions. We currently use Lagrange interpolation polynomials of fourth order ( $n_p=5$ ) as element functions. The Lagrange interpolation polynomials have the property of being 1 at one grid point and zero at all the others. With this choice of element functions the expansion coefficients of the orbitals and potentials become the amplitude of the functions in each grid point.

In this numerical basis we construct an energy function

$$E = \sum_{ij} h_{ij} \Gamma_{ij} + \frac{1}{2} \sum_{ijkl} g_{ijkl} \Gamma_{ijkl}, \quad (1)$$

where  $h_{ij}$  and  $g_{ijkl}$  are the one- and two-electron integrals, respectively, and  $\Gamma_{ij}$  and  $\Gamma_{ijkl}$  are the one- and two-particle density matrices. The energy is optimized with respect to the expansion parameters of the orbitals, i.e., the amplitude of the orbitals in each grid point, and

TABLE III. The *s*, *sp*, *spd*, *spdf*, and *spdfg* limits of the total energy of  $\text{Li}(^2S)$  (in a.u.).

$n^a$	<i>s</i>	<i>sp</i>	<i>spd</i>	<i>spdf</i>	<i>spdfg</i>
2	-7.432 727	-7.456 860	-7.459 127		
3	-7.447 568	-7.472 196	-7.474 867	-7.475 370	
4	-7.448 476	-7.473 454	-7.476 238	-7.476 880	-7.477 041
5	-7.448 611	-7.473 714	-7.476 577	-7.477 267	-7.477 485
6	-7.448 644	-7.473 789	-7.476 689	-7.477 399	
7	-7.448 657	-7.473 816	-7.476 733		
8	-7.448 663	-7.473 827	-7.476 752		
9	-7.448 664	-7.473 832	-7.476 760		
10	-7.448 666	-7.473 834			
11	-7.448 667				
12	-7.448 667				

<sup>a</sup>See footnote a of Table I.

TABLE IV. The  $s$ ,  $sp$ ,  $spd$ ,  $spdf$ , and  $spdfg$  limits of the Fermi contact term of  $\text{Li}(^2P)$  (in a.u.).

$n^a$	$s$	$sp$	$spd$	$spdf$	$spdfg$
1	0.0000				
2	-0.2143	-0.2060	-0.2066		
3	-0.1517	-0.1466	-0.1412	-0.1411	
4	-0.2302	-0.2573	-0.2459	-0.2456	-0.2456
5	-0.1916	-0.2227	-0.2127	-0.2120	-0.2120
6	-0.2334	-0.2330	-0.2231	-0.2214	
7	-0.2267	-0.2260	-0.2157		
8	-0.2278	-0.2294	-0.2192		
9	-0.2273	-0.2272	-0.2171		
10	-0.2275	-0.2277	-0.2176		
11	-0.2274	-0.2276			
$\infty^b$	-0.2274	-0.2276	-0.2175	-0.2158	

<sup>a</sup>The number of active shells are  $ns1p$ ,  $nsnp$ ,  $nsnp(n-1)d$ ,  $nsnp(n-1)d(n-2)f$ , and  $nsnp(n-1)d(n-2)f(n-3)g$  in the  $s$ ,  $sp$ ,  $spd$ ,  $spdf$ , and  $spdfg$  limit calculations, respectively.

<sup>b</sup>Estimated limits.

with respect to the expansion parameters of the configuration state functions, i.e., the CI coefficients, with imposed orthonormality constraints on the occupied orbitals and the CI vector. In the orbital optimization, the optimization parameters constitute actually the non-redundant set of angles of rotations from the virtual space into the occupied orbitals. The occupied-virtual part of the Fock matrix is constructed in the Lagrange interpolation basis, and transformed to a basis where the occupied set of orbitals are orthonormal against each other and against the virtual space. In this new basis the occupied-virtual Fock matrix becomes the exact gradient for rotations between the occupied space and the virtual one. The rotations of the virtuals into the occupied space are performed by using a generalized exponential mapping technique. The numerical procedure is discussed in detail in Ref. 1.

TABLE V. The Fermi contact term for  $\text{Li}(^2P)$  (in a.u.).

	Value	Reference
$s$ limit	-0.2274	This work
$sp$ limit	-0.2276	This work
$spd$ limit	-0.2175	This work
$spdf$ limit	-0.2158	This work
NR limit	-0.2158(15)	This work
Rel. and finite mass corrected	-0.2159(15)	This work <sup>a</sup>
Semitheoretical	-0.2148(8)	This work <sup>b</sup>
NR limit, Hy	-0.2162	7
MBPT	-0.2210	11
Experiment	-0.2135(10)	20 <sup>c</sup>

<sup>a</sup>The relativistic correction is  $-0.00011$  a.u. (Ref. 11). The finite nuclear mass correction is  $0.00005$  a.u. obtained using the relative factor of Table II.

<sup>b</sup>See text.

<sup>c</sup>Recalculated using conversion factors of Ref. 9. The experimental value is  $-9.838(48)$  MHz (Ref. 20).

In the multiconfigurational self-consistent field (MCSCF) procedure, both the orbital and CI coefficients are optimized to self-consistency. The CI problem is solved using a Slater-determinant-based direct CI algorithm<sup>22</sup> in  $D_{\infty h}$  symmetry. The  $\sigma$  vector is constructed in a Slater determinant basis from the CI expansion in the same basis. In the Davidson diagonalization algorithm, the vectors are transformed into the configuration state basis. The coupling between the orbital and the CI parameters is partly taken into account by using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) quasi-Newton optimization technique.<sup>4,23</sup> When the CI problem is solved the density matrices of equation (1) are constructed from the CI vector. The one- and two-electron integrals are recalculated for each set of occupied orbitals, i.e., the optimization algorithm does not involve any integral transformations. The MCSCF method is based on the complete-active-space (CAS) self-consistent-field (SCF) approach<sup>24</sup> and its extension, the restricted-active-space (RAS) method.<sup>22</sup>

In the CAS method, the orbital space is divided into three subspaces: the inactive, the active, and the virtual ones. The inactive orbitals are doubly occupied in all configurations, the virtual orbitals are all unoccupied and are involved only in the optimization of the occupied ones, and the active space is a full CI space. The spin-polarization calculations are carried out using the RAS method.<sup>22</sup>

The hyperfine parameters

$$a_c = \sum_{ij} \delta_{l(i),0} \delta_{l(i),l(j)} \langle \phi_i | 2\delta(r) | \phi_j \rangle \Gamma_{ij}^{\text{spin}}, \quad (2a)$$

$$a_l = \sum_{ij} \delta_{l(i),l(j)} \delta_{m(i),m(j)} m(j) \langle \phi_i | r_j^{-3} | \phi_j \rangle \Gamma_{ij}, \quad (2b)$$

$$a_d = \sum_{ij} (16\pi/5)^{1/2} \langle Y_{l(i)}^{m(i)} | Y_2^0 | Y_{l(j)}^{m(j)} \rangle \langle \phi_i | r_j^{-3} | \phi_j \rangle \Gamma_{ij}^{\text{spin}}, \quad (2c)$$

TABLE VI. The  $s$ ,  $sp$ ,  $spd$ ,  $spdf$ , and  $spdfg$  limits of the spin-dipolar term of  $\text{Li}(^2P)$  (in a.u.).

$n^a$	$s$	$sp$	$spd$	$spdf$	$spdfg$
1	-0.011 72				
2	-0.011 76	-0.011 87	-0.013 44		
3	-0.011 76	-0.011 95	-0.012 08	-0.012 10	
4	-0.011 77	-0.012 07	-0.013 73	-0.013 75	-0.013 76
5	-0.011 77	-0.012 09	-0.013 27	-0.013 29	-0.013 29
6	-0.011 78	-0.012 09	-0.013 52	-0.013 55	
7	-0.011 78	-0.012 09	-0.013 36		
8	-0.011 78	-0.012 09	-0.013 46		
9	-0.011 78	-0.012 10	-0.013 41		
10	-0.011 78	-0.012 10	-0.013 44		
11	-0.011 78	-0.012 10			
$\infty^b$	-0.011 78	-0.012 10	-0.013 43	-0.013 46	

<sup>a</sup>See footnote a of Table IV.<sup>b</sup>Estimated limits.

$$b_q = \sum_{ij} (16\pi/5)^{1/2} \langle Y_{l(i)}^{m(i)} | Y_2^0 | Y_{l(j)}^{m(j)} \rangle \langle \phi_i | r_j^{-3} | \phi_j \rangle \Gamma_{ij}, \quad (2d)$$

are evaluated using  $LS$ -coupled wave functions with  $M_L=L$  and  $M_S=S$ . In Eq. (2),  $\Gamma_{ij}$  and  $\Gamma_{ij}^{\text{spin}}$  are the elements of the one-body density and spin-density matrices, respectively.  $\delta_{l(i),l(j)}$  is the Kronecker delta, and  $\delta(r)$  is the Dirac  $\delta$  function.

### III. RESULTS AND DISCUSSION

#### A. $\text{Li}(^2S)$

In Table I, the obtained Fermi contact term of  $\text{Li}(^2S)$  as a function of the active space is reported. About ten energy optimized  $s$  shells are needed to reach the  $s$  limit of the Fermi contact term. The first two  $p$  shells take about 90% of the effect of  $p$  shells into account, but the convergence for the last percent of the  $p$  effect is very slow. When adding  $d$ ,  $f$ , and  $g$  shells, the first few shells

have negative contributions to the Fermi contact term, but when the third  $d$  shell and fourth  $f$  shell are added the differential contribution changes sign, and further, the fourth  $d$  shell causes a very large change in the Fermi contact term. The contributions from  $g$  shells probably behave similarly as when  $f$  shells are added. The fully energy optimized shells are not the most efficient set of shells to obtain accurate hyperfine parameters. As seen in Table I, there are lots of overcompensation effects that cause oscillating hyperfine parameters with an increasing size of the active set of shells. As mentioned above, the hyperfine parameters are very sensitive to the quality of the wave function. To ensure that the hyperfine parameters have converged in the calculation the energy threshold for the convergence was set to  $10^{-10}$ . The orbital CI coupling becomes very strong and slows down the convergence when the highest occupied orbitals have occupation numbers of the order  $10^{-7}$  to  $10^{-8}$ . By rotating the orbitals into canonical ones, the Hamilton matrix becomes more diagonal dominant, and a faster convergence in the Davidson diagonalization procedure is obtained. In the orbital optimization procedure, natural orbitals yield the fastest convergence.

By using the estimated limits of Table I, and neglecting all contributions from  $g$  shells and shells of higher symmetries, the nonrelativistic limit becomes 2.9039 a.u. This is a lower limit, because when adding further  $f$  shells the Fermi contact term will increase, and the  $g$ -shell differential contribution will change sign when the third or fourth shell is added. By adding the relativistic and finite nuclear mass corrections, a value of 2.9049(20) a.u. is obtained. This value is only 0.0012 a.u. less than the experimental value.<sup>16,17</sup> In Table II, the present calculated values are compared to earlier theoretical and experimental values.

To obtain an excellent agreement between theory and experiment, King<sup>9</sup> introduced the new proper conversion factors between MHz and a.u. obtained by using the new accurate values for the fundamental constants.<sup>25</sup> However, when considering the relativistic effects, which were neglected, the discrepancy between the theoretical and experimental values increases from  $-0.0004$  to  $0.0013$

TABLE VII. The spin-dipolar term of  $\text{Li}(^2P)$  (in a.u.).

	Value	Reference
$s$ limit	-0.011 78	This work
$sp$ limit	-0.012 10	This work
$spd$ limit	-0.013 43	This work
$spdf$ limit	-0.013 46	This work
NR limit	-0.013 46(2)	This work
Rel. and finite mass corrected	-0.013 46(2)	This work <sup>a</sup>
NR limit	-0.013 42	7
MBPT	-0.013 48	11
Experiment	-0.013 57(9)	20 <sup>b</sup>

<sup>a</sup>The relativistic correction is  $-0.000004$  a.u. (Ref. 11). The finite nuclear mass correction is  $0.000003$  a.u. obtained using the relative factor of Table II.

<sup>b</sup>Recalculated using conversion factors of Ref. 9. The experimental value is  $-1.876(12)$  MHz (Ref. 20).

TABLE VIII. The  $s$ ,  $sp$ ,  $spd$ ,  $spdf$ , and  $spdfg$  limits of the orbital term of  $\text{Li}(^2P)$  (in a.u.).

$n^a$	$s$	$sp$	$spd$	$spdf$	$spdfg$
1	0.058 58				
2	0.058 78	0.059 47	0.060 04		
3	0.058 81	0.059 86	0.061 71	0.061 78	
4	0.058 83	0.060 63	0.062 68	0.062 80	0.062 83
5	0.058 84	0.060 72	0.062 74	0.062 91	0.062 94
6	0.058 90	0.060 74	0.062 78	0.062 99	
7	0.058 90	0.060 76	0.062 79		
8	0.058 90	0.060 77	0.062 80		
9	0.058 90	0.060 78	0.062 80		
10	0.058 90	0.060 78	0.062 80		
11	0.058 90	0.060 78			
$\infty^b$	0.058 90	0.060 78	0.062 80	0.063 01	0.063 04

<sup>a</sup>See footnote a of Table IV.

<sup>b</sup>Estimated limits.

a.u. The relativistic correction<sup>11</sup> is actually about three times larger than the finite nuclear mass correction, with the opposite sign, and must not be neglected.

The calculations in this work support the recalculated experimental value of 2.906 06 a.u. (Refs. 9, 16, and 17) instead of the old one of 2.909 6 a.u. In Table III, the total energy of  $\text{Li}(^2S)$  with respect to the number of active shells per symmetry is reported.

### B. $\text{Li}(^2P)$

In Table IV, the Fermi contact term of  $\text{Li}(^2P)$  as function of the active space is given. In the Hartree-Fock approximation, the Fermi contact term vanishes, and nine energy optimized  $s$  shells are needed to obtaining the  $s$  limit. The  $p$  limit is almost equal to the  $s$  limit. The first few  $p$  shells changes the Fermi contact term significantly. However, when adding the sixth  $p$  shell to the active space, cancellations cause the net contribution from the  $p$

shells to become almost zero. In Table IV, it is seen that higher symmetries reduce, in absolute value, the Fermi contact term. Also for the  $^2P$  state the obtained  $spdf$  limit is a lower limit to the nonrelativistic value of the Fermi contact term. In Table V, the calculated limits of the Fermi contact term are compared with earlier theoretical values and experiment. The relativistic corrections to the hyperfine parameters are taken from Ref. 11.

The convergence of the spin-dipolar term with respect to the size of the active space is shown in Table VI. The spin-dipolar term converges fast with increasing  $l$  quantum number. The convergence with respect to the number of  $d$  shells is slow and oscillating. In Table VII, the obtained spin-dipolar terms are compared with literature values.

The orbital term versus active spaces is shown in Tables VIII. The  $spdfg$  limit of the orbital term is a lower limit to the nonrelativistic value. Additional contributions, obtained by adding further  $f$  and  $g$  shells will increase the orbital term, and further higher symmetries will also have positive contributions. This is rather obvious, because the correlating orbitals of higher symmetries have about the same average radial radius, but larger  $m$  quantum numbers. In Table IX, the limits of the orbital term are compared with literature.

The by far least accurate experimental magnetic hyperfine coupling constant of  $\text{Li}(^2P)$  is the off-diagonal  $A_{3/2,1/2}$  parameter which has error bars of about 3%.<sup>20</sup> A more accurate set of interaction parameters in the uncoupled representation is obtained by adapting the theoretical spin-dipolar term. The final value for the spin-dipolar term  $a_d$  (Table VI) has an uncertainty of about 0.000 02 a.u. Assuming that the spin-dipolar term is  $-0.013 46(2)$  a.u. [ $-1.8608(28)$  MHz], which is very close to the earlier literature values of  $-0.013 42$  (Ref. 7) and  $-0.013 48$  a.u. (Ref. 11) obtained from a Hylleraas calculation and a many-body perturbation calculation, respectively. The diagonal magnetic hyperfine coupling constants  $A_{1/2}$  and  $A_{3/2}$  are 45.914(25) and  $-3.055(14)$  MHz, respectively. The semitheoretically estimated values for the Fermi contact term  $a_c$  and the orbital term  $a_0$  obtained from

TABLE IX. The orbital term for  $\text{Li}(^2P)$  (in a.u.).

	Value	Reference
$s$ limit	0.058 90	This work
$sp$ limit	0.060 78	This work
$spd$ limit	0.062 80	This work
$spdf$ limit	0.063 01	This work
NR limit	0.063 04(8)	This work
Rel. and finite mass corrected	0.063 03(8)	This work <sup>a</sup>
Semitheoretical	0.063 07(16)	This work <sup>b</sup>
NR limit, HY	0.063 4	7
MBPT	0.063 08	11
Experiment	0.062 63(27)	20 <sup>c</sup>

<sup>a</sup>The relativistic correction is 0.000 004 a.u. (Ref. 11). The finite nuclear mass correction is  $-0.000 015$  a.u. obtained using the relative factor of Table II.

<sup>b</sup>See text.

<sup>c</sup>Recalculated using conversion factors of Ref. 9. The experimental value is 8.659(37) MHz (Ref. 20).

TABLE X. The  $s$ ,  $sp$ ,  $spd$ ,  $spdf$ , and  $spdfg$  limits of the electric field gradients at the nucleus of  $\text{Li}(^2P)$  (in a.u.).

$n^a$	$s$	$sp$	$spd$	$spdf$	$spdfg$
1	-0.023 43				
2	-0.023 51	-0.023 66	-0.018 89		
3	-0.023 53	-0.023 86	-0.020 79	-0.020 80	
4	-0.023 53	-0.024 15	-0.024 58	-0.024 65	-0.02466
5	-0.023 54	-0.024 19	-0.020 80	-0.020 89	-0.02090
6	-0.023 56	-0.024 20	-0.023 78	-0.023 82	
7	-0.023 56	-0.024 20	-0.021 57		
8	-0.023 56	-0.024 21	-0.022 96		
9	-0.023 56	-0.024 21	-0.022 17		
10	-0.023 56	-0.024 21	-0.022 61		
11	-0.023 56	-0.024 21			
$\infty^b$	-0.023 56	-0.024 21	-0.022 45	-0.022 52	

<sup>a</sup>See footnote a of Table IV.

<sup>b</sup>Estimated limits.

$$A_{3/2} = a_c + a_0 + a_d \quad (3a)$$

and

$$A_{1/2} = -a_c + 2a_0 - 10a_d \quad (3b)$$

become  $-9.897(39)$  MHz [ $-0.2148(8)$  a.u.] and  $8.703(22)$  MHz [ $0.063\,07(16)$  a.u.], respectively. The theoretical value for the orbital term is very close to the semitheoretical estimate, and the error bars of the theoretical and semitheoretical values for the Fermi contact overlap. Additional  $f$  shells would further lower, in absolute magnitude, the Fermi contact term and an even better agreement would be obtained. The off-diagonal parameter,  $A_{3/2,1/2}$ , is obtained from the parameters of the uncoupled representation by equation (4).

$$A_{3/2,1/2} = -a_c + a_0/2 - 5a_d/4 \quad (4)$$

The semitheoretical value of  $A_{3/2,1/2}$  becomes  $11.923(85)$  MHz, which is in good agreement with experimental value of  $11.85(35)$  MHz.<sup>20</sup>

The  $nl$  convergence of the electric-field gradient is

TABLE XI. The electric field gradient at the nucleus of  $\text{Li}(^2P)$  (in a.u.).

	Value	Reference
$s$ limit	-0.023 56	This work
$sp$ limit	-0.024 21	This work
$spd$ limit	-0.022 45	This work
$spdf$ limit	-0.022 52	This work
NR limit	-0.022 53(8)	This work
Rel. and finite mass corrected	0.022 53(8)	This work <sup>a</sup>
NR limit, Hy	-0.022 36	7
Rel. corrected	-0.022 66	11

<sup>a</sup>The relativistic correction is  $-0.000\,001$  a.u. (Ref. 11). The finite nuclear mass correction is  $0.000\,005$  a.u. obtained using the relative factor of Table II.

given in Table X. The convergence towards the  $spd$  limit is slow, and the  $f$  and  $g$  shells hardly contribute to the electric field gradient. Though the theoretically determined electric field gradient at the nucleus of  $\text{Li}(^2P)$  should have an accuracy of about 0.35% (see Table XI), it does not lead to any improvement of the nuclear quadrupole moments of the  $^7\text{Li}$  nor the  $^6\text{Li}$  nuclei, because the uncertainty of the nuclear quadrupole coupling constant is about 10%. The best available value for the nuclear quadrupole moment of  $^7\text{Li}$  is  $-0.040\,55(80)$  barn obtained from molecular calculations on  $\text{LiH}$  (Ref. 26) and  $\text{LiF}$  (Ref. 27). The energy of  $\text{Li}(^2P)$  versus active spaces is given in Table XII.

### C. Spin-polarized calculations

As seen in Tables I, IV, VI, VIII, and X, the hyperfine parameters converge slowly with an increasing number of energy optimized shells. A faster convergence can be obtained by adding polarization orbitals to the active space. The spin- and orbital-polarization orbitals for the  $^2P$  state are obtained by the following procedure: The Hartree-Fock  $1s$  shell is kept frozen, and only single excitations to the spin-polarization  $2s$  and  $1d$  shells and to the orbital-polarization  $2d$  shell, which are optimized, are allowed. The polarization orbitals affect the energy slightly, only 0.17% of the  $spd$  correlation energy is obtained in the  $2s1p2d$  calculation. In the subsequent CAS calculations the active space is augmented with energy optimized shells of  $s$ ,  $p$ , and  $d$  symmetries, while the diffuse polarization shells and the  $1s$  shell are kept frozen. A  $6s6p5d$  CAS calculation, which includes the polarization shells in the active space, yields the same Fermi contact term as an  $8s8p7d$  CAS calculation with energy optimized shells. The  $6s6p5d$  polarization calculation yields a spin-dipolar term that is only  $1 \times 10^{-5}$  a.u. smaller than the  $spd$  limit, and an electric field gradient that is  $3 \times 10^{-5}$  a.u. larger than the estimated  $spd$  limit. For comparison, the  $10s10p9d$  CAS calculation, with energy optimized shells,

TABLE XII. The  $s$ ,  $sp$ ,  $spd$ ,  $spdf$ , and  $spdfg$  limits of the total energy of  $\text{Li}(^2P)$  (in a.u.).

$n^a$	$s$	$sp$	$spd$	$spdf$	$spdfg$
1	-7.365 070				
2	-7.380 123	-7.401 376	-7.403 692		
3	-7.381 031	-7.404 239	-7.407 136	-7.407 644	
4	-7.381 167	-7.404 823	-7.408 254	-7.408 909	-7.409 071
5	-7.381 197	-7.405 050	-7.408 628	-7.409 338	-7.409 557
6	-7.381 211	-7.405 119	-7.408 739	-7.409 485	
7	-7.381 219	-7.405 143	-7.408 780		
8	-7.381 222	-7.405 152	-7.408 797		
9	-7.381 223	-7.405 156	-7.408 806		
10	-7.381 223	-7.405 158	-7.408 811		
11	-7.381 224	-7.405 159			

<sup>a</sup>See footnote a of Table IV.

yields an electric field gradient that is  $1.6 \times 10^{-4}$  a.u. from the  $spd$  limit. The convergence of the orbital term with respect to the size of the active space is not improved.

To speed up the convergence of the Fermi contact term for  $\text{Li}(^2S)$ , a similar procedure was used. The spin-polarization shell is obtained by the following procedure: A CAS calculation with  $3s$  active is performed. The  $1s$  shell is kept frozen and only single excitations are allowed to the  $4s$  shell. In the subsequent CAS calculations, the four  $s$  shells are kept frozen, and the active set is augmented with energy optimized shells. The convergence of the Fermi contact term to the  $s$  limit is faster than with the energy optimized shells. A  $7s$  CAS calculation yields a Fermi contact term that is  $3 \times 10^{-4}$  a.u. smaller than the  $s$  limit. However, when adding  $p$  and  $d$  shells to the active space to reach the  $spd$  limit the convergence becomes even slower than with energy optimized shells. When the initial  $3s$  CAS calculation in this procedure was replaced by a HF calculation, the convergence towards the  $s$  limit became very slow. Further investigations on the optimal use of polarizing shell are in progress.

#### IV. CONCLUSION

The feasibility of large-scale MCHF calculations on atoms using the finite element method has been demonstrated. The largest CI expansions of the present calculations consists of 11 514 CSF's for  $\text{Li}(^2S)$ , and 10 864 CSF's for  $\text{Li}(^2P)$  in  $D_{\infty h}$  symmetry. The hyperfine parameters of  $\text{Li}(^2S)$  and  $\text{Li}(^2P)$  converge slowly with an increasing number of active shells, but by using systematic sequences of active spaces the extrapolation to the respective limits is obvious. By adding spin-polarized shells to the active space, shorter expansions are needed for obtaining accurate hyperfine parameters of  $\text{Li}(^2P)$ . However, for  $\text{Li}(^2S)$  the procedure involving spin-polarized shells did not in general lead to improved convergence.

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