



# LUND UNIVERSITY

## Large Multiconfigurational Hartree-fock Calculations On the Hyperfine-structure Constants of the Li-7 2s 2s and 2p 2p States

Carlsson, J; Jonsson, P; Fischer, Charlotte

*Published in:*  
Physical Review A (Atomic, Molecular and Optical Physics)

*DOI:*  
[10.1103/PhysRevA.46.2420](https://doi.org/10.1103/PhysRevA.46.2420)

1992

[Link to publication](#)

*Citation for published version (APA):*  
Carlsson, J., Jonsson, P., & Fischer, C. (1992). Large Multiconfigurational Hartree-fock Calculations On the Hyperfine-structure Constants of the Li-7 2s 2s and 2p 2p States. *Physical Review A (Atomic, Molecular and Optical Physics)*, 46(5), 2420-2425. <https://doi.org/10.1103/PhysRevA.46.2420>

*Total number of authors:*  
3

### General rights

Unless other specific re-use rights are stated the following general rights apply:  
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

Read more about Creative commons licenses: <https://creativecommons.org/licenses/>

### Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

LUND UNIVERSITY

PO Box 117  
221 00 Lund  
+46 46-222 00 00

## Large multiconfigurational Hartree-Fock calculations on the hyperfine-structure constants of the ${}^7\text{Li } 2s \text{ } ^2S$ and $2p \text{ } ^2P$ states

Jörgen Carlsson and Per Jönsson

*Department of Physics, Lund Institute of Technology, P.O. Box 118, S-221 00 Lund, Sweden*

Charlotte Froese Fischer

*Department of Computer Science, Vanderbilt University, Nashville, Tennessee 37235*

(Received 18 February 1992)

Accurate hyperfine-structure parameters for the ground and first excited states of lithium are reported. Hyperfine parameters are calculated from multiconfiguration Hartree-Fock (MCHF) wave functions using a recently written hyperfine-structure program, being a part of the MCHF Atomic Structure Package. Convergence of the hyperfine-structure parameters is studied as the active set of orbitals is increased. The relativistic, finite-nuclear-size, and finite-nuclear-mass-corrected values of the magnetic hyperfine-structure constants of the  $2s \text{ } ^2S_{1/2}$  and  $2p \text{ } ^2P_{1/2,3/2}$  states of  ${}^7\text{Li}$  were determined to be  $A_{1/2} = 401.70$  MHz and  $A_{1/2} = 45.94$  MHz,  $A_{3/2} = 3.098$  MHz, respectively. The final values are compared with experiments and with the most reliable theoretical values obtained with other methods.

PACS number(s): 31.20.Tz, 31.30.Gs

### I. INTRODUCTION

The hyperfine structure of the atomic energy levels is caused by the interaction between the electrons and the electromagnetic multipole moments of the nucleus. The contribution to the Hamiltonian can be represented by an expansion in multipoles of order  $K$ ,

$$H_{\text{hfs}} = \sum_{K \geq 1} T^{(K)} \cdot M^{(K)}, \quad (1)$$

where  $T^{(K)}$  and  $M^{(K)}$  are spherical tensor operators of rank  $K$  in the electronic and nuclear space, respectively [1]. The  $K=1$  term represents the magnetic dipole interaction and the  $K=2$  term represents the electric quadrupole interaction. For the  $J = \frac{3}{2}$  state of this study, higher-order interactions can be neglected and for the  $J = \frac{1}{2}$  states they are identically zero.

For  ${}^7\text{Li}$  the electronic tensor operators are, in atomic units [1,2],

$$\begin{aligned} T^{(1)} = & \frac{\alpha^2}{2} \sum_{i=1}^3 \{ 2g_l s^{(1)}(i) r_i^{-3} \\ & - g_s \sqrt{10} [C^{(2)}(i) \times s^{(1)}(i)]^{(1)} r_i^{-3} \\ & + g_s \frac{8}{3} \pi \delta(\mathbf{r}_i) s^{(1)}(i) \} \end{aligned} \quad (2)$$

and

$$T^{(2)} = - \sum_{i=1}^3 C^{(2)}(i) r_i^{-3}, \quad (3)$$

where  $g_l = (1 - m_e/7m_p) = 0.99922$  and  $g_s = 2.0023193$  are the orbital and electron-spin  $g$  factors.  $\delta(\mathbf{r})$  is the three-dimensional  $\delta$  function.

The magnetic dipole operator (2) represents the magnetic field due to the electrons at the site of the nucleus. The first term of the operator represents the field caused

by orbital motion of the electrons and is called the orbital term. The second term represents the dipole field due to the spin motions of the electron and is called the spin-dipole term. The last term represents the contact interaction between the nucleus and the electron spin and contributes only for  $s$  electrons. The electric quadrupole operator (3) represents the electric-field gradient at the site of the nucleus.

The nuclear tensor operators  $M^{(1)}$  and  $M^{(2)}$  are related to the nuclear magnetic dipole moment  $\mu_I$  and the electric quadrupole moment  $Q$  (assuming  $M_I = I$ )

$$\langle \gamma_I II | M_0^{(1)} | \gamma_I II \rangle = \mu_I, \quad (4)$$

$$\langle \gamma_I II | M_0^{(2)} | \gamma_I II \rangle = \frac{Q}{2}. \quad (5)$$

The hyperfine interaction couples the electronic ( $J$ ) and nuclear ( $I$ ) angular momenta to a total angular momentum  $F = I + J$ . In this representation the diagonal and off-diagonal hyperfine energy corrections are given by

$$W_{M1}(J, J) = \frac{1}{2} A_J C, \quad (6)$$

$$\begin{aligned} W_{M1}(J, J-1) = & \frac{1}{2} A_{J, J-1} [(K+1)(K-2F) \\ & \times (K-2I)(K-2J+1)]^{1/2}, \end{aligned} \quad (7)$$

$$W_{E2}(J, J) = B_J \frac{(3/4C(C+1) - I(I+1)J(J+1))}{2I(2I-1)J(2J-1)}, \quad (8)$$

where  $C = F(F+1) - J(J+1) - I(I+1)$  and  $K = I + J + F$ .

The coupling constants are

$$A_J = \frac{\mu_I}{I} \frac{1}{[J(J+1)(2J+1)]^{1/2}} \langle \gamma_J J || T^{(1)} || \gamma_J J \rangle, \quad (9)$$

$$A_{J,J-1} = \frac{\mu_I}{I} \frac{1}{[J(2J-1)(2J+1)]^{1/2}} \times \langle \gamma_J J \| T^{(1)} \| \gamma_J (J-1) \rangle, \quad (10)$$

$$B_J = 2Q \left[ \frac{2J(2J-1)}{(2J+1)(2J+2)(2J+3)} \right]^{1/2} \langle \gamma_J J \| T^{(2)} \| \gamma_J J \rangle. \quad (11)$$

Together with the nuclear magnetic dipole and electric quadrupole moments, these coupling constants yield separate values of the more theoretically interesting electronic hyperfine parameters  $a_l$ ,  $a_{sd}$ ,  $a_c$ , and  $b_q$  (assuming  $M_L = L$  and  $M_S = S$ ):

$$a_l = \langle \gamma L S L S | \sum_i l_0^{(1)}(i) r_i^{-3} | \gamma L S L S \rangle, \quad (12)$$

$$a_{sd} = \langle \gamma L S L S | \sum_i 2C_0^{(2)}(i) s_0^{(1)}(i) r_i^{-3} | \gamma L S L S \rangle, \quad (13)$$

$$a_c = \langle \gamma L S L S | \sum_i 2s_0^{(1)}(i) r_i^{-2} \delta(r_i) | \gamma L S L S \rangle, \quad (14)$$

$$b_q = \langle \gamma L S L S | \sum_i 2C_0^{(2)}(i) r_i^{-3} | \gamma L S L S \rangle. \quad (15)$$

For the  $2s^2S$  state of  ${}^7\text{Li}$  the coupling constant  $A_{1/2}$  has been determined very accurately with the atomic-beam magnetic-resonance technique [3]. The experimental value  $A_{1/2} = 401.752\,043\,3(5)$  MHz gives, together with the magnetic moment  $\mu_I = 3.256\,426\,8(17) \mu_N$  [4], where  $\mu_N$  is the nuclear magneton, and a Fermi contact term of  $a_c = 2.906\,02$  a.u. However, Esquivel, Bunge, and Núñez [5] have argued that the value  $a_c = 2.909\,40$  a.u. should be used. The latter value has been calculated from the experimental value using an electron-spin  $g$  factor of 2 instead of the QED corrected value.

For the  $2p^2P$  state, the diagonal coupling constants have been measured in an optical double-resonance experiment, giving the values  $A_{1/2} = 45.914(25)$  and  $A_{3/2} = -3.055(14)$  MHz [2]. These values, together with data from earlier level crossing experiments, give an off-diagonal parameter  $A_{3/2,1/2} = 11.823(81)$  MHz [2]. The orbital, spin-dipole, and Fermi contact term can then be determined to  $a_l = 0.062\,76(27)$ ,  $a_{sd} = -0.013\,57(9)$ , and  $a_c = -0.2135(10)$  a.u., respectively. There exists no accurate measurement of the  $B_{3/2}$  constant. Also, it has not yet been possible to determine the quadrupole moment of  ${}^7\text{Li}$  directly with nuclear physics techniques. The best value  $B_{3/2} = -0.221(29)$  MHz [2] gives, together with the nuclear quadrupole moment  $Q = -0.040\,55(80)$  b obtained from molecular calculations on LiH [6] and LiF [7], a quadrupole term  $b_q = -0.0232(30)$  a.u., which is far too inaccurate to be compared with the theoretical values. This is unfortunate, since there is a rather large difference between the quadrupole terms obtained from the different theoretical calculations.

The excited-state lifetimes and hyperfine parameters in lithium are a natural test case for theoretical calculations, and thus they have been studied with many different methods. For the excited-state lifetimes two accurate experimental determinations exist, giving the values

27.29(0.04) [8] and 27.22(0.20) ns [9], respectively, for the lifetime of the  $2p^2P$  states. All *ab initio* calculations give lifetime values that are shorter, typically by 1%. This includes the most recent multiconfiguration Hartree-Fock (MCHF) [10] and many-body perturbation theory (MBPT) calculations [11,12].

Although it is possible, calculating the hyperfine parameters accurately has been shown to be difficult. In order to reach an inaccuracy of less than 1% in a MBPT calculation, three-particle effects have to be included [13]. In a Hylleraas (Hy) calculation the energy must approach the nonrelativistic limit to give reliable values for the hyperfine parameters. A rather extreme example of this is the two Hy calculations by Ahlenius and Larsson [14,15] where the electric quadrupole parameter changed from  $-0.020\,16$  to  $-0.022\,36$  a.u. when the energy was lowered from  $-7.409\,99$  to  $-7.410\,078$  a.u. The spin dependence of the hyperfine structure makes it sensitive to spin-dependent interactions between the valence electron and the core. These interactions lead to admixtures of triplet-core configurations that are obtained directly in MBPT, whereas in variational calculations they enter through their effect on the total energy, which may be very small. To describe the spin polarization correctly in a MCHF calculation, large configuration expansions have to be used where all orbitals are optimized simultaneously.

The purpose of the present work is to test the recently written hyperfine-structure program and to see what accuracy on the hyperfine parameters can be reached with the MCHF method using large configuration expansions. Also the convergence of the hyperfine parameters is studied as the active orbital space is increased.

## II. METHOD OF CALCULATION

The wave functions were generated with the MCHF code of Froese Fischer [16], where the wave function  $\psi$  for a state labeled  $\gamma_J L S J$  is expanded in terms of configuration state functions (CSF's) with the same  $LS$  term:

$$\psi(\gamma_J L S J) = \sum_j c_j \phi_j(\gamma_J L S J). \quad (16)$$

In the numerical MCHF approach the CSF's are sums of products of spin orbitals, where the radial part of the spin orbital is represented by its numerical value in a number of grid points. In the multiconfigurational self-consistent field (MC SCF) procedure, both the orbital and the expansion coefficients are optimized to self-consistency. The calculation of the parameters (12)–(15) from the MCHF wave functions was done with a newly written hyperfine-structure program [17], being a part of the MCHF atomic structure package of Froese Fischer [16].

For the generation of wave functions, sequences of active spaces were used. In this approach all possible configuration states of a particular parity are generated from an active set of orbitals. The active set was increased stepwise by adding orbitals with the same principal quantum number  $n$ , but with different angular quantum number  $l$ . In each step the principal quantum num-

ber was increased by one. This approach was applied by Sundholm and Olsen in a hyperfine-structure calculation of Li [18] and by Froese Fischer in a variational prediction of transition energies and electron affinities [19]. The size of the configuration space grows rapidly with the increasing active set. Orbitals with high  $l$  values have very small influence on the hyperfine structure, and therefore only orbitals with  $l < 5$  were included in the expansion. To further reduce the size of the space, only single and double excitations from the reference configuration  $1s^2 2s$  and  $1s^2 2p$ , respectively, were allowed for orbitals with  $n > 5$ .

Any orthogonal transformation of orbitals with the same angular momenta transforms the expansion coefficients of the total wave function, but does not change the energy. Hence the variational procedure for determining the radial function does not have a unique solution. One way to solve this problem is to perform a rotational analysis and select the particular solution for which the off-diagonal Lagrange parameters are zero [20]. Another is to delete from the configuration space those CSF's that differ from a major component of the wave function by one electron without a change in the spin angular coupling, so that an orthogonal transformation will not generate the same configuration set. This is referred to as applying the generalized Brillouin theorem, and it is known that this leads to faster convergence and more stable solutions [19]. The deleted configurations are then introduced in a final configuration-interaction (CI) calculation for the full space.

### III. RESULTS AND DISCUSSION

#### A. $2s^2S$

In the Hartree-Fock approximation the closed  $s$  shell does not contribute to the Fermi contact term. However, spin polarization of the shell induces very large contributions. The admixture of spin-polarizing states is determined through the effect on the total energy and as many as 13 energy-optimized  $s$  orbitals were needed to get a converged value of the Fermi contact term. For the higher angular momenta, consecutively fewer orbitals

TABLE I. The Fermi contact term (in a.u.) of the  $2s^2S$  term.

Active set	$a_c$
$2sp$	2.0731
$3spd$	2.8274
$4spdf$	2.8269
$5spdfg$	2.9071
$6spdfg$	2.8884
$7spdfg$	2.9051
$8spdf$	2.9039
$9spdf$	2.9046
$10spd$	2.9043
$11spd$	2.9049
$12sp$	2.9046
$13sp$	2.9048
Extrapolated	2.9047

TABLE II. The Fermi contact term (in a.u.) of the  $2s^2S$  term for equivalent MCDF and MCHF calculations. The relativistic and finite-nuclear-size correction, obtained by multiplying the extrapolated nonrelativistic Fermi contact term  $a_c = 2.9047$  with  $(\text{MCDF})/(\text{MCHF}) - 1$ , is compared with the correction estimated by Lindgren (Ref. [24]).

	MCDF	MCHF	(MCDF)/(MCHF)	Correction
$2s$	2.094 43	2.093 23	1.000 58	0.001 67
$2sp$	2.074 36	2.073 10	1.000 61	0.001 76
$3spd$	2.828 89	2.827 40	1.000 53	0.001 53
				0.001 65 <sup>a</sup>

<sup>a</sup>Correction from Ref. [24].

TABLE III. The Fermi contact term (in a.u.) of the  $2s^2S$  term.

	Value	Reference
HF	2.0932	This work
Extrapolated NR value	2.9047	This work
Corrected value <sup>a</sup>	2.9057	This work
Finite-element MCHF	2.9049	Ref. [18]
MBPT	2.9188	Ref. [24]
MBPT	2.8999	Ref. [11] <sup>b</sup>
Relativistic MBPT	2.9112	Ref. [12] <sup>b</sup>
CI	3.014	Ref. [27]
CI-spin-density convergence	2.909 53	Ref. [5]
Hylleraas	2.9074	Ref. [29] <sup>c</sup>
Experiment	2.906 02	Ref. [3] <sup>d</sup>

<sup>a</sup>Corrected for relativistic, finite-nuclear-size and finite-nuclear-mass effects.

<sup>b</sup>Calculated from published values of the magnetic dipole constant.

<sup>c</sup>The relativistic and finite-nuclear-size correction 0.001 65 a.u. from Ref. [24] has been added.

<sup>d</sup>Calculated from experiment with  $g_s = 2.002\,319\,3$  and  $\mu_I = 3.256\,426\,8\,\mu_N$ .

TABLE IV. Total energy (in a.u.) of the  $2s^2S$  term.

Active set	Energy
$2sp$	-7.454 565
$3spd$	-7.473 184
$4spdf$	-7.476 210
$5spdfg$	-7.477 160
$6spdfg$	-7.477 512
$7spdfg$	-7.477 648
$8spdf$	-7.477 698
$9spdf$	-7.477 714
$10spd$	-7.477 721
$11spd$	-7.477 725
$12sp$	-7.477 726
$13sp$	-7.477 726
Nonrelativistic limit	-7.478 060 34(20) <sup>a</sup>

<sup>a</sup>Reference [30].

TABLE V. The Fermi contact, spin-dipolar, orbital, and electric quadrupole terms (in a.u.) of the  $2p^2P$  term.

Active set	$a_c$	$a_{sd}$	$a_l$	$b_q$
2sp	-0.2143	-0.011 76	0.058 78	-0.023 51
3spd	-0.1450	-0.013 53	0.060 44	-0.019 07
4spdf	-0.2575	-0.012 26	0.062 29	-0.020 94
5spdfg	-0.2119	-0.013 75	0.062 83	-0.024 67
6spdfg	-0.2226	-0.013 30	0.062 95	-0.020 93
7spdfg	-0.2131	-0.013 56	0.062 99	-0.021 66
8spdf	-0.2179	-0.013 41	0.063 00	-0.021 79
9spdf	-0.2154	-0.013 47	0.063 01	-0.023 01
10spd	-0.2156	-0.013 45	0.063 02	-0.022 33
11spd	-0.2155	-0.013 48	0.063 03	-0.022 77
Extrapolated	-0.2155	-0.013 46	0.063 05	-0.022 55

had to be included. As shown by Sundholm and Olsen [18], the effect of adding further  $f$  and  $g$  orbitals should be to increase the value of the Fermi contact term toward the experimental value. In Table I the Fermi contact term is reported as a function of the increasing active set of orbitals. For the four largest spaces the MCHF variational procedure exhibited convergence problems, and it was not possible to vary all the orbitals simultaneously. One way to overcome this is to freeze the orbitals from the previous active set and vary the new ones. Another is to vary as many of the outer orbitals as possible and freeze only the innermost orbitals. Of the two ways, the latter was chosen, since it reduces the oscillatory behavior of the Fermi contact term and converges faster to the nonrelativistic limit as the size of the space increases.

The extrapolated nonrelativistic value of 2.9047 a.u. must be corrected for relativistic, finite-nuclear-size and finite-nuclear-mass effects, before being compared with experiment. The finite nuclear mass  $M_{\gamma_{Li}}$  leads to a scaling of the Schrödinger equation that changes the Fermi contact term with a factor  $(1 + m_e/M_{\gamma_{Li}})^{-3} = 0.999\,765$ . Relativistic corrections can be included in the MCHF atomic structure package through the Breit-Pauli approximation [21]. In this approach the total wave function for a state  $\gamma_J J$  is expanded in terms of CSF's with different  $LS$  terms:

$$\psi(\gamma_J J) = \sum_j c_j \phi_j(\gamma_J L_j S_j J), \quad (17)$$

where the radial part of the spin orbitals is taken from the preceding MCHF calculations. The expansion coefficients are then obtained by diagonalizing the Breit-Pauli interaction matrix. The most significant effect of the relativistic correction is the contraction of the valence orbital, leading to an increasing value of the Fermi contact parameter. This is in part counterbalanced by the effects of the finite nuclear size, which decreases the Fermi contact term. In an accurate calculation the latter must also be included by adding the level field shift operator to the Breit-Pauli Hamiltonian [22]. Work to include this operator in the CI program of the MCHF package and to evaluate its effect on the hyperfine structure is in progress [23]. In this study, however, relativistic and finite-nuclear-size corrections to the hyperfine parameters are taken from Lindgren [24]. To estimate the uncertainty in the corrections, contact terms obtained from MCHF and equivalent multiconfiguration Dirac-Fock (MCDF) calculations [25] are compared in Table II. In the MCDF calculations a Fermi nuclear charge density and pointlike nuclear moments have been used [26].

The relativistic finite-nuclear-size and finite-nuclear-mass-corrected value of the Fermi contact term is 2.9057 a.u., which is very close to the experimental value 2.906 02 a.u. Our values are in very good agreement with the finite element MCHF calculations of Sundholm and Olsen [18]. The difference between their value of 2.9049 a.u. and the present could be explained by the fact that our calculation included more  $f$  and  $g$  orbitals, the effect

TABLE VI. The Fermi contact, spin-dipolar, orbital, and electric quadrupole terms (in a.u.) of the  $2p^2P$  term.

Method	$a_c$	$a_{sd}$	$a_l$	$b_q$	Reference
HF	0.0000	-0.011 71	0.058 57	-0.023 43	This work
Extrapolated NR value	-0.2155	-0.013 46	0.063 05	-0.022 55	This work
Corrected values <sup>a</sup>	-0.2156	-0.013 46	0.063 04	-0.022 55	This work
Finite-element MCHF	-0.2159	-0.013 46	0.063 03	-0.022 53	Ref. [18]
Semitheoretical	-0.2148	-0.013 46	0.063 07		Ref. [18]
MBPT	-0.2210	-0.013 48	0.063 08	-0.022 66	Ref. [24]
CI	-0.2129	-0.0138	0.0625	-0.0247	Ref. [28]
Hylleraas	-0.2162	-0.013 42	0.0634	-0.020 16	Ref. [14]
Experiment	-0.2135(10)	-0.013 57(9)	0.062 76(27)	-0.0232(30)	Ref. [2]

<sup>a</sup>Corrected for relativistic, finite-nuclear-size, and finite-nuclear-mass effects.

TABLE VII. Total energy (in a.u.) of the  $2p^2P$  term.

Active set	Energy
$2sp$	-7.380 123
$3spd$	-7.404 588
$4spdf$	-7.407 851
$5spdfg$	-7.409 167
$6spdfg$	-7.409 578
$7spdfg$	-7.409 730
$8spdf$	-7.409 786
$9spdf$	-7.409 803
$10spd$	-7.409 811
$11spd$	-7.409 814
Nonrelativistic limit	-7.410 16 <sup>a</sup>

<sup>a</sup>Reference [31].

of which is to increase the value of the contact term. In Table III the present value is compared with other calculations and in Table IV the total energy is reported as a function of the active set.

### B. $2p^2P$

All three magnetic dipole as well as the electric quadrupole hyperfine parameters are present in the  $2p^2P$  term. In Table V the hyperfine parameters are reported as a function of the active set of orbitals. Of the magnetic hyperfine parameters the Fermi contact has drawn most of the attention. In the Hartree-Fock approximation the Fermi contact term vanishes, but the spin polarization of the  $s$  shell induces a large contact term. Eleven energy-optimized  $s$  orbitals were needed to describe the spin polarization. As for the  $2s$  state, fewer and fewer orbitals were needed for the higher symmetries. The contact term has a highly oscillatory behavior in the beginning, but after  $n=8$  the convergence is fast and the extrapolation to the nonrelativistic value  $-0.2155$  a.u. is obvious. The convergence of the spin-dipole term is slow and oscillatory. The nonrelativistic value was determined to  $-0.01346$  a.u. The orbital term is the only hyperfine parameter that shows monotonic convergence. The conver-

gence is slow and it is difficult to do an extrapolation.  $0.06305$  a.u. is a lower limit, since the addition of orbitals with high orbital quantum numbers will increase the orbital term. Of all the hyperfine parameters the electric-field gradient  $b_q$  is the only one that is not properly converged. The final nonrelativistic value is taken as the mean value of the two last values in the sequence. This gives a value of  $-0.02255$  a.u.

As in the  $2s$  calculation the MCHF variational procedure exhibited convergence problems for the largest spaces, and the innermost orbitals had to be frozen while as many as possible of the outer orbitals were simultaneously optimized. All calculations in this work were carried out on a DEC 3100 workstation. Due to limited internal memory, 24 Mbyte, only about 1500 CSF's could be optimized in the MC SCF procedure. When more than 1500 CSF's were present in the optimization, swapping to the external disk slowed down the program operation, making the calculations unfeasible. For the two largest configuration spaces only CSF's with weights larger than  $0.000001$  were allowed in the optimization procedure. The full configuration space was then included in a final CI calculation. The largest CI expansion for the  $2p$  states consisted of 2030 CSF's.

The final results, collected in Table VI and corrected for relativistic, finite-nuclear-size and finite-nuclear-mass effects, are compared with experimental values and values from other calculations. Our values are almost identical to the values of Sundholm and Olsen [18]. The values of the spin-dipolar and orbital terms are also in very good agreement with values obtained from a MBPT calculation [24]. The Fermi contact term, however, differs substantially from the MBPT value. This is not surprising considering the fact that the deviation from the Hartree-Fock value is very large for the Fermi contact term.

The calculated spin-dipole value is most likely more accurate than the experimental value. Combined with the two accurate experimental diagonal magnetic hyperfine coupling constants  $A_{1/2}$  and  $A_{2/3}$ , the calculated spin-dipole value yields accurate semitheoretical values of the Fermi contact term and the orbital term [18]. The sem-

TABLE VIII. Magnetic dipole constants (in MHz) for the  $2s^2S_{1/2}$  and  $2p^2P_{1/2,3/2}$  states and electric quadrupole constant (in MHz) for the  $2p^2P_{3/2}$  state.

Method	A			B <sup>a</sup>	Reference
	$2s_{1/2}$	$2p_{1/2}$	$2p_{3/2}$	$2p_{3/2}$	
HF	289.55	32.32	6.463	-0.2232	This work
MCHF	401.71	45.94	-3.098	-0.2148	This work
Finite-element MCHF	401.60	45.95	-3.113	-0.2146	Ref. [18] <sup>b</sup>
MBPT	403.53	46.24	-3.344	-0.2159	Ref. [24] <sup>b</sup>
MBPT	400.903	45.789	-2.879	-0.2160	Ref. [11]
Relativistic MBPT	402.47	45.96	-3.070	-0.2162	Ref. [12]
Hylleraas	401.94	46.01	-3.05	-0.1921	Refs. [29,14] <sup>b,c</sup>
CI-spin-density convergence	402.24				Ref. [5] <sup>b</sup>
Experiment	401.752 043	45.914(25)	-3.055(14)	-0.219(29)	Refs. [3,2]

<sup>a</sup>Electric quadrupole constants have been calculated using the semiexperimental value  $Q = -0.04055$  b of Refs. [6] and [7].

<sup>b</sup>Calculated from published values of the hyperfine-structure parameters with  $g_s = 2.0023193$  and  $\mu_I = 3.2564268 \mu_N$ .

<sup>c</sup>Magnetic dipole constant of the  $2s_{1/2}$  state has been calculated from the relativistic and finite-nuclear-size-corrected value from Table III.

theoretical values are shown in Table VI. In Table VII the total energy is reported.

In the relativistic formalism the hyperfine interaction has the simple form [2]

$$T^{(1)} = -i\alpha \sum_{j=1}^3 r_j^{-2} \alpha_j \cdot \mathbf{l}(j) C^{(1)}(j). \quad (18)$$

In order to compare our results with the relativistic calculations the hyperfine coupling constants  $A_{1/2}$  and  $A_{3/2}$  are calculated from the hyperfine parameters. In Table VIII our values are compared with experiment and other theoretical values.

#### IV. SUMMARY AND CONCLUSIONS

We report large-scale MCHF calculations where systematic sequences of active orbitals sets were used to gen-

erate the configuration space. This allows for extrapolation of the hyperfine parameters to the nonrelativistic limit. It also gives an internal check on the accuracy of the calculations. Although the energies obtained in the calculations are higher than energies obtained with Hylleraas methods, the hyperfine parameters compare favorably. Since the MCHF method is very general, large-scale calculations should be able to predict hyperfine parameters accurately for more complicated systems where relativistic effects are small.

#### ACKNOWLEDGMENTS

The present research has been supported by the Swedish Natural Science Research Council and by the U.S. Department of Energy, Office of Basic Energy Sciences.

- 
- [1] I. Lindgren and A. Rosén, *Case Stud. At. Phys.* **4**, 93 (1974).
  - [2] H. Orth, H. Aackermann, and E. W. Otten, *Z. Phys. A* **273**, 221 (1975).
  - [3] A. Beckmann, K. D. Böklen, and D. Elke, *Z. Phys.* **270**, 173 (1974).
  - [4] P. Raghavan, *At. Data Nucl. Data Tables* **42**, 189 (1989).
  - [5] R. O. Esquivel, A. V. Bunge, and M. A. Núñez, *Phys. Rev. A* **43**, 3373 (1991).
  - [6] S. Sundholm, P. Pyykkö, L. Laaksonen, and A. J. Sadlej, *Chem. Phys. Lett.* **112**, 1 (1984).
  - [7] G. H. F. Dierksen, A. J. Sadlej, D. Sundholm, and P. Pyykkö, *Chem. Phys. Lett.* **143**, 163 (1988).
  - [8] A. Gaupp, P. Kuske, and H. J. Andrä, *Phys. Rev. A* **26**, 3351 (1982).
  - [9] J. Carlsson and L. Sturesson, *Z. Phys. D* **14**, 281 (1989).
  - [10] C. Froese Fischer, *Nucl. Instrum. Methods Phys. Res. B* **31**, 265 (1988).
  - [11] A.-M. Mårtensson and A. Ynnerman, *Phys. Scr.* **41**, 329 (1990).
  - [12] S. A. Blundell, W. R. Johnson, Z. W. Liu, and J. Sapirstein, *Phys. Rev. A* **40**, 2233 (1989).
  - [13] A. Ynnerman, Licentiate thesis, Göteborg University, 1990.
  - [14] T. Ahlenius and S. Larsson, *Phys. Rev. A* **8**, 1 (1973).
  - [15] T. Ahlenius and S. Larsson, *Phys. Rev. A* **18**, 1329 (1978).
  - [16] C. Froese Fischer, *Comput. Phys. Commun.* **64**, 369 (1991).
  - [17] P. Jönsson, C.-G. Wahlström, and C. Froese Fischer, *Comput. Phys. Commun.* (to be published).
  - [18] D. Sundholm and J. Olsen, *Phys. Rev.* **42**, 2614 (1990).
  - [19] C. Froese Fischer, *Phys. Rev. A* **41**, 3481 (1989).
  - [20] C. Froese Fischer, *Comput. Phys. Rep.* **3**, 275 (1986).
  - [21] C. Froese Fischer, *Comput. Phys. Commun.* **64**, 473 (1991).
  - [22] C. Cohen-Tannoudji, B. Diu, and F. Laloë, *Quantum Mechanics* (Wiley, New York, 1977), Vol. 2.
  - [23] P. Jönsson and C. Froese Fischer (unpublished).
  - [24] I. Lindgren, *Phys. Rev. A* **31**, 1273 (1985).
  - [25] P. Jönsson, C. Froese Fischer, and F. A. Parpia (unpublished).
  - [26] F. A. Parpia and A. K. Mohanty *Phys. Rev. A* (to be published).
  - [27] A. Hibbert, *J. Phys. B* **3**, 585 (1970).
  - [28] R. Glass and A. J. Hibbert, *J. Phys. B* **9**, 875 (1976).
  - [29] F. W. King, *Phys. Rev. A* **40**, 1735 (1989).
  - [30] D. K. McKenzie and G. W. F. Drake, *Phys. Rev. A* **44**, R6973 (1991).
  - [31] A. W. Weiss, *Astrophys. J.* **138**, 1262 (1963).