PHYSICAL REVIEW A VOLUME 52, NUMBER 5 NOVEMBER 1995

Multiconfiguration Hartree-Fock calculations of low-lying excited ^2S states in lithium

Per Jönsson and Charlotte Froese Fischer
Department of Computer Science, Vanderbilt University, Box 1679 B, Nashville, Tennessee 37235

Jacek Bieroń*
Atomic Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

(Received 27 June 1995)

The hyperfine interaction constants, specific-mass-shift parameters, and total energies for the $3s\ ^2S$ and $4s\ ^2S$ states in lithium were calculated using the multiconfiguration Hartree-Fock method. The configuration expansions were obtained with the active space method, where configuration state functions are generated by excitations from the reference configuration to an active set of orbitals. The active set was increased in a systematic way, allowing the convergence of the studied parameters to be monitored. The obtained nonrelativistic energies are close to the lowest-upper-bound estimates from Hylleraas calculations. Whereas the convergence rate of the hyperfine interaction constants with respect to the increasing basis in the Hylleraas calculations degrades appreciably for higher states in the Rydberg series, no such effect could be seen for the multiconfiguration Hartree-Fock calculations. The uncertainties of the calculated hyperfine interaction constants are estimated to be less than three parts in a thousand for both of the studied states. The value for the $3s\ ^2S$ state is in excellent agreement with results from relativistic many-body perturbation theory calculations, but is well outside the error bars from a recent precision measurement using Stark spectroscopy.

PACS number(s): 31.15.−p

During the last few years a number of very accurate calculations of hyperfine structures have been performed for ground states or states lowest in their symmetry. For many of these states extremely accurate experimental values from atomic beam magnetic resonance (ABMR) measurements are available, and a detailed comparison shows that in favorable cases the theoretical and experimental values agree to within a few parts in a thousand (see, for example, Ref. [1] and references therein). By contrast, few calculations have been performed for excited states. The reason for this is mainly the lack of accurate experimental values available for a comparison. Recently, however, the hyperfine structure of the $3s\ ^2S$ state of ^{7}Li was measured with an accuracy of less than three parts in a thousand using Stark spectroscopy of Rydberg states [2]. The obtained value of the hyperfine interaction constant disagrees appreciably with theoretical values both from relativistic many-body perturbation theory (RMBPT) [3] and accurate Hylleraas calculations [4]. This is notable, considering the great success of these calculations for the lithium ground state, where the obtained values agree with the accurate AMBR value to within less than two parts in a thousand. In an effort to resolve this discrepancy and to test the applicability of the multiconfiguration Hartree-Fock (MCHF) method for Rydberg states, we performed large-scale MCHF calculations of the hyperfine interaction constants for the $3s\ ^2S$ and $4s\ ^2S$ states of ^{7}Li. To check the consistency with the Hylleraas calculations, we also evaluated the specific-mass-shift parameters.

In the nonrelativistic MCHF approach [5] the wave function ψ for a state labeled γLS, where γ represents the configuration and any other quantum numbers required to specify the state, is expanded in terms of configuration state functions (CSFs) with the same LS term:

$$\psi(\gamma LS)=\sum_{j=1}^{m} c_j\Phi(\gamma_j LS). \tag{1}$$

The CSFs are antisymmetrized linear combinations of products of spin orbitals

$$\phi_{nlm_lm_s}=\frac{1}{r}P_{nl}(r)Y_{lm_l}(\theta,\varphi)\xi_{m_s}(\sigma), \tag{2}$$

where the radial functions $P_{nl}(r)$ are represented by their numerical values at a number of grid points. The radial functions are required to be orthonormal within each l symmetry:

$$\int_0^\infty P_{n'l}(r)P_{nl}(r)dr=\delta_{n'n}. \tag{3}$$

In the multiconfiguration self-consistent field (MC-SCF) procedure both the radial functions and the expansion coefficients are determined so as to leave the energy functional

$$\langle\gamma LS|H|\gamma LS\rangle \tag{4}$$

stationary. For states that are the lowest of their symmetry this is a minimization problem, and the approximate eigenvalue approaches the exact eigenvalue from above; i.e.,

$$E_{\text{exact}}\leqslant\langle\gamma LS|H|\gamma LS\rangle, \tag{5}$$

---

*Permanent address: Instytut Fizyki, Uniwersytet Jagielloński, Reymonta 4, 30-059 Kraków, Poland.

TABLE I. The specific-mass-shift parameter, magnetic dipole interaction constant, total energy, and number of CSFs (NCSF) for the $1s^2 3s\ ^2S$ state in Li as functions of the active set of orbitals. The configuration expansions were generated by allowing all SDT excitation from the reference configuration, with the restriction that there should be at least one electron with $n \leqslant 4$ in all configurations. The $2s$ orbital was taken from a HF calculation and was kept fixed in all subsequent calculations. Also shown are the values from a CI calculation for the CAS generated by all SDT excitations to $10s9p8d7f6g5h4i3k2l1m$. The Hylleraas values of Ref. [4] are included for a comparison.

Active set	S (a.u.)	A (MHz)	E (a.u.)	NCSF
HF	0.000 000	67.149	−7.310 212	1
$3s2p1d$	0.318 090	68.159	−7.336 406	27
$4s3p2d1f$	0.294 036	92.435	−7.351 833	110
$5s4p3d2f1g$	0.293 336	90.778	−7.353 291	338
$6s5p4d3f2g1h$	0.292 820	93.176	−7.353 680	726
$7s6p5d4f3g2h1i$	0.292 570	92.454	−7.353 845	1 356
$8s7p6d5f4g3h2i1k$	0.292 405	93.133	−7.353 934	2 256
$9s8p7d6f5g4h3i2k1l$	0.292 300	92.911	−7.353 985	3 466
$10s9p8d7f6g5h4i3k2l1m$	0.292 231	93.089	−7.354 016	5 026
CAS-CI	0.292 233	93.088	−7.354 016	13 306
Hylleraas	0.292 120	92.7	−7.354 076	

where E_{exact} is the exact nonrelativistic eigenvalue. For excited states, the Hylleraas-Undheim theorem [6] states that the kth eigenvalue of the $m \times m$ Hamiltonian matrix

$$H_{ij} = \langle \gamma_i LS | H | \gamma_j LS \rangle \tag{6}$$

is an upper bound to the exact energy of the kth-lowest excited state of the given angular symmetry and parity, and the radial functions and the expansion coefficients are determined by minimizing this eigenvalue.

Once the radial functions and the expansion coefficients have been determined, the specific-mass-shift parameter (in a.u.)

$$S = \left\langle \gamma LS \left| \sum_{i<j}^{3} \nabla_i \cdot \nabla_j \right| \gamma LS \right\rangle \tag{7}$$

and the hyperfine interaction constant A (in MHz)

$$A = 95.410\,67 \left(\frac{g_s \mu_I}{3I} \right) \left\langle \gamma LS \left| \sum_{i=1}^{3} 4\pi\delta(\mathbf{r}_i)\sigma_{zi} \right| \gamma LS \right\rangle \tag{8}$$

can be evaluated by using standard Racah algebra techniques [7,8]. The nuclear parameters $I = \frac{3}{2}$ and $\mu_I = 3.256\,462\,53 \mu_N$ needed for the evaluation of the hyperfine interaction constant were taken from Raghavan [9].

The configuration expansions for the MCHF calculations were obtained with the active space method [10,11], where the CSFs of the ^2S symmetry were generated by allowing all single (S), double (D), and triple (T) excitations from the Hartree-Fock reference configuration to the active set of orbitals, with the restriction that in all the generated CSFs there should be at least one orbital with principal quantum number less than or equal to 4. To study the convergence of the calculated hyperfine interaction constants and specific-mass-shift parameters, the active sets of orbitals were increased in a systematic way, leading to consecutively larger configuration expansions. The notation of the active sets of orbitals follows the conventions used in quantum chemistry, where, for example, the set $3s2p1d$ contains three s orbitals, two p orbitals, and one d orbital. Except for the reference configuration, principal quantum numbers have no significance other than defining the order in which the orbitals are introduced.

During the calculations for the $3s\ ^2S$ state, it was observed that the MC-SCF procedure was unstable when all the orbitals in the active set were optimized simultaneously. To avoid this, the $2s$ orbital was taken as the $1s^2 2s\ ^2S$ Hartree-Fock orbital and was kept fixed, whereas all the other orbitals were optimized simultaneously. Similar stability problems were encountered for the $4s\ ^2S$ state. Here the $2s$ and $3s$ orbitals were taken, respectively, as the $1s^2 2s\ ^2S$ and $1s^2 3s\ ^2S$ Hartree-Fock (HF) orbitals and were kept fixed, whereas all the other orbitals were optimized simultaneously. For the calculations with a large enough active set, the restriction on the $2s$ and $3s$ orbitals could be relaxed. Tests showed, however, that this relaxation did not change the value of the total energy nor that of the calculated parameters. Finally, to see the importance of the neglected triple excitations, configuration-interaction (CI) calculations were performed for complete active space (CAS) expansions obtained by allowing all SDT excitations from the reference configurations to the largest active sets of orbitals from the MCHF calculations.

In Tables I and II the specific-mass-shift parameters, hyperfine interaction constants, and total energies for the $3s\ ^2S$ and $4s\ ^2S$ states are shown as functions of the increasing active sets. As can be seen from Table I, the specific-mass-shift parameter for the $3s\ ^2S$ state shows a very smooth monotonic convergence toward the very well-converged Hylleraas value. The convergence for the hyperfine interaction constant is oscillatory. The amplitude of the oscillations is, however, rapidly decreasing and the nonrelativistic limit should be close to $A(3s\ ^2S_{1/2}) = 93.089$ MHz, with an estimated uncertainty of less than two parts in a thousand.

TABLE II. The specific-mass-shift parameter, magnetic dipole interaction constant, total energy, and number of CSFs (NCSF) for the $1s^2 4s\ ^2S$ state in Li as functions of the active set of orbitals. The configuration expansions were generated by allowing all SDT excitation from the reference configuration with the restriction that there should be at least one electron with $n \leqslant 4$ in all configurations. The $2s$ and $3s$ orbitals were taken from HF calculations and were kept fixed in all subsequent calculations. Also shown are the values from CI calculation for the CAS generated by all SDT excitations to $10s9p8d7f6g5h4i3k2l1m$. The Hylleraas values of Ref. [4] are included for a comparison.

Active set	S (a.u.)	A (MHz)	E (a.u.)	NCSF
HF	0.000 000	25.388	−7.274 890	1
$4s3p2d1f$	0.315 075	26.039	−7.302 400	110
$5s4p3d2f1g$	0.292 860	35.584	−7.316 958	338
$6s5p4d3f2g1h$	0.291 155	34.252	−7.318 031	726
$7s6p5d4f3g2h1i$	0.290 692	35.148	−7.318 271	1 356
$8s7p6d5f4g3h2i1k$	0.290 497	34.856	−7.318 367	2 256
$9s8p7d6f5g4h3i2k1l$	0.290 390	35.118	−7.318 419	3 466
$10s9p8d7f6g5h4i3k2l1m$	0.290 321	35.008	−7.318 451	5 026
CAS-CI	0.290 321	35.013	−7.318 451	13 306
Hylleraas	0.290 383	35	−7.318 491	

Whereas the convergence properties of the Hylleraas calculation for the $4s\ ^2S$ state degrade considerably compared to the $3s\ ^2S$ state [4], the convergence trends for the MCHF calculation, as shown in Table II, remain almost the same. For this case the MCHF values are believed to be more accurate than the Hylleraas values. The amplitudes of the hyperfine oscillations are slightly larger than for the $3s\ ^2S$ state, and the final value $A(4s\ ^2S_{1/2}) = 35.008$ MHz has an estimated uncertainty of about three parts in a thousand. In Tables I and II also the values from the CAS-CI calculations are shown. A comparison with the corresponding MCHF values shows that the effects of the neglected triple excitations in the latter expansions are indeed small.

Before the calculated hyperfine interaction constants are compared with the experimental values, they should be corrected for finite nuclear mass and relativistic effects. The finite nuclear mass $M_{^7\mathrm{Li}}$ leads to a scaling of the Schrödinger equation that changes the hyperfine interaction constants with a factor $(1 + m_e / M_{^7\mathrm{Li}})^{-3} = 0.999\,765$. The relativistic effects were estimated by multiplying the final nonrelativistic values of the hyperfine interaction constants with the ratio between the Dirac-Fock (DF) and Hartree-Fock values. The hyperfine interaction constant for the $2s\ ^2S_{1/2}$ ground state has previously [12] been obtained from MCHF calculations similar to the ones presented here, and in Table III the MCHF values for the $2s\ ^2S_{1/2}$, $3s\ ^2S_{1/2}$, and $4s\ ^2S_{1/2}$ states are compared with the experimental values and with values obtained from RMBPT [3] and Hylleraas [4,13] calculations. As can be seen from the table, all the theoretical values agree to within less than two parts in a thousand with the accurate AMBR value for the $2s\ ^2S_{1/2}$ ground state. For the $3s\ ^2S_{1/2}$ state the calculated values all agree perfectly but are outside the error bars of experimental value from Stark spectroscopy [2]. For the $4s\ ^2S_{1/2}$ state the Hylleraas value is not properly converged and cannot be given with more than two significant digits. The MCHF value, however, should be accurate to within less than three parts in a thousand and is well within the error bars of the experimental value. As for the difference between the theoretical and experimental values for the $3s\ ^2S_{1/2}$ state, we cannot, considering the consistency of the theoretical values and the excellent agreement with the accurate experimental value for ground state, avoid the conclusion that the uncertainty of the Stark spectroscopy value may be larger than expected. Further experimental investigations are needed to resolve this discrepancy.

To summarize, we have performed MCHF calculations for the $3s\ ^2S$ and $4s\ ^2S$ states in lithium. Contrary to the Hylleraas method, the convergence properties of the calculated specific-mass-shift parameters and the hyperfine inter-

TABLE III. Theoretical and experimental values of the hyperfine interaction constant for the three lowest ^2S states in Li.

Method	$A(2s\ ^2S_{1/2})$	$A(3s\ ^2S_{1/2})$	$A(4s\ ^2S_{1/2})$	Reference
HF	289.39	67.149	25.388	[12], this work
DF	289.55	67.201	25.407	[12], this work
MCHF [a]	401.79	93.139	35.026	[12], this work
Hylleraas [b]	401.70	92.7	35	[13,4]
RMBPT [b]	402.47	93.24		[3]
Experiment	401.752 0433(5)	94.68(22)	36.4(4.0)	[14,2,15]

[a] Corrected for relativistic and finite nuclear mass effects.

[b] Corrected for finite nuclear mass effects.

action constants do not degrade for the higher Rydberg states, and it is indeed possible to calculate the hyperfine structure constants with an estimated inaccuracy of less than three parts in a thousand.

This research has been supported by the Swedish National Science Research Council (NFR) and by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy.

[1] P. Jönsson, Phys. Scr. **48**, 678 (1993).

[2] G. D. Stevens, C.-H. Iu, S. Williams, T. Bergeman, and H. Metcalf, Phys. Rev. A **51**, 2866 (1995).

[3] S. A. Blundell, W. R. Johnson, Z. W. Liu, and J. Sapirstein, Phys. Rev. A **40**, 2233 (1989).

[4] F. W. King, Phys. Rev. A **43**, 3285 (1991).

[5] C. Froese Fischer, Comput. Phys. Commun. **64**, 369 (1991).

[6] E. Hylleraas and B. Undheim, Z. Phys. **65**, 759 (1930).

[7] C. Froese Fischer, L. Smentek-Mielczarek, N. Vaeck, and G. Miecznik, Comput. Phys. Commun. **74**, 415 (1993).

[8] P. Jönsson, C.-G. Wahlström, and C. Froese Fischer, Comput. Phys. Commun. **74**, 399 (1993).

[9] P. Raghavan, At. Data Nucl. Data Tables **42**, 189 (1989).

[10] B. O. Roos, P. R. Taylor, and P. E. M. Siegbahn, Chem. Phys. Lett. **48**, 157 (1980).

[11] J. Olsen, B. O. Roos, P. Jørgensen, and H. J. Aa Jensen, J. Chem. Phys. **89**, 2185 (1988).

[12] M. Tong, P. Jönsson, and C. Froese Fischer, Phys. Scr. **48**, 446 (1993).

[13] F. W. King, Phys. Rev. A **40**, 1735 (1989).

[14] A. Beckmann, K. D. Böklen, and D. Elke, Z. Phys. **270**, 173 (1974).

[15] J. Kowalski, R. Neumann, H. Suhr, K. Winkler, and G. zu Putlitz, Z. Phys. A **287**, 247 (1978).