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Reanalysis and semi-empirical predictions of the hyperfine structure of ^{91}ZrI in the model space $(4d + 5s)^4$

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Abstract. On the basis of most of the earlier hyperfine-structure (hfs) experimental results, the hfs of the atomic zirconium has been reanalyzed by the simultaneous parameterization of the one- and two-body interactions for the model space $(4d + 5s)^4$. The values of the one- and two-body hfs parameters have been determined and the nuclear quadrupole moment, free of Sternheimer corrections up to second order, $Q(^{91}\mathrm{Zr}) = -0.23(2)b$ has been evaluated. Moreover, the values of the magnetic-dipole A and the electric-quadrupole B constants for all known levels of this model space have been predicted.

PACS. 31.30.Gs Hyperfine interactions and isotope effects

1 Introduction

The analysis of the $4d$- and $5d$-shell spectra has been performed only in a few cases until now, due to the scarcity of experimental data. Shadmi's systematic treatment of the $(4d + 5s)^n$ configurations in the neutral palladium-group atoms [1] was apparently never published, and no systematic calculation has been made for the $(4d + 5s)^{n-1}5p$ odd parity configurations in these atoms. Shadmi's calculations included Zr $(4d + 5s)^4$, and the levels of this complex were also studied by Büttgenbach *et al.* [2]; both investigations indicated the need for revisions of the Zr analysis in [3]; in the past Wyart [4,5] and recently Martin and Sugar [6] after examining available data for the odd parity energy level structures in Zr, Hf and Rf – these elements are located in the same row of the periodic table – concluded also that more complete and reliable energy level analysis are needed for a number of $4d$- and $5d$-shell spectra.

^{91}Zr is the only stable Zr isotope with the non-zero nuclear spin. It has a natural abundance of 11.3% and the nuclear spin $I = 5/2$. Half century ago the hfs of ^{91}Zr has been measured using the Fabry-Perot technique [7,8] and later Büttgenbach *et al.* [2] performed precise atomic-beam-magnetic-resonance (ABMR) measurements; but we can consider that like in the case of hafnium [9] only few hfs measurements have been achieved so far comparatively to the other elements. This is because Hf and Zr are refractory elements whose atomic beams are difficult to be produced stably. In this work we try to estimate the virtual excitation effects on the atomic structure of $4d$-elements and we use them to predict non-measured hfs splittings of the model space levels.

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2 Remarks on fine and hyperfine structure parameterizations

The method applied here for fine structure (fs) and hfs analysis was successfully used for the model space $[nd + (n + 1)s]^{N+2}$ in the $3d$-elements [10–16] and hafnium and tantalum atoms [9,17].

The procedure of fs analysis includes besides electrostatic and spin dependent interactions within model space $(4d + 5s)^4$, which are represented by the Slater integrals F^k, G^k, R^k and the spin-orbit integrals ζ_{4d} also the interactions with distant configurations. The interaction effects with distant configurations affecting the term structure have been taken into account by the three-body parameters $T(d^2s)$, $T_2(22)$, $T_3(42)$ and two-body parameters α and β representing the one- and two-electron excitations, respectively. The effects of the one-electron excitation on the spin-orbit splitting of the term (electrostatically correlated spin-orbit interaction (EL-SO)) were considered in the way reported in [11,12,17] and we express their strength by the parameters P_i defined in [11].

The fs least square fitting procedure have been carried out to 40 energy levels attributed to the model space. The details on this method can be found in [10,13,16]. With 65 parameters 11 of which were treated as free, a good fit has been achieved. In Table 1 are given the energy levels, calculated eigenvalues and percentages of first and second components of wavefunctions. In this table the calculated Landé g_J-factors, deduced from eigenvector compositions

Table 1. Comparison of the observed and calculated energy levels and g_J-factors.

Obs. energy level	Calc. eigenvalue	ΔE	Largest eigenvector component (%)	Next-largest component (%)	Calc. g_J	Obs. g_J	Δg_J
4196.850	4197.387	−0.537	74.33 ^3P	23.26 ^2P			
	15190.302		64.91 ^4P; ^3P	17.09 ^2P; ^3P			
17321.520	17235.256	86.264	56.97 ^2P; ^3P	25.46 ^4P; ^3P			
	19660.002		93.82 ^1S	3.41 ^1S			
21726.279	21736.264	69.984	99.48 ^5D	0.27 ^3P			
	29651.816		48.83 ^3P	38.92 ^3P			
4376.280	4380.257	−3.978	74.08 ^3P	23.64 ^2P; ^3P	1.50103	1.50072	−0.00031
4870.530	4869.180	1.350	99.53 ^4F; ^5F	0.28 ^2D; ^3D	0.00055		
10885.360	10878.824	6.536	99.54 ^4P; ^5P	0.30 ^3P	2.49862	2.50000	0.00138
14123.010	14119.606	3.403	68.43 ^2D; ^3D	23.29 ^2D; ^3D	0.54858	0.61000	0.06142
	15448.580		68.61 ^4P; ^3P	10.67 ^2P; ^3P	1.44866		
17059.820	17065.600	−5.779	49.60 ^2P; ^3P	26.02 ^2P; ^1P	1.37299		
	17885.166		69.85 ^2P; ^1P	13.09 ^2P; ^3P	1.13292		
21801.211	21807.820	−6.609	99.61 ^5D	0.19 ^3P	1.50089		
0.000	19.508	−19.508	96.05 ^3F	1.91 ^2F; ^3F	0.67002	0.66981	−0.00021
4186.110	4156.652	29.458	49.49 ^1D	31.75 ^3P	1.21028	1.23146	0.02118
5023.410	5027.475	−4.064	98.38 ^4F; ^5F	0.62 ^1D	1.00333	1.00081	−0.00252
5101.680	5081.541	20.140	41.56 ^3P	36.29 ^1D	1.28410	1.26472	−0.01936
11016.650	11013.411	3.239	98.97 ^4P; ^5P	0.59 ^3P	1.83099	1.82000	−0.01099
11640.720	11629.690	11.029	96.41 ^4F; ^3F	1.96 ^3F	0.67110	0.75000	0.07890
14348.780	14360.316	−11.536	71.10 ^2D; ^3D	22.58 ^2D; ^3D	1.17585	1.17000	−0.00585
15932.100	15959.384	−27.284	78.90 ^4P; ^3P	9.01 ^3P	1.49420	1.46000	−0.03420
17142.721	17213.531	−70.811	61.49 ^2P; ^3P	19.12 ^3P	1.46369		
	18717.287		63.39 ^2D; ^1D	11.42 ^2D; ^1D	1.03230		
	20251.521		92.08 ^2F; ^3F	3.22 ^3F	0.66900		
21943.740	21945.029	−1.289	99.74 ^5D	0.08 ^3P	1.50055		
	26450.754		74.15 ^2D; ^3D	20.13 ^2D; ^3D	1.16608		
1240.840	1226.014	14.826	96.71 ^3F	2.22 ^2F; ^3F	1.25010	1.24987	−0.00023
5540.540	5562.064	−21.524	99.78 ^4F; ^5F	0.16 ^2G; ^3G	1.35027	1.35012	−0.00015
8057.300	8088.182	−30.882	81.88 ^1G	16.48 ^2G; ^1G	1.00068	1.00052	−0.00016
12342.370	12312.831	29.539	50.91 ^4F; ^3F	46.12 ^2G; ^3G	1.15316	1.15000	−0.00316
12760.660	12748.477	12.184	50.53 ^2G; ^3G	46.07 ^4F; ^3F	1.14223	1.15000	0.00777
14791.280	14771.212	20.068	96.06 ^2H; ^3H	1.69 ^2G; ^3G	0.80670	0.77000	−0.03670
17752.730	17759.313	−6.582	79.61 ^2G; ^1G	15.85 ^1G	0.99991	1.00000	0.00010
	20145.145		92.20 ^2F; ^3F	3.16 ^3F	1.24956		
22398.000	22385.242	12.758	99.51 ^5D	0.26 ^2F; ^3F	1.49992		
5888.930	5919.900	−30.970	99.56 ^4F; ^5F	0.44 ^2G; ^3G	1.40004	1.39991	−0.00013
12772.780	12760.721	12.060	95.45 ^2G; ^3G	2.61 ^2H; ^3H	1.19632	1.20000	0.00368
14988.510	14968.516	19.994	96.42 ^2H; ^3H	2.62 ^2G; ^3G	1.03788	1.03000	−0.00788
18738.939	18817.252	−78.313	99.60 ^2H; ^1H	0.25 ^2G; ^3G	1.00057	1.02000	0.01943
15119.660	15098.171	21.489	99.17 ^2H; ^3H	0.83 ^3H	1.16705	1.15000	−0.01705

mean square error $\sigma = 31\,\mathrm{cm}^{-1}$
number of independent parameters = 11
number of levels fitted = 40
degrees of freedom = 29

Table 2. Fs parameters values (in cm^{-1}) of the model space $(4d+5s)^4$ of zirconium atom.

Configuration	$4d^25s^2$	$4d^35s^1$	$4d^4$
E_{av}	5473(14)	15211 (8)	31780 (16)
$F^2(4d,4d)$	30281(137)	25567 (64)	21141[a]
$F^4(4d,4d)$	17756(265)	15171(56)	14354[a]
$G^2(4d,5s)$	–	8551(25)	–
$T_2(22)$	–	−62	−62
$T_3(42)$	–	−47	−47
$T(d^2s)$	−311	−311	–
Values of parameters common to all configurations:			
$\zeta(4d,4d) = 387(17)$; $P_1 = 125(32)$;			
$P_2 = 24(39)$; $P_3 = 16.08$ [b];			
$\alpha = 32(2)$; $\beta = -138(39)$.			
Values of configuration interaction parameters:			
$4d^25s^2$–$4d^35s^1$, $R^2(4d4d,4d5s) = -12226(50)$;			
$4d^35s^1$–$4d^4$, $R^2(5s5s,4d4d) = 8551$[c];			
$4d^35s^1$–$4d^4$, $R^2(4d5s,4d4d) = -10092(63)$.			

[a] Taken in a ratio to parameters of $4d^35s^1$ configuration.
[b] Taken in a ratio to P_2.
[c] Taken as an equal to $G^2(4d,5s)$.

are compared to experimental ones. Table 2 contains the values of fs radial parameters.

We would like to remind that the attribute of the method, we use for the description of the fs spin-dependent interactions and hfs interactions, is the assumption that the orbital $4d$ and also the open $n'l'$- and the inner $n''l''$-shell orbitals are common to all states within the model space.

Concerning the hfs analysis we follow the many-body parameterization method [10–12] which allows to take advantage of similarities between configuration interaction effects observed independently in spin-orbit and hyperfine splittings.

The assumption mentioned above allows to replace the familiar one-configuration parameters $a_{nl}^{\kappa k}(l^{N+M}s^{2-M})$ by the model space parameter $a_{nl}^{\kappa k}$ [10]:

$$\begin{aligned} a_{nl}^{\kappa k}(l^{N+M}s^{2-M}) = a_{nl}^{\kappa k} &+ [2/(2l+1)][1-(N+M)]a_1 \\ &- [2/(2l+1)]^{1/2}(2-M)a_4 \\ &+ [2/(2l+1)]a_5\delta(M,0) \end{aligned} \quad (1)$$

for $\kappa k = 01, 12$. In the case of $\kappa k = 10$ we have:

$$\begin{aligned} a_{nl}^{10}(l^Ns^2) &= a_{nl}^{10} \\ a_{nl}^{10}(l^{N+1}s) &= a_{nl}^{10} - [2/(2l+1)]a_9 \\ a_{nl}^{10}(l^{N+2}) &= a_{nl}^{10} + [2/(2l+1)](a_{10}-a_9). \end{aligned} \quad (2)$$

These relations can also help to compare our results with those given in [2]. Another consequence of the above assumption is the formula:

$$\frac{a_i}{a_{4d}^{\kappa k}} = \frac{b_i}{b_{4d}^{\kappa k}} = \frac{P_i}{\zeta(4d,4d)}, \quad i = 1,\,2,\,3 \quad (3)$$

which gives the possibility to compare the effects of the virtual excitations on the fine- and hyperfine structure or to introduce in hfs-fit fixed relations between radial parameters (in case of the scarcity of experimental data).

It should be mentioned that in case of the $4d$-elements there exists the excitation from closed and $3d$-shell into the open $4d$-shell. However, these excitations deliver no new angular dependency and cause only the screening effects for the excitations open shell → empty shell, which already have been taken into account.

3 Hfs results and discussion

The essential formulae for prediction of the A and B constant values of the levels belonging to the considered $(4d+5s)^4$ configurations read as follows:

$$\begin{aligned} A(\psi) &= \sum_{\phi,\phi'} c(\psi,\phi)c(\psi,\phi') \\ &\quad \times \underbrace{\left[\sum_{\kappa k,nl} \alpha_{nl}^{\kappa k}(\phi,\phi')a_{nl}^{\kappa k} + \sum_i \alpha_i(\phi,\phi')a_i\right]}_{A((\phi,\phi))} \\ &= \sum_{\kappa k,nl} \alpha_{nl}^{\kappa k}(\psi)a_{nl}^{\kappa k} + \sum_i \alpha_i(\psi)a_i \end{aligned} \quad (4)$$

and

$$\begin{aligned} B(\psi) &= \sum_{\phi,\phi'} c(\psi,\phi)c(\psi,\phi') \\ &\quad \times \underbrace{\left[\sum_{\kappa k,nl} \beta_{nl}^{\kappa k}(\phi,\phi')b_{nl}^{\kappa k} + \sum_i \beta_i(\phi,\phi')b_i\right]}_{B((\phi,\phi))} \\ &= \sum_{\kappa k,nl} \beta_{nl}^{\kappa k}(\psi)b_{nl}^{\kappa k} + \sum_i \beta_i(\psi)b_i \end{aligned} \quad (5)$$

where $a_{nl}^{\kappa k}$ and $b_{nl}^{\kappa k}$ are hfs one-body radial parameters, whereas $\alpha_{nl}^{\kappa k}(\phi,\phi')$ and $\beta_{nl}^{\kappa k}(\phi,\phi')$ stand for the angular coefficients originating in the first-order hfs operator. The two-body hfs radial parameters and their angular coefficients are represented by a_i, b_i and $\alpha_i(\phi,\phi'), \beta_i(\phi,\phi')$ respectively [10]. In calculations of the $\alpha_{nl}^{\kappa k}(\psi)$, $\beta_{nl}^{\kappa k}(\psi)$, $\alpha_i(\psi)$, $\beta_i(\psi)$ coefficients the $c(\psi,\phi)$ amplitudes of intermediate coupling eigenvectors, which were obtained from semi-empirical analysis of fs, are used (Tabs. 3 and 4).

The radial parameters $a_{nl}^{\kappa k}$, $b_{nl}^{\kappa k}$, a_i and b_i have been evaluated by fitting them to experimentally determined hfs constants A and B [2] using the theoretical expressions (4, 5). However, the number of A and B experimental values of ^{91}ZrI is much smaller than the number of one and two body parameters predicted by theory. According to our knowledge, the constants A and B were measured for only 7 levels of ground configuration [2]. For this reason additional assumptions, which are taken from relativistic

Table 3. The coefficients of the hfs magnetic dipol interaction parameters of the model space for each fine structure state under study.

	$\alpha^{01}(4d)$	$\alpha^{12}(4d)$	$\alpha^{10}(4d)$	$\alpha^{10}(5s)$
	α^{12}_{IC}	α_1	α_2	α_3
	α_4	α_5	α_6	α_7
	α_8	α_9	α_{10}	α_{11}
b $^3F_2$	1.32922	0.17172	−0.32603	−0.00319
	−0.03026	−0.61963	0.32878	0.03882
	−2.64191	0.58999	−0.03944	−0.02824
	0.01061	−0.00019	0.00019	−0.00779
c $^5F_2$	0.99667	−0.05932	−0.00359	0.00693
	−0.01563	−0.74691	0.39816	0.06287
	−0.84502	0.36866	0.02390	−0.00630
	−0.00098	0.00528	−0.00528	−0.00017
b $^3F_3$	0.91666	0.03385	0.08252	0.00082
	−0.01044	−0.39377	0.21124	0.02828
	−1.66999	0.37311	−0.01115	−0.02202
	0.00400	0.00003	−0.00003	0.00201
c $^5F_3$	0.75019	−0.04008	0.18054	0.06927
	0.00201	−0.56808	0.29473	0.05580
	−0.63516	0.28274	0.01395	0.00018
	0.00008	0.00545	−0.00545	−0.00011
b $^3F_4$	0.75048	−0.02413	0.24676	0.00276
	0.00345	−0.30297	0.15776	0.02187
	−1.27155	0.28373	0.00801	−0.02345
	0.00015	0.00023	−0.00023	0.00630
c $^5F_4$	0.65054	−0.00648	0.25844	0.09102
	0.00251	−0.51524	0.24555	0.06275
	−0.57610	0.25681	0.00280	0.00030
	0.00001	0.00293	−0.00293	−0.00005
c $^5F_5$	0.60089	−0.01596	0.29911	0.10000
	−0.00086	−0.46795	0.21511	0.07703
	−0.52316	0.22494	0.00543	−0.00003
	0.00006	0.00017	−0.00017	−0.00001

b: $4d^2 5s^2$ configuration; c: $4d^3 5s$ configuration.

Table 4. The coefficients of the hfs electric quadrupole interaction parameters of the model space for each fine structure state under study.

	β^{02}	β^{13}	β^{11}	β^{02}_{IC}
	β_1	β_2	β_3	β_4
	β_5	β_6	β_7	β_8
b $^3F_2$	0.18583	−0.05005	−0.06687	−0.06038
	−0.07510	0.04340	0.00481	−0.33072
	0.07287	0.05670	−0.01441	0.00809
c $^5F_2$	−0.05630	−0.03500	0.05204	0.00522
	0.04374	0.01584	−0.02457	0.05326
	−0.02251	−0.02100	−0.00038	0.00087
b $^3F_3$	0.21183	−0.04212	0.08098	−0.07776
	−0.08587	0.04818	0.00528	−0.37637
	0.08296	0.06920	−0.01618	0.00848
c $^5F_3$	−0.09116	−0.04599	0.10757	−0.00002
	0.07293	0.02856	−0.04392	0.08153
	−0.03640	−0.03023	0.00004	−0.00004
b $^3F_4$	0.28357	0.03964	0.19912	−0.10716
	−0.11495	0.06393	0.00685	−0.50387
	0.11085	0.09247	−0.02222	0.01206
c $^5F_4$	−0.17065	−0.03068	0.15934	−0.00010
	0.13653	0.05376	−0.08309	0.15261
	−0.06818	−0.05729	0.00007	−0.00008
c $^5F_5$	0.28321	0.03341	0.20370	0.00054
	−0.22657	0.08933	−0.13802	−0.25332
	0.11034	0.09393	0.00001	−0.00004

b: $4d^2 5s^2$ configuration; c: $4d^3 5s$ configuration

Hartree-Fock calculations [18] and from fs analysis (see Eq. (3)) had to be included in our hfs-fitting procedure. The value of hfs parameters are presented in Table 5. Some of the hfs two-body parameters, which are expected to be small, have been fixed to zero and they are not listed in Table 5. In Table 6 the results of hfs calculations together with predicted A and B hfs constants are presented. Differences between the experimental and calculated A and B values are small and they can origin from low degree of freedom in the hfs least square fitting procedure.

Usually the hfs parameters are discussed for each configuration separately. Using the equations (1, 2) the corresponding parameters for each configuration can be deduced (Tab. 7) from the model space parameters (Tab. 5).

The configuration radial integrals are given in Table 8, together with the results of Büttgenbach *et al.* [2] and also Hartree-Fock (HF) and Optimized-Hartree-Fock-Slater (OHFS) calculations made by Lindgren and Rosen [18] and by Olsson and Rosen [19] for comparison.

In principle the experimental value $\langle r^{-3}\rangle^{10}_{4d,exp}$ reflects relativistic effects and core polarization contribution due to the Fermi contact term [20]:

$$\langle r^{-3}\rangle^{10}_{4d,exp} = \langle r^{-3}\rangle^{10}_{4d,rel} + \langle r^{-3}\rangle^{10}_{4d,contact}. \qquad (6)$$

The relativistic parts $\langle r^{-3}\rangle^{10}_{4d,rel}$ evaluated from *ab initio* theoretical calculations [18,19] contribute only a few percent to the experimental values [2,21,31]. The main contribution to the experimental contact parameter for the d-electrons is therefore configuration interaction [22].

Table 5. The hfs radial parameters for the model space $(4d + 5s)^4$ (in MHz).The uncertainties given in parentheses are the standard deviations.

Parameter	value (MHz)	parameter	value (MHz)
a_{4d}^{01}	-124.28 (0.69)	b_{4d}^{02}	-131.94 (1.14)
$a_{4d}^{12} = 1.0789\, a_{5d}^{01}$	-134.09[a]	b_{4d}^{13}	-4.51 (1.40)
a_{4d}^{10}	3.47 (1.06)	$b_{4d}^{11} = -0.426\, b_{4d}^{13}$	1.92
a_{4s}^{12}	$-1716.1(5.5)$		
a_{IC}^{12}	0	b_{IC}^{02}	0
a_1	-37.02 (1.51)	b_1	-42.49 (2.66)
$a_2 = 0.195\, a_1$	-7.22[b]	$b_2 = 0.195\, \beta_1$	-8.29[b]
$a_3 = 0.130\, a_1$	-4.81[b]	$b_3 = 0.130\, \beta_1$	-5.52[b]
$a_9 = 0.20725\, a_{5s}^{10}$	-356[c]		
$a_{11} = -0.54985\, a_{5s}^{10}$	944[c]		

[a] Ratio of the parameters taken from the Hartree-Fock calculations [12].

[b] Ratio of the parameters taken from fs calculations (see text).

[c] Ratio average of the parameters taken from hfs fit for Ta [17] and Ti [32].

From the definition of hfs radial integral [10]

$$\langle r^{-3}\rangle_{4d,contact}^{10} = \frac{16\pi}{3} \sum_{n'',n'''} \frac{E(n''s4d, 4dn'''s)\psi_{n'',s}(0)\psi_{n'''s}(0)}{(2l+1)\Delta E(n''s, n'''s)} \quad (7)$$

one can see that core polarization effect observed for the $4d^3 5s$ configuration differs from that for the $4d^2 5s^2$ configuration by contributions of electron excitations of the type $n''s \to 5s$ and $5s \to n'''s$. The closed shell $5s^2$ does strongly reduce the effect of core polarization. Due to the scarcity of experimental data and then to the limited number of possible free parameters we took here $\langle r^{-3}\rangle_{4d}^{10}(4d^4) = \langle r^{-3}\rangle_{4d}^{10}(4d^3 5s)$. In reality $\langle r^{-3}\rangle_{4d}^{10}(4d^4)$ can be slightly bigger than $\langle r^{-3}\rangle_{4d}^{10}(4d^3 5s)$ (around 11% in the case of Ti [23,24] for example). Let us point out that the core polarization behaviour is different as far as p-electrons are concerned [25–27]. This problem will be discussed in details in another paper about odd configurations.

4 Determination of the nuclear quadrupole moment

In order to determine the nuclear quadrupole moment Q the radial parameters a_{nl}^{01}, a_{nl}^{12}, and b_{nl}^{02} are commonly used. The values of these parameters were still disturbed by the effect of electrostatic interactions with far configurations called "Sternheimer effects". The Q value obtained in that way must be corrected by calculated Sternheimer shielding or antishielding factors [28].

The new parameterization method [10] used in this work allows the evaluation of SL- and N-dependent contributions to the observed hfs splitting, which arise from the mixing of far configurations *via* coulomb interaction. Thus, if Q values are evaluated from the following equation [10]:

$$Q = \frac{2\mu_I g_I}{e^2} \frac{b_{nl}^{02}(1 + \Delta_{ll'}^{(01)1})}{a_{nl}^{01}(1 + \Delta_{ll'}^{(02)2})} \frac{F^{01}}{R^{02}} \quad (8)$$

where F^{01} and R^{02} are relativistic correction factors [18] and $\Delta_{ll'}^{\kappa k}$ are the contributions of one-body excitations of closed shells to empty shells [29]. The contributions $\Delta_{ll'}^{(\kappa k)1,2}$ of one-body excitations of full shells to empty shells are not known, because they cannot be determined experimentally. Neglecting these contributions we can derive $Q = -0,22(2)b$.

The above mentioned SL- and N-dependent contributions to the A and B constants have been separated by the use of an independent set of two-body hfs parameters a_i and b_i. This permits the determination of the nuclear quadrupole moment Q_i free from Sternheimer corrections from this independent set of two-body hfs parameters [10].

$$Q_1 = \frac{2\mu_I g_I}{e^2} \frac{b_1}{a_1}\,. \quad (9)$$

Since the magnetic dipole moment of ^{91}Zr has been measured by NMR method; ($\mu_I = -1.29802(2)\mu_N$ [30]) it is possible to derive $Q_1 = -0.24(3)b$.

The difference between the both Q-values quoted above is within experimental uncertainties and indicates the effects of inner shell $\to$ empty shell excitation can be neglected. Hence we prefer the average value $Q = -0,23(2)b$ as the final result, which is quasi free of Sternheimer corrections.

5 Conclusion

For the first time the nuclear quadrupole moment of the zirconium, quasi free of Sternheimer corrections up to second order has been determined using successfully the hfs parameterization method proposed in [10], as regards $4d$-electrons this time.

Table 6. Predicted A and B hfs constants of ^{91}Zr (in MHz). The rows printed in bold are related to the levels with experimentally measured hfs splitting [2]. A_{calc} and B_{calc} are given with uncertainties originated from pure statistical error.

Energy	Designation		A_{exp}	A_{calc}	ΔA	B_{exp}	B_{calc}	ΔB
$J = 1$								
4376.280 f	I	^{3}P		−43.157			−17.98	
4870.530 f	II	^4F; ^5F		246.414			6.66	
10855.360 f	II	^4P; ^5P		−577.998			−4.08	
14123.010 f	II	^2D; ^3D		306.252			13.90	
15449*	II	^4P; ^3P		146.293			10.97	
17059.820 f	II	^2P; ^3P		−798.318			−1.42	
17885*		^2P; ^1P		353.701			7.00	
21801.211 f	III	^5D		55.194			−15.91	
$J = 2$								
0.000 f,	**I**	**^{3}F**	**−170.7696**	**−170.7857**	**0.0161**	**−21.500**	**−21.616**	**0.116**
4186.110 f,	I	^1D		−117.121			30.25	
5023.410 f,	**I**	**^{4}F; ^{5}F**	**−105.7264**	**−105.3757**	**−0.3507**	**5.587**	**5.754**	**−0.167**
5101.6 f	II	^3P		−98.303			32.85	
11016.650 f	II	^4P; ^5P		−400.186			39.53	
11640.720 f	II	^4F; ^3F		−298.236			18.51	
14348.780 f	II	^2D; ^3D		−279.578			21.42	
15932.100 f	II	^4P; ^3P		163.713			−32.43	
17142.721 f	II	^2P; ^3P		−335.526			8.23	
18717*	II	^2D; ^1D		−101.417			22.09	
20251*	II	^2F; ^3F		204.521			−21.49	
21943.740 f	III	^5D		47.004			−9.90	
$J = 3$								
570.410 f	I	^3F	**−104.9441**	**−104.7764**	**−0.1677**	**−24.187**	**−24.383**	**0.196**
5249.070 f	II	**^{4}F; ^{5}F**	**−189.1413**	**−189.5090**	**0.3677**	**9.606**	**9.216**	**0.390**
11258.880 f	II	^4P; ^5P		−309.600			−39.33	
11956.330 f	II	^4F; ^3F		−13.224			13.26	
12503.440 f	II	^2G; ^3G		96.056			−11.70	
14697.030 f	II	^2D; ^3D		−372.629			27.88	
20198*	II	^2F; ^3F		−137.856			−23.10	
21767*	II	^2F; ^1F		−107.965			−30.14	
22145.311 f	III	^5D		35.622			11.36	
$J = 4$								
1240.840 f,	**I**	**^{3}F**	**−77.8878**	**−78.0836**	**−0.8042**	**−33.476**	**−32.889**	**−0.586**
5540.540 f	**I**	**^{4}F; ^{5}F**	**−217.5720**	**−219.3718**	**1.7998**	**17.320**	**16.930**	**0.390**
8057.300 f	II	^1G		−107.403			−110.57	
12342.370 f	II	^2G; ^3G		−32.393			1.83	
12760.660 f	II	^4F; ^3F		−40.773			0.76	
14791.280 f	II	^2H; ^3H		63.752			−67.97	
17752.730 f	II	^2G; ^1G		−72.942			−38.28	
20145*	II	^2F; ^3F		−305.033			−24.90	
22398.000 f	III	^5D		22.491			46.27	
$J = 5$								
5888.930 f	**II**	**^{4}F; ^{5}F**	**−229.6590**	**−227.7779**	**−1.8811**	**27.684****	**−27.09**	
12772.780 f	II	^2G; ^3G		−266.058			26.32	
14988.510 f	II	^2H; ^3H		−132.845			12.68	
18738.939 f	II	^2H; ^1H		−81.934			14.26	
$J = 6$								
15119.660 f	II	^2H; ^3H		−237.882			13.88	

* calculated energy ** not introduced in the fit calculation (see Sect. 5)

f: level taken to fs least-square fit

I: $4d^2 5s^2$ II: $4d^3 5s$ III: $4d^4$

Table 7. Hfs radial parameters in one-configuration approximation deduced from (1) and (2). All values are given in MHz.

	a^{01}_{4d}	a^{12}_{4d}	a^{10}_{4d}	a^{10}_{4d}	b^{02}_{4d}	b^{13}_{4d}	a^{11}_{4d}	
$4d^2 5s^2$	−102.8	−251.7	−9.1		−119.3	−14.8	3.3	[8]
	−109.48	−119.28	3.5		−114.8	−4.4	1.9	[this work]
$4d^3 5s$	−95.5	−52.4	62.5	-1889	−87.9	−3.2	13.8	[8]
	−94.68	−104.48	145.9*	-1716	−96.6	−4.4	1.9	[this work]
$4d^4$	−79.88	−89.68	145.9		−78.4	−4.4	1.9	[this work]

Table 8. Theoretical and experimental radial integral values (in a_0^{-3}).

	Magnetic dipole interaction			Electric quadrupole interaction			
	$\langle r^{-3}\rangle^{01}_{4d}$	$\langle r^{-3}\rangle^{12}_{4d}$	$\langle r^{-3}\rangle^{10}_{4d}$	$\langle r^{-3}\rangle_{5s}$	$\langle r^{-3}\rangle^{02}_{4d}$	$\langle r^{-3}\rangle^{13}_{4d}$	$\langle r^{-3}\rangle^{11}_{4d}$
$4d^2 5s^2$							
HF	2.299	2.444	−0.0654*		2.310	0.300	−0.112
OHFS	2.475	2.636	−0.0727*		2.487	0.333	−0.125
Exp. [8]	2.070	5.1	0.2				
This work	2.210	2.408	−0.071		2.020	0.077	−0.033
$4d^3 5s$							
HF	1.949	2.082	−0.0606*		1.958	0.267	−0.103
OHFS	2.090	2.257	−0.0771*	58.7	2.098	0.320	−0.129
Exp. [8]	1.92	1.1	−1.3	38.0			
This work	1.911	2.109	−2.945	34.64	1.699	0.077	−0.033
$4d^4$							
HF	1.634	1.763	−0.060*		1.640	0.246	−0.100
OHFS	1.785	1.96	−0.081*		1.790	0.312	−0.133
Exp. [8]	1.74						
This work	1.612	1.810	−2.945		1.379	0.077	−0.033

* Relativistic party only

As one can see in Table 8 more reliable data and better agreement with *ab initio* calculations has been obtained in this work. Furthermore, with only 7 hfs experimental data of two configurations, we have been able to predict the hfs splitting of the remaining levels of the system, resorting to a model space parameterization.

Büttgenbach *et al.* gave $B(4d^2 5s\,{}^5F_5)$ positive [8]. Later in his book [31] he repeated the same data. Considering then that is not a misprint we suggest to our colleagues to perform some experimental measurements to check the sign of this value because in Table 4 the coefficient of b^{02} (0.28321) is positive and $b^{02} = -131.94$ MHz (Tab. 5) then the B constant of this level should be negative.

We hope that this work can be a stimulus for further experimental and theoretical hfs investigations in the zirconium atomic spectrum: this element is light and then the expected Doppler width of lines is surely consequent; so the predicted A and B constants given in Table 6 can help to simulate the shapes of lines under study with laser spectroscopy and to recognize the saturated hyperfine components even if the classical relative ratios of these components change totally.

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