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Calculation of the Magnetic Hyperfine Structure of the ^1D, ^3D, ^1F, and ^3F States of $^7\mathrm{Li}^+$

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The separations of the magnetic-hyperfine-structure levels of the ^1D, ^3D, ^1F, and ^3F states of the ion $^7\mathrm{Li}^+$ have been calculated taking into account the mixing of singlet and triplet functions which arises from each configuration ($1snd$) and ($1snf$) by the spin-orbit and spin-spin interactions of Breit's Hamiltonian and the magnetic interaction between the nucleus and the $1s$ electron (Fermi-contact term). The electronic wave functions used are linear combinations of Slater determinants built on hydrogenic orbitals. The calculated distribution of levels is in agreement with experimental results and confirms the coupling rules introduced by Herzberg and Moore for the interpretation of the spectra. The calculations predict an apparent hyperfine structure of the singlet states of $^7\mathrm{Li}^+$ which is analogous to that observed in the n^1D states of $^3\mathrm{He}$.

I. INTRODUCTION

The spectra of the ^1D, ^3D, ^1F, and ^3F states of the ion $^7\mathrm{Li}^+$ which have been studied by Herzberg and Moore[1] do not show the usual fine and hyperfine splittings. The lines corresponding to the transitions $3\,^3D$–$n\,^3F$ show a splitting of the $3\,^3D$ level very much larger than one might expect and each of the singlet lines $3\,^1D$–$n\,^1F$ is doubled while classical theory would predict a negligible hyperfine structure for singlet states. These observations may be explained by a very large interaction between the nucleus and the internal electron; in this case the separation of the hyperfine levels would become as large, if not larger, than the separation of the fine-structure levels and even of the same order of magnitude as the separation of singlet and triplet levels for the nF states.

We thus believed it would be of interest to calculate the hyperfine structure of the $n\,^1D$, $n\,^3D$, $n\,^1F$, and $n\,^3F$ states of $^7\mathrm{Li}^+$ using a method similar to the one which was used to interpret the experimental results for the separation of the hyperfine levels of $n\,^1D$ of $^3\mathrm{He}$.[2,3]

II. CALCULATION

In the present case the hyperfine-structure Hamiltonian cannot be considered as a perturbation of a state of total angular momentum J of the electrons, and the usual expressions for calculating the energy levels as a function of the magnetic hyperfine constants $a(J)$ are no longer valid.

Each atomic wave function Ψ_F is an eigenfunction of the total angular momentum F^2 of the atom. It is taken to be the product of a nuclear wave function by a linear combination of singlet and triplet electronic wave functions associated with each configuration ($1snd$) and ($1snf$) of the electrons.

The energy levels W_F and the corresponding functions Ψ_F are obtained by diagonalizing the total Hamiltonian of the atom. The Hamiltonian $\mathcal{H}$, which we have used, contains, in addition to the usual electrostatic interaction H_{LS}, the fine-structure interaction H_J including the spin-orbit term of Landé, the spin-other-orbit and spin-spin interactions of the Breit operator, and the Fermi-contact hyperfine-structure term H_F. The other contributions to the hyperfine structure are quite negligible here. We have for $\mathcal{H}$,

$$\mathcal{H}=H_{LS}+H_J+H_F\,,$$

$$H_{LS}=\sum_i\left(-\tfrac{1}{2}\Delta_i-\frac{Z}{r_i}\right)+\sum_{i<j}\frac{1}{r_{ij}}\,,$$

$$H_J=\tfrac{1}{2}\alpha^2Z\sum_i \mathbf{l}_i\cdot\mathbf{s}_i\frac{1}{r_i^3}-\tfrac{1}{2}\alpha^2\sum_{i\neq j}\frac{(\mathbf{r}_{ij}\Lambda\mathbf{p}_i)}{r_{ij}^3}(\mathbf{s}_i+2\mathbf{s}_j)+\tfrac{1}{2}\alpha^2\sum_{i\neq j}\frac{1}{r_{ij}^3}\left[\mathbf{s}_i\cdot\mathbf{s}_j-3\frac{(\mathbf{s}_i\cdot\mathbf{r}_{ij})(\mathbf{s}_j\cdot\mathbf{r}_{ij})}{r_{ij}^2}\right],$$

$$H_F=(8\pi/3)g_s\beta\boldsymbol{\mu}_N\cdot\sum_i\delta(\mathbf{r}_i)\mathbf{s}_i\,.$$

The Hamiltonian H_{LS} will act only to determine the singlet-triplet separation of the levels.

If, in addition to the electrostatic interaction H_{LS}, we consider only [calculation (a)] the contribution arising from the Fermi-contact term, the calculated energy levels then correspond to all possible values of the angular momentum G, where $\mathbf{G}=\mathbf{I}+\mathbf{S}$ and $|I-S|\leqslant G\leqslant I+S$. It would have been natural to start from this coupling to make a complete calculation (b)

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[1] G. Herzberg and H. R. Moore, Can. J. Phys. **35**, 1293 (1959).

[2] N. Bessis, H. Lefebvre-Brion, and C. M. Moser, Phys. Rev. **135**, A957 (1964).

[3] M. Descoubes, B. Descombs, and J. Brossel, Compt. Rend. **258**, 4005 (1964).

TABLE I. Values of parameters for $n\,D$ states (cm^{-1}).

	ζ_{nd}			ξ_{nd}	η_{nd}	$E_{LS}(^1D)-E_{LS}(^3D)$		
	Hydrogenic orbitals	HF orbitals ^3D	^1D	Hydrogenic orbitals		Hydrogenic orbitals	HF orbitals	Average expt. distances
3*d*	0.3463	0.3454	0.3489	−0.3517	0.0326	41.6960	42.1394	~30
4*d*	0.1461	0.1455		−0.1491	0.0137	23.6334	23.4840	~17.5
5*d*	0.0748	0.0736		−0.0765	0.0070	13.5148	13.6075	~10.2
6*d*	0.0433	0.0438		−0.0443	0.0040	8.2627	8.3401	~6.5
7*d*	0.0273	0.0263		−0.0279	0.0025	5.3703	5.2674	~4.5
8*d*	0.0183	0.0175		−0.0187	0.0017	3.6701	3.7311	~3.7

including the Hamiltonian H_J to obtain the different levels W_F, where $\mathbf{F}=\mathbf{G}+\mathbf{L}$ and, for each value of G, $|G-L|\leqslant F\leqslant G+L$.

However, the W_F values of calculation (b) can be obtained in the usual LSJ formalism where one calculates the eigenfunctions and eigenvalues of F^2 ($\mathbf{F}=\mathbf{I}+\mathbf{J}$) and introduces all possible values of J, $|L-S|\leqslant J\leqslant L+S$. There are then fewer matrix elements of H_J to calculate.

In both coupling schemes the matrix elements of H_J and H_F are products of reduced nuclear and electronic matrix elements multiplied by $9j$ Wigner coefficients.[4] An automatic program for the CDC 3600 computer has been written to calculate these angular coefficients. The nuclear matrix elements only introduce the magnetic-dipole moment $\mu_{^7\mathrm{Li}}$ of the nucleus ($\mu_{^7\mathrm{Li}}=3.25598\,\mu_N$[5]). The electronic singlet and triplet functions used to calculate the reduced electronic matrix elements are, for each configuration ($1snd$) and ($1snf$), linear combinations of Slater determinants built on hydrogenic orbitals with effective charges $Z(1s)=3$ and $Z(nd)=Z(nf)=2$.

Finally, the results are expressed in terms of four calculated parameters ζ_{nl}, ξ_{nl}, η_{nl}, and α_s, which correspond, respectively, to the Landé spin-orbit, spin-other-orbit, and spin-spin interactions of H_J and to the Fermi-contact term (see Appendix). An automatic program has been written to calculate the two-electron spin-orbit and spin-spin integrals between linear combinations of Slater orbitals using the general formulas of Blume and Watson[6] as well as a program for expanding hydrogenic orbitals in terms of Slater orbitals.

TABLE II. Values of parameters for $n\,F$ states (cm^{-1}).

	ζ_{nf}		ξ_{nf}	η_{nf}	$E_{LS}(^1F)-E_{LS}(^3F)$
	Hydrogenic orbitals	HF orbitals	Hydrogenic orbitals		
4*f*	0.0522	0.0526	−0.0783	0.0058	0.1507
5*f*	0.0267	0.0263	−0.0401	0.0030	0.1255
6*f*	0.0155	0.0158	−0.0232	0.0017	0.0896
7*f*	0.0097	0.0105	−0.0146	0.0011	0.0633
8*f*	0.0065	0.0070	−0.0098	0.0007	0.0455

The electronic wave functions of the singlet and of the triplet states were also calculated using the numerical Hartree-Fock program of C. Froese. The parameter α_s, as well as the integrals $\langle nl|r^{-3}|nl\rangle$ and consequently the parameter ζ_{nl}, have nearly the same value whether obtained from singlet and triplet numerical orbitals or from hydrogenic orbitals (see Tables I and II). The numerical method gives only a total expectation value of the spin-orbit interaction.

III. RESULTS

To determine the theoretical spectra of ^{7}Li$^+$, we have used, in calculation (a), the approximation $\mathcal{H}\sim H_{LS}+H_F$ and, in calculation (b), the total Hamiltonian $\mathcal{H}=H_{LS}+H_J+H_F$. The results are compared to the experimental results of Herzberg and Moore. They are evidently quite different from those which would be obtained using constants $a(J)$ for each J state of the electrons.

A. Hyperfine Structure of ^1D and ^3D States

In Tables III and IV are collected the results for the $n\,^1D$ and $n\,^3D$ states ($n=3$ to 8). The levels W_F we obtain [calculation (b)] are grouped together for each G value, $G=\frac{3}{2}$ for the $n\,^1D$ states and $G=\frac{1}{2}$, $\frac{3}{2}$, and $\frac{5}{2}$ for the $n\,^3D$ states, in agreement with the observed spectra. Yet, this G splitting of the levels is well given by the approximate results of calculation (a) because the diagonal elements of the Landé spin-orbit and spin-other-orbit Hamiltonians are of the same order of magnitude but of opposite sign, and the spin-spin elements are very small (see Table I). However, calculation (b), which includes the Hamiltonian H_J, does bring out the apparent hyperfine structure of the singlet states ($F=\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$, $\frac{7}{2}$ for $G=\frac{3}{2}$). We obtain a hyperfine structure for the $n\,^3D$ states for which the calculated distribution of levels ($F=\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$, $\frac{7}{2}$, $\frac{9}{2}$ for $G=\frac{5}{2}$; and $F=\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$, $\frac{7}{2}$ for $G=\frac{3}{2}$; and $F=\frac{3}{2}$, $\frac{5}{2}$ for $G=\frac{1}{2}$) is in agreement with the diagram of Herzberg and Moore.

The expression for the wave functions which is given in Table III shows that the coupling (ISG) is quite appropriate for the study of the hyperfine structure of the $n\,D$ states. For each of the groups of the triplet

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[4] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, N. J., 1960).

[5] H. Kopferman, *Nuclear Moments* (Academic Press Inc., New York, 1958).

[6] M. Blume and R. E. Watson, Proc. Roy. Soc. (London) **270**, 127 (1962).

TABLE III. Magnetic hyperfine structure of 3 ^1D and 3 ^3D states of ^{7}Li$^+$.

		Energy levels W_F (cm^{-1})			Coefficients of wave functions (b)							
						^3D		^1D		^3D		^1D
G	F	Expt.	Calc. (a)	Calc. (b)	$J=1$	$J=2$	$J=3$	$J=2$	$G=\frac{1}{2}$	$G=\frac{3}{2}$	$G=\frac{5}{2}$	$G=\frac{3}{2}$
$\frac{3}{2}$	$\frac{1}{2}$	30.47	42.324	42.332	0	0.0036	0.0176	0.9998	0	−0.0090	−0.0180	0.9997
	$\frac{3}{2}$			42.330	0.0065	0.0139	−0.0061	0.9999	−0.0028	−0.0080	0.0032	0.9999
	$\frac{5}{2}$			42.326	0.0074	0.0079	−0.0087	0.9999	−0.0035	−0.0109	0.0044	0.9999
	$\frac{7}{2}$			42.322	0	−0.0005	−0.0090	0.9999	0	−0.0150	0.0044	0.9998
$\frac{5}{2}$	$\frac{1}{2}$	1.15	0.996	1.101	0	0.9724	−0.2333	0.0006	0	0.1079	0.9940	0.0189
	$\frac{3}{2}$			1.050	0.8743	−0.4729	0.1092	0.0016	0.0542	0.2129	0.9756	−0.0014
	$\frac{9}{2}$			1.023	0	0	1	0	0	0	1	0
	$\frac{5}{2}$			0.979	0.6359	−0.6969	0.3316	0.0037	0.1011	0.1970	0.9752	−0.0017
	$\frac{7}{2}$			0.946	0	−0.7009	0.7133	0.0060	0	0.0309	0.9995	−0.0039
$\frac{3}{2}$	$\frac{5}{2}$	0.62	0.368	0.429	−0.6136	−0.1959	0.7648	0.0128	0.1736	0.9616	−0.2122	0.0120
	$\frac{3}{2}$	0.45		0.356	0.4272	0.6431	−0.6353	−0.0156	0.0705	0.9737	−0.2164	0.0086
	$\frac{7}{2}$			0.336	0	0.7133	0.7009	0.0066	0	0.9994	−0.0308	0.0151
	$\frac{1}{2}$			0.266	0	0.2333	0.9722	−0.0179	0	0.9941	−0.1081	0.0071
$\frac{1}{2}$	$\frac{5}{2}$	0	0	−0.009	0.4680	0.6898	0.5523	−0.0041	0.9796	−0.1907	−0.0630	0.0016
	$\frac{3}{2}$			−0.010	0.2302	0.6021	0.7645	−0.0052	0.9960	−0.0806	−0.0378	0.0022

levels, G is a nearly well-defined quantum number but J is not at all well defined.

The calculated singlet-triplet distances associated either with the same or with different configurations are in poor agreement with experiment as the wave functions which we use do not introduce any correlation energy. However, we obtain essentially the same results for the relative separation of the hyperfine-structure levels for each triplet or singlet state, by using the average experimental distance $E\,(^1D)-E\,(^3D)$ (Table I).

B. Hyperfine Structure of ^1F and ^3F States

In Tables V and VI are gathered the results obtained for the $n\ ^1F$ and $n\ ^3F$ states ($n=4$ to 8). In both calculations (a) and (b) we find two groups of levels which correspond well to the experimental situation where one observes a separation of about 1 cm^{-1}. The Fermi-contact term remains predominant but the singlet-triplet interaction is very important as the ^3F-^1F distance is very small (see Table II).

The expressions of the wave functions (a) are given in Table VII. The lack of ISG coupling becomes more important here. Not only is J not well defined but also the singlet and triplet functions are much more mixed than for the D states. The results (Tables V and VII) confirm the predominant coupling between spin $s=\frac{1}{2}$ of the electron 1s and the nuclear spin $I=\frac{3}{2}$, viz., $|I-s|\leqslant F_i\leqslant I+s$ ($F_i=1,2$), which was proposed by Herzberg and Moore to interpret the experimental

TABLE IV. Magnetic hyperfine structure of $n\ ^1D$ and $n\ ^3D$ states of ^{7}Li$^+$.

		Energy levels W_F (cm^{-1})														
			$n=4$			$n=5$			$n=6$			$n=7$			$n=8$	
G	F	Expt.	Calc. (a)	Calc. (b)	Expt.	Calc. (a)	Calc. (b)	Expt.	Calc. (a)	Calc. (b)	Expt.	Calc. (a)	Calc. (b)	Expt.	Calc. (a)	Calc. (b)
$\frac{3}{2}$	$\frac{1}{2}$	17.93	24.266	24.270	10.33	14.154	14.158	6.97	8.913	8.916	4.96	6.034	6.038	4.68	4.351	4.355
	$\frac{3}{2}$			24.269			14.157			8.915			6.037			4.354
	$\frac{5}{2}$			24.267			14.155			8.913			6.035			4.352
	$\frac{7}{2}$			24.264			14.152			8.910			6.032			4.349
$\frac{5}{2}$	$\frac{1}{2}$	1.05	0.996	1.040	1.05	0.996	1.018	1.05	0.996	1.009	1.05	0.996	1.004	1.05	0.996	1.002
	$\frac{3}{2}$			1.016			1.005			1.002			1.000			0.998
	$\frac{9}{2}$			1.006			1.001			0.998			0.997			0.997
	$\frac{5}{2}$			0.986			0.991			0.993			0.994			0.995
	$\frac{7}{2}$			0.973			0.984			0.989			0.992			0.993
$\frac{3}{2}$	$\frac{5}{2}$	0.39	0.364	0.390	0.39	0.357	0.370	0.39	0.346	0.354	0.39	0.332	0.337	0.39	0.315	0.318
	$\frac{3}{2}$			0.360			0.354			0.344			0.330			0.313
	$\frac{7}{2}$			0.353			0.352			0.345			0.332			0.316
	$\frac{1}{2}$			0.320			0.333			0.332			0.322			0.307
$\frac{1}{2}$	$\frac{5}{2}$	0	0	−0.001	0	0	0		0	0	0	0	0	0	0	0
	$\frac{3}{2}$			−0.003												

Table V. Magnetic hyperfine structure of 4 ^1F and 4 ^3F states of $^7\mathrm{Li}^+$.

		Energy levels W_F (cm^{-1})			Coefficients of wave functions (b)			
					^3F			^1F
G	F	Expt.	Calc. (a)	Calc. (b)	$J=2$	$J=3$	$J=4$	$J=3$
$\frac{3}{2}$	$\frac{3}{2}$	1.07	1.105	1.199	−0.0865	−0.5875	0	0.8045
	$\frac{5}{2}$	($F_1=2$)		1.177	−0.1233	−0.5077	0.3301	0.7862
	$\frac{7}{2}$			1.141	0.1260	0.3889	−0.5198	−0.7501
	$\frac{9}{2}$			1.091	0	0.2294	−0.7139	−0.6616
$\frac{5}{2}$	$\frac{1}{2}$		0.996	1.011	1	0	0	0
	$\frac{11}{2}$			1.002	0	0	1	0
	$\frac{3}{2}$			0.999	0.9403	−0.3149	0	−0.1288
	$\frac{5}{2}$			0.979	0.8286	−0.5068	0.0708	−0.2270
	$\frac{7}{2}$			0.953	−0.6308	0.6765	−0.1505	0.3490
	$\frac{9}{2}$			0.918	0	0.8123	−0.2340	−0.5341
$\frac{3}{2}$	$\frac{9}{2}$	0	0.051	0.123	0	0.5362	0.6600	−0.5262
	$\frac{7}{2}$	($F_1=1$)		0.074	−0.2032	0.2397	0.8201	−0.4782
	$\frac{5}{2}$			0.036	−0.1377	0.0665	0.9186	−0.3644
	$\frac{3}{2}$			−0.058	0.3291	0.7454	0	0.5798
$\frac{1}{2}$	$\frac{7}{2}$		0	−0.024	0.7382	0.5776	0.1859	0.2947
	$\frac{5}{2}$			−0.047	0.5284	0.6936	0.2053	0.4445

Table VI. Magnetic hyperfine structure of $n\,^3F$ and $n\,^1F$ state of $^7\mathrm{Li}^+$.

		Energy levels W_F (cm^{-1})											
			$n=5$			$n=6$			$n=7$			$n=8$	
G	F	Expt.	Calc. (a)	Calc. (b)	Expt.	Calc. (a)	Calc. (b)	Expt.	Calc. (a)	Calc. (b)	Expt.	Calc. (a)	Calc. (b)
$\frac{3}{2}$	$\frac{3}{2}$	1.0	1.078	1.131	1.05	1.054	1.084	1.14	1.037	1.056	1.18	1.025	1.038
	$\frac{5}{2}$	($F_2=2$)		1.117	($F_2=2$)		1.076	($F_2=2$)		1.050	($F_2=2$)		1.034
	$\frac{7}{2}$			1.096			1.063			1.042			1.028
	$\frac{9}{2}$			1.063			1.043			1.029			1.019
$\frac{5}{2}$	$\frac{1}{2}$		0.996	1.003		0.996	1.000		0.996	0.999		0.996	0.998
	$\frac{11}{2}$			0.999			0.998			0.997			0.997
	$\frac{3}{2}$			0.998			0.997			0.997			0.997
	$\frac{5}{2}$			0.989			0.993			0.994			0.995
	$\frac{7}{2}$			0.978			0.987			0.991			0.993
	$\frac{9}{2}$			0.969			0.983			0.988			0.991
$\frac{3}{2}$	$\frac{9}{2}$	0	0.044	0.079	0	0.032	0.053	0	0.023	0.036	0	0.017	0.026
	$\frac{7}{2}$	($F_1=1$)		0.053	($F_1=1$)		0.037	($F_1=1$)		0.026	($F_1=1$)		0.019
	$\frac{5}{2}$			0.028			0.021			0.016			0.012
	$\frac{3}{2}$			−0.013			−0.001			0.002			0.003
$\frac{1}{2}$	$\frac{7}{2}$		0	−0.009		0	−0.004		0	−0.002		0	−0.001
	$\frac{5}{2}$			−0.016			−0.007			−0.004			−0.002

spectra. The two levels $F_1=1$ and $F_2=2$ are split according to the coupling scheme

$$|F_i-j_2|\leqslant F\leqslant|F_i+j_2|\,,$$

where $\mathbf{F}=\mathbf{F}_i+\mathbf{j}_2$ and $\mathbf{j}_2$ is the total angular momentum of the nf electron ($j_2=\frac{5}{2},\frac{7}{2}$).

Table VII. Coefficients of wave functions (a). $\mathcal{H}\sim H_{LS}+H_{\mathrm{Fermi}}$ approximation.

G	^3D	^1D	^3F	^1F
$\frac{3}{2}$	−0.0115	0.9999	0.5554	0.8316
$\frac{5}{2}$	1	0	1	0
$\frac{3}{2}$	0.9999	0.0115	0.8316	−0.5554
$\frac{1}{2}$	1	0	1	0

The complete calculation (b) predicts an apparent hyperfine structure of the $n\,^1F$ states more important than for the $n\,^1D$ states. The relative distances of the four hyperfine levels of the $n\,^1F$ states diminish with n:

$$W_{3/2\;5/2}\sim 0.022\ \mathrm{cm}^{-1}\ (n=4)\ \text{to}\ 0.004\ \mathrm{cm}^{-1}\ (n=8),$$

$$W_{5/2\;7/2}\sim 0.036\ \mathrm{cm}^{-1}\ (n=4)\ \text{to}\ 0.006\ \mathrm{cm}^{-1}\ (n=8),$$

$$W_{7/2\;9/2}\sim 0.050\ \mathrm{cm}^{-1}\ (n=4)\ \text{to}\ 0.009\ \mathrm{cm}^{-1}\ (n=8).$$

On the contrary, the separation of the levels of the $n\,^1D$ states remains essentially constant with n:

$$W_{1/2\;3/2}\sim 0.002\ \mathrm{cm}^{-1}\ (n=3)\ \text{to}\ 0.001\ \mathrm{cm}^{-1}\ (n=4\ \text{to}\ 8),$$

$$W_{3/2\;5/2}\sim 0.004\ \mathrm{cm}^{-1}\ (n=3)\ \text{to}\ 0.002\ \mathrm{cm}^{-1}\ (n=4\ \text{to}\ 8),$$

$$W_{5/2\;7/2}\sim 0.004\ \mathrm{cm}^{-1}\ (n=3)\ \text{to}\ 0.003\ \mathrm{cm}^{-1}\ (n=4\ \text{to}\ 8).$$

The values for the $n\,{}^1D$ states of ${}^7\mathrm{Li}^+$ are of the same order of magnitude as the separation of levels in the $n\,{}^1D$ states of ${}^3\mathrm{He}$ [2] ($W_{3/2\;5/2}\sim 0.004$ cm^{-1}).

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APPENDIX: EXPRESSIONS FOR MATRIX ELEMENTS OF H_J AND H_F

If $T_N{}^K$ is a tensorial operator of rank K and depends only on nuclear coordinates, and $T_e{}^{k_L}$ and $T_e{}^{k_S}$ are tensorial operators of rank k_L and k_S and depend only on the space coordinates and spin coordinates of the electrons, respectively, the general expression of the matrix element of a state F with $M_F=F$ is given by[4]:

In the coupling scheme ISG; $\mathbf{G}=\mathbf{I}+\mathbf{S}$, $\mathbf{F}=\mathbf{G}+\mathbf{L}$:

$$\begin{aligned}&\langle (IS)GLF\,M_F=F\,|\,T_N{}^K\\&\quad\times\{T_e{}^{k_L}T_e{}^{k_S}\}^K\,|\,(IS')G'L'F\,M_F=F\rangle\\&=(-)^{k_S+k_L}[(2K+1)(2k_L+1)(2F+1)\\&\quad\times(2G+1)(2G'+1)]^{1/2}\begin{Bmatrix}L & L' & k_L\\ G & G' & k_L\\ F & F & 0\end{Bmatrix}\begin{Bmatrix}I & I & K\\ S & S' & k_S\\ G & G' & k_L\end{Bmatrix}\\&\quad\times\langle I\|T_N{}^K\|I\rangle\langle LS\|T_e{}^{k_L}T_e{}^{k_S}\|L'S'\rangle.\end{aligned}$$

In the coupling scheme LSJ; $\mathbf{J}=\mathbf{L}+\mathbf{S}$, $\mathbf{F}=\mathbf{I}+\mathbf{J}$:

$$\begin{aligned}&\langle (LS)JIF\,M_F=F\,|\,T_N{}^K\\&\quad\times\{T_e{}^{k_L}T_e{}^{k_S}\}^K\,|\,(L'S')J'IF\,M_F=F\rangle\\&=(-)^K(2K+1)[(2F+1)(2J+1)(2J'+1)]^{1/2}\\&\quad\times\begin{Bmatrix}J & J' & K\\ I & I & K\\ F & F & 0\end{Bmatrix}\begin{Bmatrix}L & L' & k_L\\ S & S' & k_S\\ J & J' & K\end{Bmatrix}\\&\quad\times\langle I\|T_N{}^K\|I\rangle\langle LS\|T_e{}^{k_L}T_e{}^{k_S}\|L'S'\rangle.\end{aligned}$$

These general formulas have been used to calculate the different terms of the Hamiltonian (see Sec. II) and the electronic reduced matrix elements are given in Table VIII.

The electronic reduced matrix elements are obtained from the explicit expression of the electronic wave functions ($M_J=J$) and are calculated directly as a function of single-electron and two-electron integrals by the usual Slater rules. We introduce, for the diagonal matrix elements ($M_J=J$), the notation

$$\zeta_{nl}=Z(\tfrac{1}{2}\alpha^2)\langle nl|r^{-3}|nl\rangle,$$

$$\eta_{nl}=\tfrac{1}{2}(\tfrac{1}{2}\alpha^2)\langle 1s(r_1)1s(r_2)|r^{-3}\epsilon(r_1-r_2)|nl(r_2)nl(r_2)\rangle,$$

where

$$\begin{aligned}\epsilon(x)&=1,\quad\text{if}\quad x>0\\&=0,\quad\text{if}\quad x<0\end{aligned}$$

$$\alpha_s=(8\pi/3)g_s\beta\mu_{^7\mathrm{Li}}\times\tfrac{1}{2}[(1s)_{r=0}]^2.$$

For a hydrogenic orbital $(1s)_{r=0}=[Z(1s)]^{3/2}/\sqrt{\pi}$. The nondiagonal singlet-triplet matrix elements of the spin-other-orbit interaction cannot be expressed as a function of the ξ_{nl}'s. They remain a linear combination of two-electron integrals.

TABLE VIII. Electronic reduced matrix elements as functions of the calculated parameters.

Reduced matrix element	Landé spin-orbit terms $(K=0, k_L=k_S=1)$	Spin-other-orbit terms	Spin-spin terms $(K=0, k_L=k_S=2)$	Fermi-contact term $(K=1, k_L=0, k_S=1)$
$\langle {}^3D\|T_e{}^{k_L}T_e{}^{k_S}\|{}^1D\rangle$	$(\sqrt{\tfrac{5}{2}})\zeta_{nd}$		0	$-(\sqrt{15})\alpha_S$
$\langle {}^3D\|T_e{}^{k_L}T_e{}^{k_S}\|{}^3D\rangle$	$(3\sqrt{5})\zeta_{nd}$	$-(3\sqrt{15})\xi_{nd}$	$(5\sqrt{105})\eta_{nd}$	$(\sqrt{30})\alpha_S$
$\langle {}^3F\|T_e{}^{k_L}T_e{}^{k_S}\|{}^1F\rangle$	$-(3\sqrt{7})\zeta_{nf}$		0	$(\sqrt{21})\alpha_S$
$\langle {}^3F\|T_e{}^{k_L}T_e{}^{k_S}\|{}^3F\rangle$	$(3\sqrt{14})\zeta_{nf}$	$-(2\sqrt{42})\xi_{nf}$	$(6\sqrt{70})\eta_{nf}$	$(\sqrt{42})\alpha_S$